

X-ray Diffraction Analysis of the Particulate Matter in Residual Oil Flyash

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KEYWORDS: Particulate Matter, Characterization, X-ray Diffraction

ABSTRACT

X-ray diffraction studies are reported on a series of PM samples produced by combustion of residual fuel oil. The residual oil flyash (ROFA) from four oils of varying sulfur content were aerodynamically separated into <2.5 micron and >2.5 micron fractions using a cyclone. The analysis of their x-ray diffraction measurements indicated sharp lines due to the presence of crystalline components superposed on two broad peaks due to amorphous carbon. The intensity of the crystalline components tends to be higher in the <2.5 micron fractions and in oils with the higher sulfur content. The sharp lines have been identified with various sulfites and sulfates of Zn, V, Ni, Pb, Fe, Cu and Ca.

INTRODUCTION

Particulate Matter (PM) is composed of a mixture of particles directly emitted into the air and the particles formed in air from the chemical transformation of gaseous pollutants (secondary particles). The earlier focus of the US Environmental Protection Agency (EPA) was on the particulate matter less than 10 microns in diameter (PM_{10}). In July 1997, EPA adopted a new rule that, for the first time, addressed particulate matter with diameter less than 2.5 microns (fine PM or $PM_{2.5}$) [1]. The implementation of this new rule requires the acquisition of important scientific information regarding the effects of $PM_{2.5}$ on public health and welfare. These adverse health effects include premature mortality, aggravation of respiratory and cardiovascular symptoms and illness, change in lung structure, and altered respiratory defense mechanisms [2-4]. Two controversial studies (the Harvard University six-city study and the American Cancer Society study) have linked the presence of fine particulate matter to premature mortality [5]. Generally, fine particles are considered to be more hazardous than coarse particles. Therefore, the analysis have to be done at molecular levels. In order to understand the molecular speciation and its parameters such as valency, solubility, acidity, and composition, it is essential to identify and analyze the elements and compounds present accurately by employing several analytical tools. Huffman et al., have carried out X-ray absorption fine structure (XAFS) analysis to investigate several elements in ROFA samples [6].

In this work, we have employed x-ray diffraction for the identification and analysis of the compounds present in $PM_{2.5}$ samples. The technique of x-ray diffraction allows identification of any crystalline material, elements or compounds, present in a sample. In this work, x-ray diffraction was used to investigate the suite of residual oil flyash (ROFA) samples separated aerodynamically into fractions <2.5 ($PM_{2.5}$) and >2.5 microns ($PM_{2.5+}$) in diameter. The ROFA samples were generated by combustion of residual fuel oil at the EPA laboratory at the Research Triangle Park in experiments conducted by Miller et al [7]. A series of eight samples were analysed. All the PM samples measured possess sharp lines superposed on two broad peaks. We could identify the sharp lines due to various sulfates of Zn, V, Ni, Pb Fe, Cu and Ca. The two broad peaks are due to presence of amorphous carbon [8].

EXPERIMENTAL

The combustion experiments were carried out in a North American three-pass fire tube package boiler, which is a practical, commercially available heavy fuel oil combustion unit. A detailed description of this boiler is given elsewhere [7]. Samples were

separated aerodynamically by a cyclone into fractions that were nominally < and > 2.5 microns in diameter, hereafter referred to as PM_{2.5} and PM_{2.5+}. The sampling system consists of a large dilution sampler capable of isokinetically sampling 0.28m³/min (10ft³/min) of flue gas using a Source Assessment Sampling System (SASS) cyclone. The SASS cyclone produces 50 and 95% collection efficiencies at approximately 1.8 and 2.5 micron diameter, respectively. The resulting PM is collected on large (65 cm) Teflon coated glass fiber filters, transferred to sampling jars, and made available for analysis.

Although burnout was fairly complete (>99.7%), the inorganic content of the oils was quite low (0.02-0.10 wt.% ash), and the dominant element of the ROFA is carbon. Loss on ignition (LOI) measurements indicate that the carbon content of the PM_{2.5} ranged from 64 to 87 wt.% and that of the PM_{2.5+} from 88 to 97%. S content of the PM samples was ~ 1 to several wt.%, while the V content ranged from 0.5 to 5.9 wt.% and the Ni content from 0.08 to 0.8 wt.%. As reported in the paper by Miller et al. [7], the metals are typically more concentrated in the PM_{2.5} samples than they are in the PM_{2.5+} samples by factors ~3 to 6.

These samples were investigated using a Wide Angle X-ray Diffractometer (WAXD). The WAXD used is a Rigaku diffractometer (Model D/MAX) using Cu K α radiation with a wavelength λ of 1.542 Å. The other experimental conditions include ½' divergence and scatter slits, 0.15mm receiving slits, step scans with 0.04' steps and 30sec, counting time at each step, and intensity measured in counts. This relatively slow scan process enabled us to obtain the diffraction pattern with resolved sharp lines due to various compounds. The analysis of the X-ray patterns have been carried out using Jade software package produce by MDI (Materials Data Inc.) and the JCPDS data files.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the two ROFA samples (oil #5) are shown in Figures 1 (<2.5 microns) and 2 (>2.5 microns). Figure 1 shows well defined sharp lines superposed on two broad peaks at $2\theta \cong 26^\circ$ and 44° due to amorphous carbon[8]. The inorganic components have been identified as CaSO₄; Zn₄SO₄(OH)₆ · 5H₂O; Zn(SO₃)₂ · 2.5H₂O; VOSO₄; NiSO₄ · 6H₂O; PbS₂O₃; Fe₃(SO₄)₄ · 14H₂O; ZnSO₄ · xH₂O; Ca(SO₄)(H₂O)₂; Cu₂SO₄. All these phases are identified and labeled as shown in the Figs. 1, 2 and 3. Figure 2 shows only CaSO₄ phase and the two broad peaks due to carbon [7]. In a similar fashion a total of eight samples were analyzed and the inorganic phases identified are summarized in Table 1. The samples are found to contain various sulfates and sulfites of Zn, V, Ni, Pb, Fe, Ca and Cu. The intensities of the x-ray diffraction lines for these compounds is the largest for the ROFA samples obtained from the high sulfur No. 6 oil and for the PM_{2.5} fraction of No. 5 oil (BL5FH). This is understandable since the high sulfur content would tend to produce higher levels of the sulfates. The other noticeable trend is the higher concentrations of the sulfates in the PM_{2.5} fraction as compared to the PM_{2.5+} fraction.

The major contribution of the present investigation using x-ray diffraction is that we have been able to identify various compounds and their water content in the ROFA samples. In making the identifications, we compared the diffraction patterns of all appropriate compounds available in the JCPDS files. Since the studies by Miller et al [7] had given the percentages of various elements present in these samples, our search was primarily confined to the various compounds of these elements. The information reported here on the various compounds should be useful for developing appropriate models for the formation of these compounds. Some of these compounds may have appropriate band gaps for the photocatalytic absorption of solar radiation [9]. In addition, some of these materials being acidic, may have the catalytic ability to crack hydrocarbons and create free radicals. Further work along these lines is needed to understand the harmful effects of PM_{2.5}. A more detailed description of our

investigations, including comparison with the findings obtained by other techniques, will be published elsewhere.

ACKNOWLEDGEMENT

Support of this research under the U.S. Department of Energy contract No. DE-AC26-99BC15220 is gratefully acknowledged. We thank Dr. G. P. Huffman for providing the samples used in these investigations.

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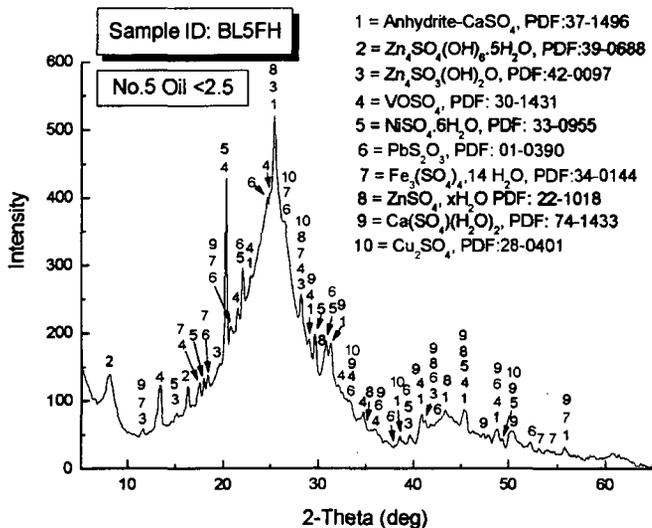


Fig. 1 Room temperature x-ray diffractogram of sample BL5FH. Lines due to various crystalline components are identified.

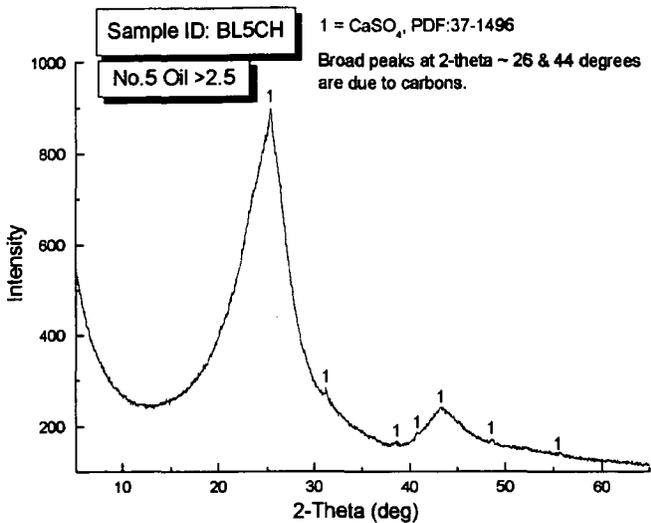


Fig. 2 Room temperature x-ray diffractogram of sample BL5CH. Lines only due to CaSO₄ are present. The broad peaks near 2θ ~ 26° and 44° are due to amorphous carbons (see Ref. 8).

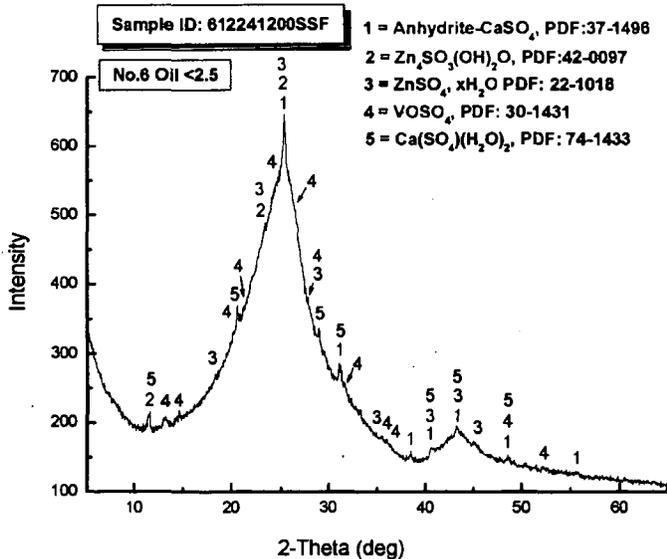


Fig. 3 Room temperature x-ray diffractogram of sample 612241200SSF. Lines due to various crystalline components are identified. The broad peaks are due to amorphous carbon.

Table 1: Identification of the compounds in the ROFA samples

Sample	Compound (PDF File)
BL5FH (#5 oil) <2.5	CaSO ₄ (37-1496); Zn ₄ SO ₄ (OH)6.5H ₂ O (39-0688); Zn(SO ₃) ₂ .2.5H ₂ O (42-0097); VOSO ₄ (30-1431); NiSO ₄ .6H ₂ O (33-0955); PbS ₂ O ₃ (01-0390); Fe ₃ (SO ₄) ₄ .14H ₂ O (34-0144); ZnSO ₄ xH ₂ O (22-1018); Ca(SO ₄)(H ₂ O) ₂ (74-1433); Cu ₂ SO ₄ (28-0401)
BL5CH (#5 oil) >2.5	CaSO ₄ (37-1496)
701291400SSF (#6 oil) high sulfur <2.5	Same as BL5FH
70129400SSC (#6 oil) high sulfur >2.5	Same as BL5FH
612241200SSC (#6 oil) medium sulfur >2.5	CaSO ₄ (37-1496); Zn(SO ₃) ₂ .2.5H ₂ O (42-0097); Ca(SO ₄)(H ₂ O) ₂ (74-1433)
612241200SSF (#6 oil) medium sulfur <2.5	CaSO ₄ (37-1496); Zn(SO ₃) ₂ .2.5H ₂ O (42-0097); ZnSO ₄ xH ₂ O (22-1018); VOSO ₄ (30-1431); Ca(SO ₄)(H ₂ O) ₂ (74-1433)
701071200SSF (#6 oil) low sulfur <2.5	CaSO ₄ (37-1496); Zn(SO ₃) ₂ .2.5H ₂ O (42-0097); VOSO ₄ 1.5H ₂ O (31-1444); NiSO ₄ (34-0144); Ca(SO ₄)(H ₂ O) ₂ (74-1433)
807161300SSF baseline filter	CaSO ₄ (37-1496); VOSO ₄ (30-1431); NiSO ₄ .6H ₂ O (33-0955); PbS ₂ O ₃ (01-0390); Fe(NO ₃) ₃ .9H ₂ O (01-0124); ZnSO ₄ xH ₂ O (22-1018); Ca(SO ₄)(H ₂ O) ₂ (74-1433); Cu ₂ SO ₄ (28-0401); NaAl(SO ₄) ₂ .6H ₂ O (19-1186)

XAFS Spectroscopy and SEM Investigation of Fine Particulate Matter from Residual Fuel Oil Combustion

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Keywords: particulate matter, PM_{2.5}, XAFS, NMR, molecular structure, SEM, particle size distribution

Introduction

The EPA is currently considering new regulations for fine airborne particulate matter (PM) less than 2.5 microns in diameter (PM_{2.5}). Such regulations should be based on the best scientific data, particularly with regard to fine particle characterization. Although there are many analytical techniques for determining the elemental composition of PM_{2.5}, information on molecular speciation is much more difficult to obtain. Since the health effects of PM_{2.5} are closely related to speciation parameters such as valence, solubility and acidity, it is essential to identify and evaluate analytical methods that can accurately speciate the molecular structure of critical elements.

X-ray absorption fine structure (XAFS) spectroscopy is a synchrotron radiation – based technique that is uniquely well suited to characterization of the molecular structure of individual elements in complex materials. In previous research, we have used XAFS spectroscopy to determine the molecular forms of environmentally important elements (S, Cl, As, Cr, Hg, Ni, etc.) in coal, oil, flyash, and sorbents.⁽¹⁻⁷⁾ Our initial investigations of PM indicate that XAFS will also be a powerful tool in this area.^(8,9)

In the current work, XAFS spectroscopy was used to investigate several elements in a suite of residual oil flyash (ROFA) samples separated aerodynamically into fractions <2.5 (PM_{2.5}) and >2.5 microns (PM_{2.5+}) in diameter. The ROFA was generated by combustion of residual fuel oil at the EPA National Risk Management Laboratory.⁽¹⁰⁾ Complementary data were obtained using computer-controlled scanning electron microscopy (CCSEM), ¹³C NMR, GC/MS, and XRD. In the current paper, some examples of the XAFS, CCSEM, and NMR data are presented. The XRD data are discussed in a separate paper presented in this symposium by Seehra and Mannivanan.⁽¹¹⁾

Experimental Procedure

The combustion experiments were carried out in a North American three-pass fire tube package boiler, which is a practical, commercially available heavy fuel oil combustion unit. A detailed description of this boiler is given elsewhere.⁽¹⁰⁾ Samples were separated aerodynamically by a cyclone into PM_{2.5} and PM_{2.5+} fractions. The sampling system consists of a large dilution sampler capable of isokinetically sampling 0.28 m³/min (10 ft³/min) of flue gas using a Source Assessment Sampling System (SASS) cyclone. The SASS cyclone produces 50 and 95% collection efficiencies at approximately 1.8 and 2.5 micron diameter, respectively. The resulting PM is collected on large (65 cm) Teflon coated glass fiber filters, transferred to sampling jars, and made available for analysis.

Although burnout was fairly complete (>99.7%), the inorganic content of the oils was quite low (0.02-0.10 wt.% ash), and the dominant element of the ROFA is carbon. Loss on ignition (LOI) measurements indicates that the carbon content of the PM_{2.5} ranged from 64 to 87 wt.% and that of the PM_{2.5+} from 88 to 97 wt.%. S content of the PM samples was ~ 1 to several wt.%, while the V content ranged from 0.5 to 5.9 wt.%, and the Ni content from 0.08 to 0.8 wt.%. The metals are typically more concentrated in the PM_{2.5} samples than they are in the PM_{2.5+} samples by factors ~3 to 6.⁽¹⁰⁾

The samples were investigated by XAFS spectroscopy at the Stanford Synchrotron Radiation Laboratory (SSRL) and the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. All measurements were carried out in the fluorescent mode using either a Lytle detector or a multi-element Ge array detector, as described

elsewhere.⁽¹⁻⁴⁾ The XANES regions of the spectra were analyzed by deconvolution, derivative, and comparative analysis methods, as discussed in earlier papers.⁽¹⁻⁷⁾

Results and Discussion

CCSEM examination of the PM_{2.5} was carried out on samples dispersed on a nucleopore filter, prepared as discussed elsewhere.⁽¹²⁾ Since the particles were predominantly carbon rich, C was by far the dominant element detected in the energy dispersive x-ray (EDX) spectra. S, V and Ni were observed as minor components. Because the sample contained both a large particle component and a small particle component, quantitative particle size distributions have not yet been obtained. However, measurements of the spread of the PSD were obtained by examining fields containing primarily small particles at magnifications ~1000X and fields containing large particles at a magnification of 50X. Examples are shown in Figure 1. It is seen that the PSD of the small particle component peaks at 1-3 microns and that of the large particle component at 10-15 microns.

Typical S K-edge XANES spectra of ROFA PM_{2.5} and PM_{2.5+} samples are shown in Figure 2. The spectra are deconvoluted by a least squares computer analysis into a series of peaks (50% Lorentzian-50% Gaussian) and two rounded arctangent step functions, as discussed elsewhere.^(1,2) Most of the peaks represent 1s→3p transitions of photoelectrons excited from the K-shell by x-ray absorption. Both the position and relative intensity of these peaks vary significantly with the electronic state of the S atom, increasing with increasing valence. By using calibration data generated from mixtures of standard compounds, the peak area percentages can be translated into percentages of S contained in different molecular forms.^(1,2)

The results of this analysis for the ROFA PM samples are summarized in Table 1. For comparison, the results for the PM derived from combustion of a Pittsburgh No. 8 coal in the same boiler are also included. The dominant molecular forms of S observed are sulfate and thiophenic S. Sulfate was greater in the PM_{2.5} samples than in the PM_{2.5+} samples, reflecting the greater degree of carbon burnout for the smaller particles. Additional components, including elemental S and inorganic sulfides, are present in lower percentages. The origin of the elemental S is not clear at this time. The S in the PM_{2.5} of the ROFA from a high S residual oil burned in a second furnace where carbon burnout was much more complete was 100% sulfate. It is seen that both the PM_{2.5} and PM_{2.5+} from the Pittsburgh #8 coal are also predominantly sulfate.

Table 1. XANES results for the weight percentages of different S forms.

Sample	PM size	Sulfate	Thiophene	Elemental S	Inorganic sulfide	Other forms
Baseline # 5 oil	<2.5	55	24	5	11	5
Baseline # 5 oil	>2.5	32	37	8	19	4
Low S #6 oil	<2.5	84	14	--	--	2
Low S #6 oil	>2.5	58	34	6	--	2
Med. S #6 oil	<2.5	73	13	6	--	8
Med. S #6 oil	>2.5	55	35	6	--	3
High S #6 oil	<2.5	54	29	5	11	1
High S #6 oil	>2.5	26	39	9	26	--
Pitt. #8 coal	<2.5	95	5	--	--	--
Pitt. #8 coal	>2.5	85	14	--	--	1

Analysis of the XANES spectra from V and Ni in the ROFA PM samples indicates that they are present predominantly as sulfates. Most of the V XANES spectra closely resemble the spectrum of vanadyl sulfate (VO•SO₄•xH₂O). This is brought out clearly by the first derivative of the XANES spectra, which exhibited peaks in nearly identical positions and with similar intensities to the first derivative of the XANES spectrum of VO•SO₄•3H₂O reported by Wong et al.⁽¹²⁾ The Ni XANES and first derivative spectra from the PM samples agree well with that of NiSO₄, and with the Ni spectra observed in an earlier investigation of ROFA⁽⁴⁾ by the current authors. Similarly, the XANES and the

first derivative spectra of the other metals examined (Fe, Zn, Cu, Mn and Pb) also identify the principal components of these metals to be sulfates. However, secondary components are present in many of the metal XAFS spectra. In most cases, these secondary components appear to be oxides. The As XANES identify the arsenic as an arsenate (As^{+5}) but do not identify the specific phase.

NMR data

Seven of the samples were examined by ^{13}C NMR. Cross polarization experiments suggested that the proton content of the samples was very low and, hence, no useful data were obtained using this experimental technique. Proton spectra taken on several samples verified the very low H/C ratios for all but the high sulfur #6 $\text{PM}_{2.5}$ sample. The ^{13}C NMR spectra were then acquired using by using block decay with a pulse repetition rate of 10 s and accumulating between 17,000 and 25,000 scans. These resulting spectra are shown in Figure 3, where FL and CY denote filter ($\text{PM}_{2.5}$) and cyclone ($\text{PM}_{2.5+}$) samples, HS, MS and LS indicate high, medium and low sulfur #6 oil, and BL indicates baseline #5 oil. The spectra indicate that the carbon in the samples is predominantly condensed in graphitic-like structures. Second moment (line width) measurements are uniform at ~ 75 ppm (FW/HH) for six of the samples. However, the second moment of the high sulfur #6 $\text{PM}_{2.5}$ (FL-HS) sample indicates a much narrower aromatic band (45 ppm). In addition, this sample is unique in that aliphatic structure is clearly present in the spectrum.

Summary and Conclusions

XAFS spectroscopy, CCSEM and ^{13}C NMR data have been obtained from a series of $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples produced by combustion of residual fuel oil in a commercial boiler. Analyses of the XANES spectra have been carried out for S and a number of metals in the PM. Deconvolution of the S XANES reveals that the dominant molecular forms of S observed are sulfate and thiophenic S. Sulfate was greater in $\text{PM}_{2.5}$ samples than in the $\text{PM}_{2.5+}$ samples, reflecting the greater degree of carbon burnout for the smaller particles. Sulfates are the dominant components of the metal spectra. CCSEM indicates that the aerodynamically separated $\text{PM}_{2.5}$ is bimodal in size, with a small particle component peaking at 1-3 microns and a large particle component peaking at 10-15 microns. The ^{13}C NMR indicated that the carbon in the PM was predominantly graphitic or soot-like in structure. However, one sample exhibited a much narrower aromatic band than the others and an aliphatic component.

Acknowledgement: Support of this research under U.S. Department of Energy (FE/NPTO) contract No. DE-AC26-99BC15220 is gratefully acknowledged. The XAFS experiments were conducted at the Stanford Synchrotron Radiation Laboratory and the National Synchrotron Light Source, which are also supported by the U.S. DOE.

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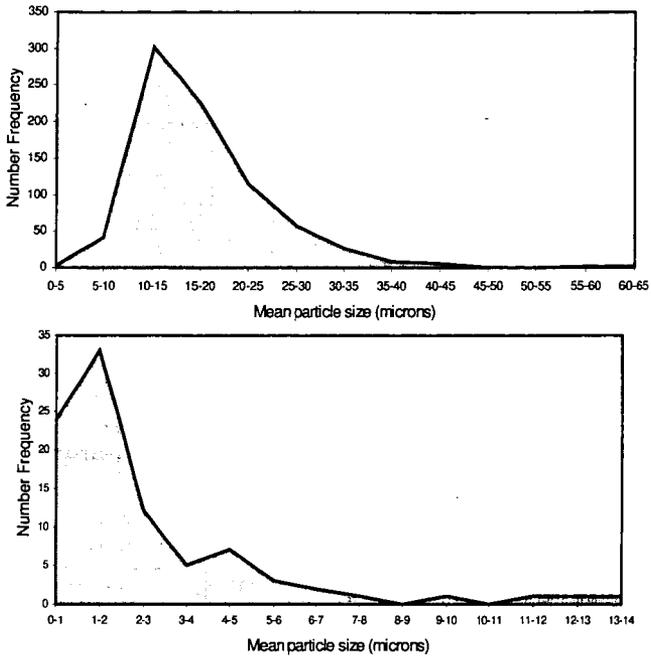


Figure 1. Particle size distributions for PM_{2.5} measured for a field of particles at a magnification of 50X and a second field at a magnification of 1000X.

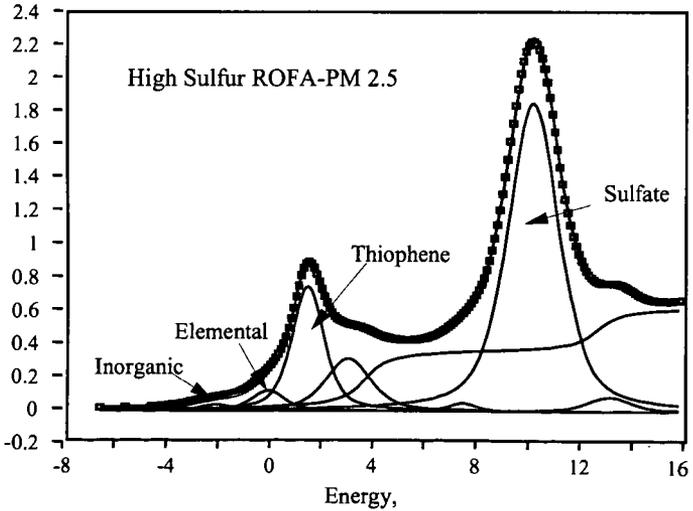


Figure 2. Typical least squares analysis of the S XANES of a ROFA PM_{2.5} sample.

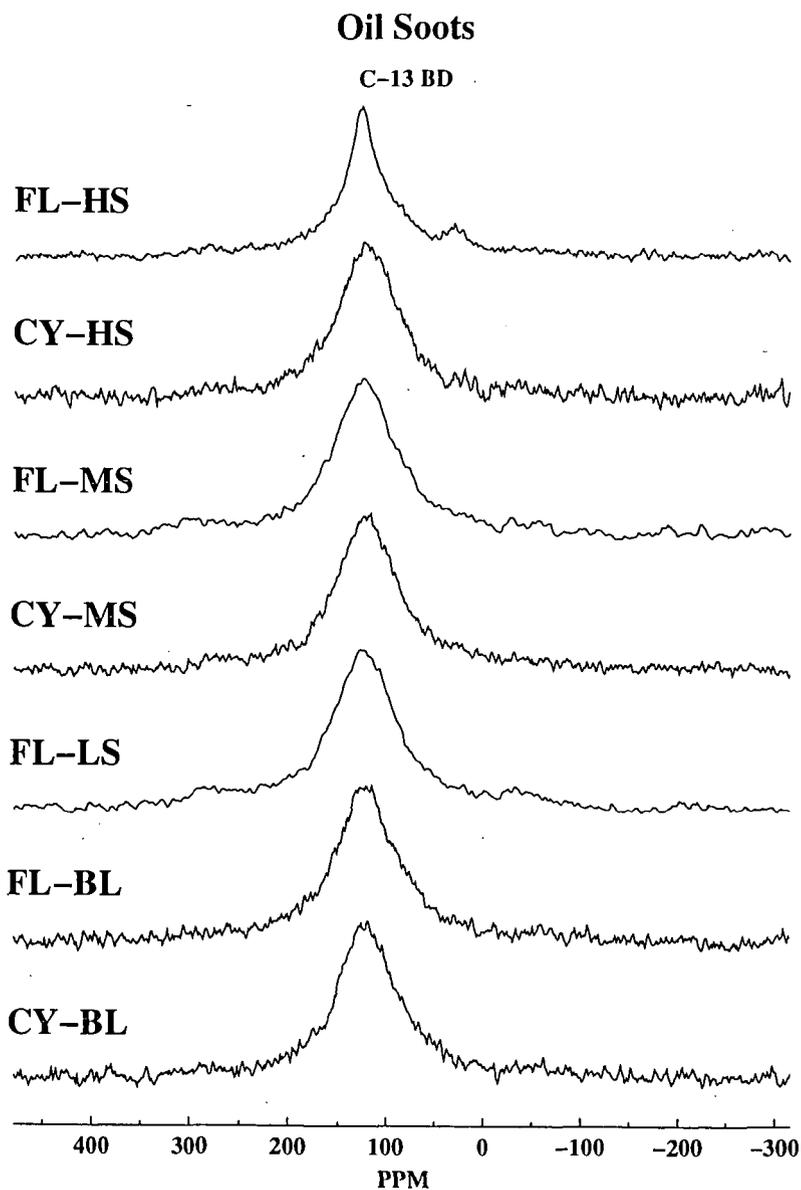


Figure 3. ^{13}C NMR Spectra of ROFA PM Samples.

SUPER-EQUILIBRIUM CONCENTRATIONS OF CARBON MONOXIDE AND HYDROCARBON IN FUEL GASES AND THEIR RELATIONSHIP WITH VOC AND METALS EMISSIONS

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KEYWORDS: Coal combustion; Emissions of CO, VOC, PAH, trace metal; modelling

INTRODUCTION

Flue gases resulting from the combustion of hydrocarbon fuels in practical systems usually contain levels of carbon monoxide that are significantly above equilibrium values. Typically, for flue gases from a utility plant containing 5% O₂, the measured level of carbon monoxide is about 300 ppm. The computed equilibrium value is extremely small with 3% O₂ and rises rapidly as the O₂ level is reduced. If combustion took place in the combustion chamber with perfectly-mixed fuel and combustion air, the lower levels of carbon monoxide would result. However, mixing is not perfect because of the formation of coherent structures and large turbulent eddies. These unburned pockets of rich mixtures are caused by incomplete mixing of fuel and air at the near-burner zone, and persist because of the slow subsequent mixing with air. They are responsible for the above equilibrium levels of hydrocarbons, namely the volatile organic compounds (VOC) found in the flue gases.

The super-equilibrium levels of carbon monoxide can also be responsible for corrosion cracking in earlier parts of certain boilers, is related to the presence of unburned hydrocarbons, and can have some influence on the chemistry of the metals emitted. In this paper, values of the super-equilibrium levels of carbon monoxide and VOC's are computed together with their influence on metal emission.

A similar situation can hold for smoke where the concentrations in the rich pocket are above those expected for a uniformly mixed gas. These higher local soot concentrations can coagulate faster and can result in sub-micron particulate matter even in lean mixtures.

EXPERIMENTAL

Thermodynamic equilibrium concentrations of major VOCs, certain polycyclic aromatic hydrocarbons (PAHs) and trace element species were determined by means of minimisation of free energy calculations using "Equitherm" (VCH scientific Software, Equitherm version 5.0).¹ The calculations presented here were designed to determine the effect of carbon monoxide levels on species for arsenic, chlorine, cadmium, mercury, nickel, lead and thallium. The system examined uses a sub-stoichiometric basis and calculates the formation of all gaseous, liquid and solid phase species at 1 atm. pressure over a range of temperatures (500 - 1800 K), and amount of air supplied (300, 250, 200 and 150 kg corresponding to between approximately 1/4 to 1/8 of stoichiometric air) and is based on 100 kg of coal. Two coals with very different properties were investigated, Thai coal and Pittsburgh #8 coal, and the analyses of which are given in Table 1.

RESULTS AND DISCUSSION

Equilibrium predictions of CO concentrations are low compared to CO₂. However, actual CO concentrations in flue gases are much higher than equilibrium values. These higher CO concentrations could arise from poor mixing in the combustion system, resulting in a drastic decrease in local O₂ concentrations, and consequently increases in CO concentration. Such a situation could be described by the formation of fuel-rich turbulent eddies, which mix, and therefore cool, relatively slowly. Within these fuel rich pockets, reactions of volatile gases, fuel and unburned or partially oxidised species take place in an oxygen deficient atmosphere. Figure 1 describes the change in CO, CH₄ and C₆H₆ concentration at 1500 K as the air supply is varied. A rapid increase in CO between 300 and 250 kg air (per 100 kg fuel) is observed. As the mixture becomes richer, benzene and methane also start to increase in concentration,

Table 1 Summary of characterisation analysis on original coal sample

	Thal coal		Pittsburgh #8	
	As determined (wt%)	Dry basis (wt%)	As determined (wt%)	Dry basis (wt%)
% ash	25.43	22.54	9.84	9.68
%carbon	56.45	50.04	74.66	73.45
%hydrocarbon	13	11.52	5.2	5.12
%nitrogen	1.69	1.50	1.7	1.67
%oxygen (difference)	3.43	3.04	8.6	8.46
%sulfur	1.98	1.76	2.19	2.15
%moisture	12.81		1.65	
concentration of metal in ppm, wt.				
As	11.28	10.0	3.36	3.31
Cd	0.58	0.5	0.03	0.029
Ni	22.58	20.0	1.70	1.67
Pb	45.12	40.0	1.85	1.82
Tl	1.13	1.0	1.02	1.0
Hg	0.11	0.1	0.12	0.12
Cl	1128.10	1000.0	0.12	0.12
kJ/kg	27110	24030	31960	31440

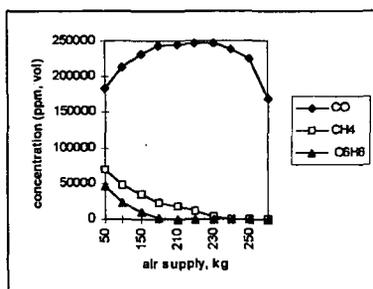


Fig 1: Thermodynamic prediction of the equilibrium concentration of CO, CH₄ and C₆H₆ at 1500K

and CO begins to decrease. If calculations are performed at leaner conditions (up to 600 kg air) the CO concentration decreases to very low levels, as do the VOC species.

Figure 2 indicates the concentration profiles with temperature of hydrocarbons at both 150 and 300kg air /100kg coal. Equilibrium conditions are not expected to be attained at lower temperature in the reaction times available.² Transient kinetic calculations indicate that the equilibrium concentrations produced at high temperature (i.e. above ~ 1273 K) are reasonable, but that the species are quenched as the rich pockets cool. The window of stability for hydrocarbons is related to O₂ concentration. Concentrations of the larger polyaromatic hydrocarbons (PAH) (C₁₀H₈ and C₂₀H₁₂) are predicted to rise rapidly at lower O₂ concentrations. The increased concentration of PAH and other reduced species results in the increased probability of soot formation and agglomeration, through collision and reaction in the rich turbulent eddies.

Throughout the temperature range studied (500-1800K) the distribution of metals can be followed as shown in Figure 3a and 3b for Pittsburgh coal. The concentration of air affects the overall distribution of the metals between the solid and gas phase. The reduction in air also influences the speciation of the metals causing many of them to be fixed in the solid phase up to a higher temperature. The presence of fuel rich "pockets" in the combustion system appears to be beneficial for many trace metals, because the formation of solid chlorides and sulphides is favoured at higher temperatures for richer pockets. E.g. for 300 kg air, the transformation of cadmium occurs in the temperature range 900 - 1000 K corresponding to the transformation of Cd metal (g) to CdS (s). A slight increase in CdCl₂ effects the distribution of cadmium. For lead, solidification of PbS vapour is expected to be independent of air concentration, and occurs at 700-800 K. The temperature for partitioning of thallium between gas and solid phases is changed slightly by changing the air concentration. In terms

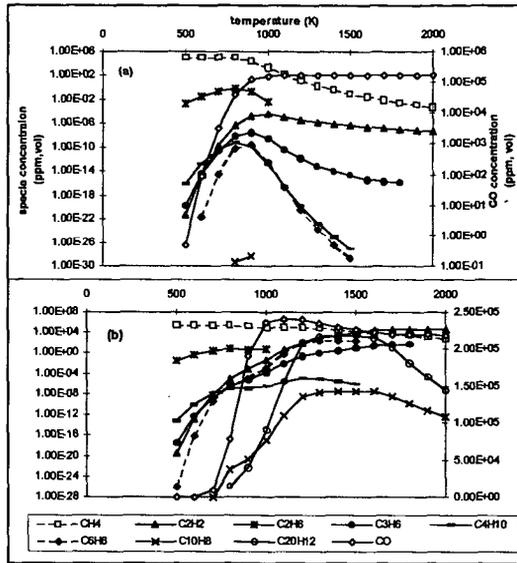


Fig 2: Thermodynamic prediction of equilibrium concentrations of gases for Thai coal: at (a) air 300 kg, and (b) air 150 kg.

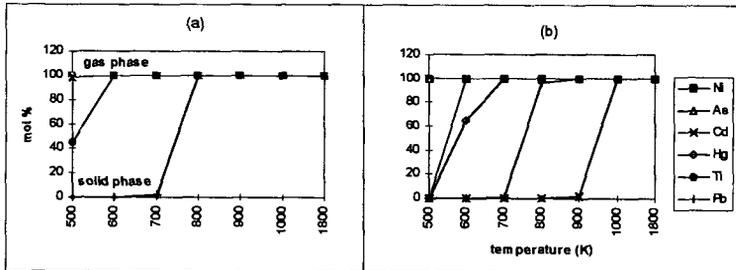


Fig 3: (a) Distribution of metal species in fuel gas and ash for Pittsburgh coal: (a) air 300 kg (b) air 200 kg

of distribution between the phases, Hg remains in the gas phase throughout the temperature range for 300 kg air/100kg fuel (Fig. 3a) predominantly as Hg (metal). At leaner conditions (Fig. 3b) mercury is in the gas phase as HgS (g), which forms a solid phase at low temperatures.

Ni and As are present in the gas phase even at low temperatures regardless of air concentration. Ni is released as $\text{Ni}(\text{CO})_4$ and appears to independent of air concentration. Even at stoichiometric air (or above), nickel carbonyl is predicted to be the most stable nickel species. Figure 4 shows the distribution of metal speciation for nickel. The higher emission for the Thai coal simply reflects the higher concentration of nickel in the original coal.

Arsenic on the other hand is very sensitive to the air concentration, as shown in Figure 5. At 350 kg air, the arsenic is predominantly $\text{AsO}(\text{g})$ over the entire temperature range. However at 300 kg air, higher temperature favours the decomposition of $\text{AsO}(\text{g})$ and the formation of the highly toxic hydride, arsene (AsH_3).

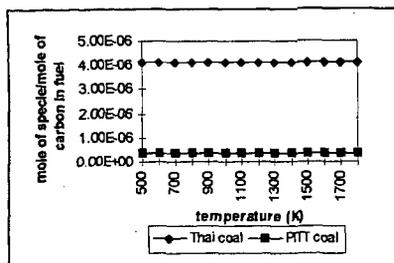


Fig 4: Equilibrium concentration of Ni(CO)₄ for Thai coal and Pittsburg coal with 300kg air/100kg coal

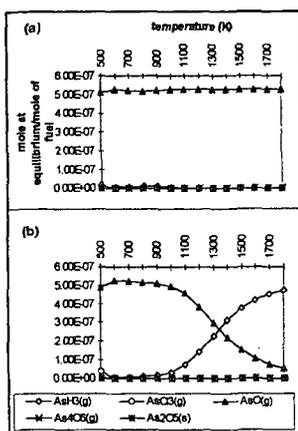


Fig 5: Equilibrium distribution of Arsenic species at 350 (a) and 300 (b) kg of air for Pittsburg #8 coal.

CONCLUSIONS

One route to the emission of VOC and PAH from combustion processes is via the formation of fuel-rich turbulent eddies in the flame. The local gaseous environment in these eddies favours the formation of super-equilibrium concentrations of all organic species. The concentration of CO may be used as a marker to calculate emissions of organic species, since a direct correlation is observed, although the nature of the fuel also influences the relative concentrations.

Trace metals, present in the fuel-rich "pockets", are predicted to change their speciation behaviour, compared to a fuel-lean situation. In some cases the thermodynamics acts in favour of decreasing the flue gas emission factor of the metal in question (e.g. thallium). However, the predictions for the influence on the emission of certain metal species (e.g. nickel and arsenic) is of concern. Possible routes to nickel carbonyl and arsene (AsH₃) are apparent.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to the Thai Government for financial assistance of Ms S Chaiklangmuang through a PhD studentship.

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FIELD TESTING OF THE ADVANCED HYBRID PARTICULATE COLLECTOR, A NEW CONCEPT FOR FINE-PARTICLE CONTROL

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KEYWORDS: Fine-particle control and coal-fired boiler

INTRODUCTION

A new concept in particulate control, called an advanced hybrid particulate collector (AHPC), is being developed at the Energy & Environmental Research Center (EERC) with U.S. Department of Energy (DOE) funding. In addition to DOE and the EERC, the project team includes W.L. Gore & Associates, Inc., Allied Environmental Technologies, Inc., and the Big Stone power station (jointly owned by three partners: Northwestern, Montana-Dakota Utilities, and Otter Tail Power Company.) The AHPC combines the best features of electrostatic precipitators (ESPs) and baghouses in a unique approach to develop a compact but highly efficient system. Filtration and electrostatics are employed in the same housing, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The AHPC provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs, and solves the problem of reentrainment and re-collection of dust in conventional baghouses.

The goals for the AHPC are as follows: >99.99% particulate collection efficiency for particle sizes from 0.01 to 50 μm , applicable for use with all U.S. coals, and cost savings compared to existing technologies.

The electrostatic and filtration zones are oriented to maximize fine-particle collection and minimize pressure drop. Ultrahigh fine-particle collection is achieved by removing over 90% of the dust before it reaches the fabric and using a GORE-TEX[®] membrane fabric to collect the particles that reach the filtration surface. Charge on the particles also enhances collection and minimizes pressure drop, since charged particles tend to form a more porous dust cake. The goal is to employ only enough ESP plate area to precollect approximately 90% of the dust. ESP models predict that 90% to 95% collection efficiency can be achieved with full-scale precipitators with a specific collection area (SCA) of less than 100 ft^2/kacfm [1]. Fabric filter models predict that face velocities greater than 12 ft/min are possible if some of the dust is precollected and the bags can be adequately cleaned. The challenge is to operate at an air-to-cloth (A/C) ratio of 12 ft/min or greater for economic benefits while achieving ultrahigh collection efficiency and controlling pressure drop. The combination of GORE-TEX[®] membrane filter media, small SCA, high A/C ratio, and unique geometry meets this challenge.

Studies have shown that fabric filter collection efficiency is likely to deteriorate significantly when the face velocity is increased [2, 3]. For high collection efficiency, the pores in the filter media must be effectively bridged (assuming they are larger than the average particle size). With conventional fabrics at low A/C ratios, the residual dust cake serves as part of the collection media, but at high A/C ratios, only a very light residual dust cake is acceptable, so the cake cannot be relied on to achieve high collection efficiency. The solution is to employ a sophisticated fabric that can ensure ultrahigh collection efficiency and endure frequent high-energy cleaning. In addition, the fabric should be reliable under the most severe chemical environment likely to be encountered (such as high SO_2). A fabric that meets these requirements

is GORE-TEX® membrane on GORE-TEX® felt. GORE-TEX® membrane filter bags consist of a microporous, expanded polytetrafluoroethylene (PTFE) membrane laminated to a felted or fabric backing material. Consequently, even fine, nonagglomerating particles do not penetrate the filter, resulting in significant improvements in filtration efficiency, especially for submicron particles. This fabric is also rugged enough to hold up under rigorous cleaning, and the all-PTFE construction alleviates concern over chemical attack under the most severe chemical environments.

Assuming that low particulate emissions can be maintained through the use of advanced filter materials and that 90% of the dust is precollected, operation at face velocities in the range from 12–24 ft/min should be possible, as long as the dust can be effectively removed from the bags and transferred to the hopper without significant redispersion and re-collection. With pulse-jet cleaning, heavy residual dust cakes are not typically a problem because of the fairly high cleaning energy that can be employed. However, the high cleaning energy can lead to significant redispersion of the dust and subsequent re-collection on the bags. The combination of a very high-energy pulse and a very light dust cake tends to make the problem of redispersion much worse. The barrier that limits operation at high A/C ratios is not so much the dislodging of dust from the bags as it is transferring the dislodged dust to the hopper. The AHPC achieves enhanced bag cleaning by employing electrostatic effects to precollect a significant portion of the dust and by trapping in the electrostatic zone the redispersed dust that comes off the bags following pulsing.

CONCEPT DEVELOPMENT AND FIELD TESTING

Phase I of the development effort consisted of design, construction, and testing of a 200-acfm working AHPC model [4, 5]. Since all of the developmental goals of Phase I were met, the approach was scaled up in Phase II to a size of 9000 acfm and installed at the Big Stone power station (see specification in Table I and top view in Figure 1).

Big Stone power plant was commissioned for service in 1975. The unit is a 450-MW-rated, Babcock and Wilcox cyclone-fired boiler. The primary fuel for the first 20 years of operation was North Dakota lignite, but four years ago, the primary fuel was switched to Powder River Basin subbituminous coal. This fuel has approximately one-half of the moisture and one-third more heat than North Dakota lignite. Almost all of the effects of this new fuel have been positive. However, one challenge that has occurred is the decreased efficiency of the ESP, due to an increase in resistivity of the fly ash. The combination of a very fine particle size produced from the cyclone-fired boiler and high ash resistivity make this a challenging test dust for the AHPC.

After completing the shakedown testing, the field AHPC unit was started on July 29, 1999. Based on shakedown testing, the initial secondary current was set at 50 mA and the bag cleaning trigger point was set at 8 in. W.C. to initiate pulsing all four rows of bags in sequence. The flow rate was set to a nominal 12 ft/min based on pitot readings. However, since the fan speed was not automatically controlled by the flow rate, there was always an increase in flow rate after pulsing. With the increase in flow after pulsing, the integrated average flow rate throughout the pulsing cycles was typically in the range from 12 to 13 ft/min during the first 6-week test period.

Over the course of the first 6 weeks, there were a number of interruptions to the operation. During this time, there were six unplanned outages to the plant ranging from a few hours up to 24 hours. In each case, the outage caused the induced-draft (ID) fan to shut down automatically, and the AHPC was then brought on-line manually when the plant was up to stable operating conditions. There were also two occurrences where significant rainfall led to water leaking into the AHPC around an insulator, which resulted in arcing and automatic shutdown of the ESP power supply. In these cases, the AHPC remained on-line, but the pulse interval increased significantly without ESP power.

While the multiple unplanned outages added difficulty to the AHPC operation, they also provided a severe test of the ruggedness of the AHPC during multiple start-ups, power outages, and moisture in the compartment. In spite of all of these interruptions, the AHPC continued to operate with a reasonable pulse-cleaning interval in the range from 10–30 minutes.

Two inlet and two outlet U.S. Environmental Protection Agency (EPA) Method 17 dust loadings were completed after 3 weeks of operation (see Table 2). Based on these measurements, the collection efficiency was at least 99.99%. However, the measured efficiency was somewhat limited by the weighing accuracy of the filters before and after sampling. The sampling time for the second outlet dust loading was extended to 17 hours to lower the detection limit. The ultrahigh collection efficiency was confirmed by the perfectly clean outlet filter, even after

sampling for 17 hours. The flue gas moisture values of 12% along with leak checks of the sampling trains before and after sampling provide quality control checks that the indicated flue gas volume was the actual volume sampled. Another indication of ultrahigh collection is that inspection of the clean plenum area of the AHPC following 6 weeks of operation showed the tube sheet to be completely clean.

Since the dust is known to cause operational difficulties for the Big Stone ESP because of high resistivity, it was expected that resistivity problems might also be an issue with the AHPC. Significant sparking and back corona were present from the first days of operation. Visual inspection through the sight ports during periods of severe sparking showed that sparking always was between the discharge electrodes and plates rather than between the electrodes and bags. In spite of a total of 150,000 sparks during the 6 weeks and some arcing when water leaked into the compartment, sparks were never observed going to the bags. In addition, after pulling bags and inspecting, there was no evidence of sparking damage.

Bag samples were analyzed using a microscope to determine if the high A/C ratio caused dust penetration. Under magnification of 10–50x, the media surface was clear of particulate matter after brushing, which indicates no dust penetration into the membrane.

The air permeability analysis of the AHPC filter bag media was performed in the lab using a Frazierometer. This device measures the amount of air that flows through a flat sample of media 3.5 in. in diameter and correlates it to a Frazier number. The Frazier number describes the volume of air (ft³/min) passing through 1 ft² of media at a differential pressure of 0.5 in. W.C. A Frazier number of 1.0 indicated 1 ft³/min/ft² at 0.5 in. W.C. Canceling units of ft², the Frazier number units are expressed as ft³/min at 0.5 in. W.C.

Samples of the three AHPC filter bags were cut from the top, middle, and bottom bag locations. The average Frazier numbers for the three bags were 1.9, 1.8, and 2.4 ft³/min at 0.5 in. W.C. Next, the samples were carefully brushed to remove the primary dust layer from the membrane surface. The samples were retested in the exact locations to measure the permeability change after brushing. The average bag permeabilities were 3.0, 3.0, and 4.6 ft³/min at 0.5 in. W.C. These media permeability values are typical of filter bags from coal-fired boiler applications. As a baseline, the new media Frazier number is generally within the range of 3.5–6.0 ft³/min at 0.5 in. W.C.

SUMMARY

After 6 weeks of operation, the bags seasoned to an on-line cleaned condition filter drag of 0.5 in. W.C./ft³/min, which is considered typical for a coal-fired boiler application, and there was no evidence of sparking to or across the media. The AHPC has met Phase II experimental objectives of operation, including A/C ratio of 12 ft³/min, dissipation of charge and spark potential, particulate release upon pulse-jet cleaning, low-particulate matter emissions, and recoverability from AHPC system upsets.

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TABLE 1

AHPC Specifications

Flow Rate	8646 acfm at 12 ft/min 11,520 acfm at 16 ft/min
Bags	32 (4 rows x 8 bags/row) 5.75 in. d. x 15 ft long
Bag Type	GORE-TEX® all ePTFE No-Stat®
Collection Plates	18 gauge, 29-in. spacing 14 ft 4 in. x 7 ft 3 in.
Discharge Electrodes	Rigid mast type with directional spikes toward plates
Discharge Electrode Spikes to Plate Distance	5 in.
Discharge Electrode Spike to Bag Distance	6.5 in.
Rappers	Pneumatic vibrator type for both plates and discharge electrodes
HV Power	ABB switched integrated rectifier (SIR)

TABLE 2

AHPC Dust Loadings Taken 8/18/99

Inlet		Sample	
Grains/scf	% H ₂ O	Time	
1.17	12.84	25 min	
1.36	12.84	15 min	

Outlet		Sample	Removal
Grains/scf	% H ₂ O	Time	Efficiency %
0.0000913	12.2	4 hr	99.993
0.0000398	11.8	17 hr	99.997

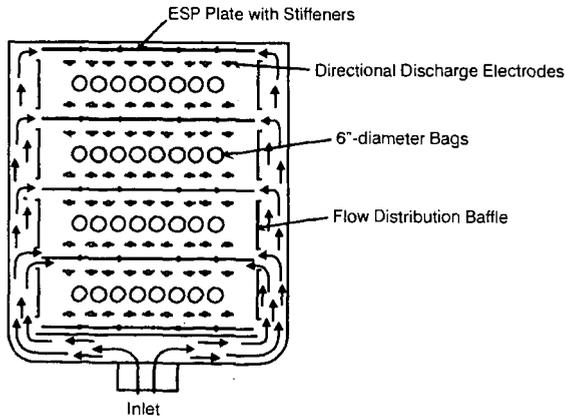


Figure 1. Top view of the 9000-acfm AHPC.

FORMATION OF ULTRA-FINE PARTICULATE MATTER FROM PULVERIZED COAL COMBUSTION

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KEYWORDS: PM2.5, coal-fired, power plants, fine particulate matter

INTRODUCTION

Although attention is focused currently on the emission of particles less than 2.5 microns (PM2.5) from stationary combustion systems, ultrafine or submicron particulate matter may prove to be an important constituent of PM2.5. Field observations¹⁻³ and theoretical considerations⁴ lead us to conclude that vaporization and condensation of ash occurs in pulverized coal-fired power plants. Furthermore, many toxic trace elements are enriched in the vaporization mode of the fly ash⁵ because many of the inorganic elements in coal are volatile at flame temperatures.^{6,7} In the flame zone, the inorganic vapors homogeneously nucleate to form an ultrafine aerosol with a primary particle size of 0.01 to 0.03 μm .⁵ Post-flame, the combustion gases cool rapidly to near room temperature in a time period of 2 to 5 s. The mean particle size of this condensation aerosol grows by coagulation. Calculations for a typical vapor loading show that the peak of the mass distribution grows to 0.03 to 0.07 μm in the range of 1 to 10 s.⁶ These ultrafine ash particles are not collected as efficiently by electrostatic precipitators as are the larger ash particles.⁹ Thus, toxic metals in the vaporization mode can be preferentially emitted to the atmosphere.

Measurements of submicron aerosol from full-scale coal-fired power plants show a distinct peak in the mass distribution falling in the range of 0.07 to 0.15 μm .^{1-3,9} These measurements are made at the ESP inlet, not in the flame zone. In one study,³ two submicron modes were observed with peak diameters at 0.07 microns and 0.4 μm . Scanning electron micrographs of the two submicrometer modes showed that the 0.4 μm particles were solid spheres, while the particles below 0.1 μm were agglomerates of ultrafine primary particles. In full-scale combustion systems, therefore, ash collected with diameters less than 0.1 to 0.2 μm could be attributed to vaporization.

The ultrafine mode can be ascribed to a vaporization-condensation mechanism.⁴ Taking into account all the observations mentioned above, the ultrafine mode has a peak (mass distribution) of 0.07 to 0.15 μm . The variation in the diameter is mostly due to the combustion conditions; coal type is a second order effect. This can be seen in the data of McElroy et al.² Six power plants of different designs were sampled. All but one were burning western sub-bituminous coals. Data are given on the fraction of the ash found in the submicron aerosol as a function of NO content in the exhaust gas (Figure 1). Since NO is related to the peak combustion temperature, Figure 1 shows that the combustion conditions have a strong effect on the amount of mass in the ultrafine mode. The type of coal and furnace design do not seem to have a strong influence on the amount of ash in the ultrafine mode. Although, it should be noted that while this data set represents most types of boilers (except cyclone-fired), five out of six of the coals are western sub-bituminous coals.

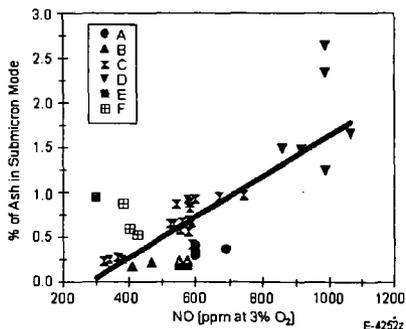


Figure 1. Mass fraction of ash in submicron mode as a function of NO for six different boilers.² Line is best fit ($r^2 = 0.57$).

The composition of the submicron mode from coal combustion varies with coal type. The most complete dataset is found in Quann and Sarofim.¹⁰ This work was both experimental and theoretical. The effects of coal rank, particle size, particle temperature and oxygen concentration were examined.

Also, a theoretical analysis on vaporization from included, excluded and atomically dispersed minerals was accomplished. This analysis indicates that the element vaporization depends on one or more of the following parameters: bulk oxygen concentration, coal rank, coal type, particle size and composition of inherent ash. Results of this effort for Si, Ca and Mg were in very good agreement with the experiments.

MODEL FORMULATION

In the present work, we used the theoretical framework of Quann and Sarofim¹⁰ to calculate the fraction of individual metal oxides (f_i) which vaporize during combustion of the char particle burning for time t_B . The total amount of metal oxides vaporized was then calculated by summing over all the major oxides. For this work, instead of calculating f_i/t_B from first principles, we used existing experimental results as reference, as described in Reference 10. The reference data were values for the fractional vaporization of a metal normalized to the char burnout time, $(f_i/t_B)_r$, the equilibrium partial pressure of the metal, $p_{i,r}$, the concentration of the element of interest in the coal particle, $C_{\alpha,r}$, and the coal particle radius (or diameter), r_x (d_w) for one bituminous and one low rank coal. The reference combustion conditions were a gas temperature of 1750 K and a bulk oxygen partial pressure of 0.2. The particle temperature under such combustion conditions was measured to be 2100 K.¹⁰ The following equations that use reference data were derived from Reference 10. For an element i found in mineral inclusions in the char particles:

$$f_v/t_B = (f_v/t_B)_r (p_i/p_{i,r}) (r_{\alpha}/r_o) (C_{\alpha}/C_o) \quad (1)$$

For an element i found primarily organically-bound to the char:

$$f_v/t_B = (f_v/t_B)_r (p_i/p_{i,r}) (r_{\alpha}/r_o)^2 (C_{\alpha}/C_o) \quad (2)$$

For an element i found in excluded mineral particles, not contained in char:

$$f_v/t_B = (f_v/t_B)_r (r_{\alpha}/r_o)^2 (C_{\alpha}/C_o) \quad (3)$$

The burnout time was computed assuming diffusion-limited combustion where the burnout time is proportional to the particle radius and the bulk oxygen concentration, p_{O_2} :

$$t_B \propto r_o^2 / \ln(1 + p_{O_2}) \quad (4)$$

The metal gaseous mole fractions, p_i and $p_{i,r}$, are calculated by assuming that the metal oxides undergo reduction during evaporation, for example:



And the partial pressure of SiO is equal to:

$$p_{SiO} = (a_{SiO_2} K_{eq} p_{CO})^{1/2} \quad (6)$$

where a_{SiO_2} is the activity coefficient and K_{eq} is the equilibrium constant. The activity coefficient is assumed to be independent of coal type and combustion conditions, so it cancels out in Eqs. (1) through (3). The equilibrium constants used were curvefits from data over a temperature range of 1500 to 2500 K as shown in Table 1.

The simple equilibria between CO and CO₂ can be used for each metal species of interest, assuming that oxygen diffusing to the char particle surface is completely consumed and that CO is

Table 1. Vaporization Equilibrium Equations and Equilibrium Coefficients - Equilibrium Constants at Temperature Char Temperature T are Calculated from $\ln(K)=A+B10^4/T$

Vaporization Equation	A	B
Na ₂ O+CO=2Na+CO ₂	17.8966	-2.8487
FeO+CO=Fe+CO ₂	11.4942	-4.2064
SiO ₂ +CO=SiO+CO ₂	18.8256	-5.9700
Al ₂ O ₃ +2CO=Al ₂ O+CO ₂	24.0505	-11.3361
MgO+CO=Mg+CO ₂	14.4976	-5.4094
CaO+CO=Ca+CO ₂	13.2182	-6.1507

the only product of combustion. In this case, the bulk oxygen concentration, p_{O_2b} , will determine the concentration of CO at the surface:

$$P_{CO_s} = 2 p_{O_2b} / (1 + p_{O_2b}) \quad (7)$$

The fraction of potassium vaporized was calculated from a separate equation, based on previous work which showed a good correlations between the fraction of potassium and sodium vaporized during coal combustion.¹²

$$f_{v-K} = 0.007706 + 0.6165746 f_{v-Na} \quad (8)$$

RESULTS

For validation purposes, we used our model to predict metal vaporization from a variety of coals burning at different conditions. Subsequently, we compared our predictions with experimental data. The purpose of this effort was to assess the accuracy of our model with respect to parameters that affect vaporization and then improve the accuracy by making proper corrections. The following parameters that affect the vaporization were examined: (a) the coal type, (b) the coal rank, (c) the coal particle diameter, (d) the oxygen concentration and (e) the element concentration in the coal. A complete set of vaporization data that involved a variety of coals, particle sizes and combustion conditions was given in Reference 10. In those experiments, vaporization from excluded minerals was negligible. Therefore, in our calculations we only accounted for vaporization from included and organically bound minerals.

Initially we calculated the fraction of Si, Na, K, Ca, Fe, Al and Mg that vaporized as oxides, namely: SiO_2 , Na_2O , K_2O , CaO , FeO , Al_2O_3 and MgO . Subsequently, the amounts of the individual amounts of vaporized oxides were estimated. Finally, the amounts of oxides vaporized were summed to get a calculated value of the total ash vaporized. As reference values for Eqs. (1) and (2), the following experimental data we used: (a) for vaporization of Na, Si, Fe and Al from bituminous coals, we used data for Illinois 6 from Quann,¹⁰ and (b) for vaporization of Na, Si, Fe, Al, Ca and Mg from sub-bituminous coals and lignites, we used data for Montana Savage lignite from Quann.¹⁰

Vaporization of major elements was predicted for Illinois 6 considering different coal particle sizes and bulk oxygen contents. Figure 2 shows the effect of oxygen concentration on vaporization from coal particles with diameters of 50 μm and 120 μm with a gas temperature of 1750 K. The model does a good job of predicting the effect of oxygen content on total vaporization. However, the effect of coal particle diameter is not modeled as well. Vaporization for large coal particles is over-predicted by two to three times.

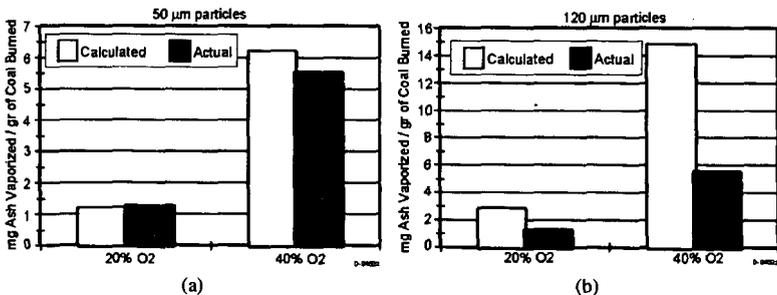


Figure 2. Effect of oxygen concentration on ash vaporization from Illinois 6 coal particles burning at a gas temperature of 1750 K for two different coal particle diameters: (a) 50 μm and (b) 120 μm .

Similar results were obtained for other bituminous coals. Figure 3 compares the amount of vaporization from 50 μm coal particles burning at a gas temperature of 1750 K for the Illinois 6 coal with two other bituminous coals. In Figure 4, the predicted and measured compositions of one of the bituminous coals are shown. The calculation tends to over-predict the amount of iron in the submicron ash for bituminous coals.

Vaporization of major elements was predicted for a Montana lignite considering different coal particle sizes and bulk oxygen contents. Figure 5 shows the effect of oxygen concentration on vaporization from low rank coal particles with diameters of 60 μm and 120 μm with a gas temperature of 1750 K. The model does a good job of predicting the effect of oxygen content and coal particle size on total vaporization.

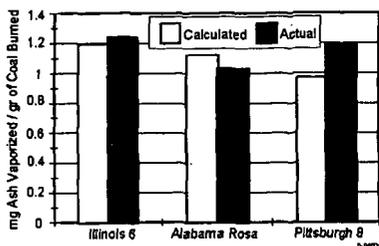


Figure 3. Predicted and measured ash vaporization from bituminous coals: 50 μm diameter particles burning in 20% oxygen with a gas temperature of 1750 K.

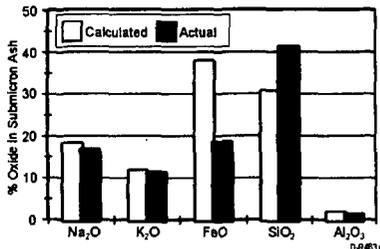


Figure 4. Predicted and measured submicron ash composition from combustion of Pittsburgh 8 coal: 50 μm diameter particles burning in 20% oxygen with a gas temperature of 1750 K.

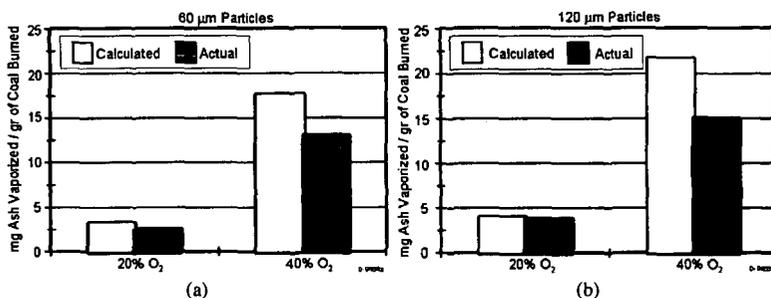


Figure 5. Effect of oxygen concentration on ash vaporization from Montana Savage lignite particles burning at a gas temperature of 1750 K for two different coal particle diameters: (a) 60 μm and (b) 120 μm .

Similar results were obtained for other low rank coals. Figure 6 compares the amount of vaporization from 60 μm coal particles burning at a gas temperature of 1750 K for the Montana Savage lignite (MO SVG L) coal with three other coals: Montana Rosebud sub-bituminous (MO RSB S), North Dakota Lignite (ND L), and Montana Powder River Basin sub-bituminous (MO PRB S).

SUMMARY

This work aimed to develop a model that predicts the vaporization of metals during coal combustion. The model is based on other existing models, experimental data and correlations of data. The main factors that affect the metal vaporization are: the coal rank, the coal type, the coal particle size, the oxygen content (and therefore the particle temperature) and the metal concentration in the coal. Our model predicts fairly accurately the amounts of ash that vaporizes and the submicron ash composition of bituminous coals based on a fixed reference condition. The effect of oxygen concentration and the metal composition of the coal on the ash vaporization are predicted well, but the effect of the coal particle diameter is not predicted accurately. Our model predicts fairly accurately the amounts of ash that vaporizes and the submicron ash composition from a variety of low rank coals based on a fixed reference condition. The model predicts the effect of coal particle size on the ash vaporization better than it does the effect of oxygen concentration, unlike the case of the bituminous coals. The modeling efforts should concentrate on the following areas: (a) the effects of coal particle size and oxygen concentration on the element evaporation and (b) the accuracy of iron and alkali vaporization.

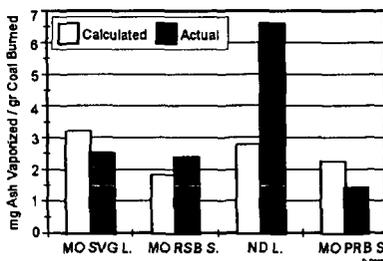


Figure 6. Predicted and measured ash vaporization from low rank coals: 60 μm diameter particles burning in 20% oxygen with a gas temperature of 1750 K. With the exception of the North Dakota lignite, the model accurately predicts the vaporization of major elements.

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The Effect of Blending Coals on Electrostatic Precipitator Performance

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Key Words: electrostatic precipitation, particulate emission, fly ash, coal, boilers

ABSTRACT

Tarong Power Station, in southern Queensland, Australia, operates 4 X 350 Mwe coal-fired boilers. The boilers fire the local, Meandu Coal from the isolated Tarong Basin. This coal contains 0.3 percent sulfur and 27 percent ash. This ash is 71 percent SiO₂, 27.5 percent Al₂O₃, and 1.9 percent TiO₂, with small amounts of other components. This coal has poor precipitation performance. With water injection, these plants emit 470 mg/Nm³ of particulate matter. Recent power plant trials blending Meandu with Jeebropilly coal from the Morton Basin (near Ipswich) and Wilke Creek Coal from the Surat Basin (near Dalby) with Meandu Coal have reduced the emissions to near 100 mg/Nm³.

The objective of this study was to identify the causes of the improved precipitator performance when Meandu Coal was blended with other coals and to determine the properties of other coals that would improve the precipitator performance. We gathered emission data from the power plant trials, measured particle size, and analyzed the fly ash for chemical composition, and electrical resistivity. We calculated drift velocities that confirm that Meandu fly ash is difficult, but Jeebropilly and Wilke Creek are easier to collect. We attributed the small difference between calculated and measured efficiency to the effect of ash resistivity. For the conditions studied, the difference in efficiencies did not primarily depend on particle size or sulfur concentration, but were related to the concentrations of alkali and alkaline earth metal in the fly ash.

INTRODUCTION

Many Australian Coals are considered difficult to precipitate. This is attributed to the low sulfur concentration of the coals and high quartz content of coal ash. This has been a consideration in purchasing Australian Export Coals for some time. Recently, Australia has begun to impose particulate emission standards on coal-fired power plants. Most of the power plants in Australia use Electrostatic Precipitators (ESP) to collect fly ash. Many Australian Coals are low in sulfur and the ashes are high in quartz. These fly ashes are difficult to collect in ESP's. The Meandu Coal, from the isolated Tarong basin, burned at Tarong Power Station has a fly ash that is particularly difficult to collect using an ESP. Table 1 shows that the Meandu Coal has 0.3 percent sulfur and 27 percent ash. The ash from Meandu Coal has 71 percent SiO₂, 27.5 percent Al₂O₃, 1.9 percent TiO₂, and small amounts of other constituents¹. Table 2 shows that the Meandu Coal, using water injection, has an emission of 470 mg/Nm³. However, blending the Meandu coal with Jeebropilly Coal, from the Morton basin near Ipswich or Wilke Creek Coal, from the Surat Basin near Dalby¹, improved the emissions to around 100 mg/Nm³. The purpose of this paper is to determine the cause of the improved collection efficiency when Meandu Coal is blended with Wilke Creek or Jeebropilly Coal.

ESP PERFORMANCE

The collection efficiency of an ESP is controlled by the Deutsch Equation^{2,4}:

$$\eta = 100 \times [1 - \exp(-w \times SCA)]$$

where η = the collect in percent

w = the drift velocity in m/s

SCA = the specific collection area in m²/m³-s

The drift velocity can be estimated by³:

$$W = k \times \epsilon \times \epsilon_0 \times E^2 \times d_{m50} / (\epsilon + 2) \times \mu$$

where: $k = 1/7$ = ratio of effective drift velocity to theoretical drift velocity
 ϵ = dielectric constant of the dust
 $\epsilon_0 = 8.85 \times 10^{-12}$ F/m = permittivity of free space
 E = electric field strength v/m
 d_{m50} = mass mean diameter of particles m
 μ = gas viscosity Pa.s

Table 1. Coal Properties¹

% AD	MEANDU	WILKE CREEK	JEBROOPILLY
H ₂ O	2.9	8.0	4.1
ASH	26.9	13.0	14.3
VOLATILES	27.5		39.8
% DAF			
C	79.5		81.1
H	5.43		6.38
N	1.45		1.61
S	0.37	0.5	0.70
O(DIFF)	13.3		10.2
% ASH			
SiO ₂	71.0		61.9
Al ₂ O ₃	27.5		32.7
Fe ₂ O ₃	0.74		1.58
CaO	0.26	1.75	0.74
MgO	0.11	1.40	0.74
Na ₂ O	0.03	0.80	1.10
K ₂ O	0.30	0.40	0.66
TiO ₂	1.86		2.13
Mn ₃ O ₄	0.01		0.01
SO ₃	0.04	0.60	0.22
P ₂ O ₅	0.02		0.04
BaO	0.02		0.07
SrO	0.02		0.06
ZnO	0.02		0.01

The ability to collect fly ash particles with an ESP depends on⁵: fundamental, mechanical, and operational limitations. In this paper, we investigate the fundamental problems associated with the characteristics of the fly ash and gas. These problems include:

- Particle
 - Resistivity
 - Size distribution
 - Structure
 - Density
 - Composition
 - Concentration
 - Agglomeration
- Gas
 - Temperature
 - Moisture
 - Flow

The ESP's at Tarong operate at 140 C, use water injection, and seem to have adequate flow patterns. We therefore concentrated on the properties of the particles that effect ESP collection efficiency.

Particle size did not seem to have a major effect on the collection efficiency for the coals studied. However, the nature of the fly ash particles did. We found resistivity to be the most important fly ash property.

The ESP's at Tarong operate at 20 kv over a 150 mm³ spacing. This is a low voltage. It is restricted by the breakdown and charging of the gas in the high gradient regions between particles. The potential could be increased if the particle resistivity was reduced.

EXPERIMENTAL

Tarong Power Station provided operating data and samples of the coal and resulting fly ash. The samples were analyzed for particle size distribution, chemical composition, and resistivity. Australian Industrial Coal Research Laboratory (ACIRL) performed the analyses⁶.

RESULTS

Table 2. shows the plant measurements for the Trials of Meandu Coal blended with Wilke Creek.

Table 2. Operating Performance of Meandu and Wilke Creek Coals^{3,7,8,9}

COAL	100 % MEANDU	50 % WILKE CK	100% WILKE CK
COAL T/H	170	138	138
% ASH	29.7	21.3	12.8
GAS DEN @140	0.88	0.88	0.88
FLUE GAS KG/S	626.2	627.6	689.1
IN DUST g/Nm ³	15.9	9.2	5.0
OUT DUST g/Nm ³	470	107	67
ESP EFF	97.0	98.8	98.8

Table 3. shows estimated efficiencies based on the Deutsch Equation. Baker, et al⁶ measured the dielectric constant for Meandu Coal as 1.79 and for Blackwater Coal (similar to Jeebropilly and Wilke Creek Coal) as 7.33. Here, we assume the dielectric constants for Jeebropilly and Wilke Creek Coals are about 10.

Table 3. Calculated Drift Velocities and ESP Efficiencies

COAL	100 % MEANDU	50 % JEEBROPILL	100 % JEEBROPILL	10 % WILKE CREEK
W cm/s	1.48	1.56	1.62	2.02
CAL EFF	97.87	98.27	98.50	99.47

Figure 1. shows that increasing alkali and alkaline earth metal concentration reduces the Meandu and Jeebropilly fly ash resistivity.

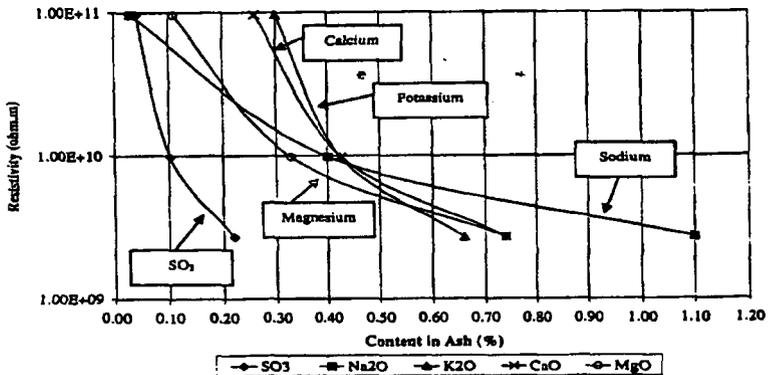


Figure 4.8: Influence of ash properties on resistivity

DISCUSSION

We find that the alkali and alkaline earth metal concentrations are the most important factors reducing the resistivity of the fly ash. This is consistent with earlier findings. Bush and Snyder¹⁰ found that sulfur, alkali metals, and water have the largest influence on fly ash resistivity. Harker and Pimparkar¹¹ reported that sulfur had limited effect on fly ash resistivity. Bush and Synder¹⁰, Bickelhaupt¹², Tidy¹³, and White¹⁴ now believe that the concentration of alkaline metals on the surface of fly ash particles are the most important factor in reducing resistivity.

Bush and Synder¹⁰ suggest that calcium and magnesium also reduce resistivity. Bickelhaupt¹² argues that potassium and lithium are key components in reducing ash resistivity. Tidy¹³ showed

that calcium, magnesium, lithium, and potassium were present on the surface of fly ash particles, but were less important in reducing resistivity than sodium. Bickelhaupt¹² thinks the reduced resistivity may be a combination of the above metals.

We find that all the alkali and alkaline earth metal reduce fly ash resistivity. The metals with the smallest ionic radii reduce fly ash resistivity the most for the coals studied. However, lithium concentration was not measured in the current study.

RECOMMENDATIONS

We will measure the lithium concentrations on the fly ash samples. In addition, we will do pilot scale combustion and ESP trials to determine the optimum amount of coal and type of coals to blend and to investigate the effect of injecting solutions of alkali and alkaline earth salts into the duct.

ACKNOWLEDGMENTS

The authors would like to acknowledge the help Tarong Power Station gave to this project. They would also like to acknowledge the work that ACIRL, Ipswich, did.

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THE CARBON MONOXIDE-ELEMENTAL CARBON LINK:
A METHODOLOGY FOR DIAGNOSING AND MONITORING SOOT IN URBAN AREAS

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BACKGROUND

Carbon monoxide (CO) and elemental carbon (soot) are produced in large quantities by incomplete combustion in urban areas. The effects of soot on health (*Dockery et al.*, 1992, 1993), photochemical processes (*Raga and Raga*, 1999) and on structural damage (*Mansfield et al.*, 1991; *Pio et al.*, 1998) has raised the scientific and public consciousness of the need to better understand and monitor soot formation, evolution, and transport, as well as its catalytic potential for surface heterogeneous reactions. The measurement and monitoring of CO is common in the large urban areas of first world countries and becoming more frequent in the cities of developing countries. The measurement of soot mass is more problematic because of its particulate nature and difficulty in quantification; however, because of its ubiquitous nature and potential for environmental damage at so many different levels, there is a serious need to assess its magnitude, both spatially and temporally. Recent measurements in Mexico City show a high correlation between CO and the light absorption coefficient, σ_a , and optical property of aerosols that is linearly related to the mass mixing ratio of soot (*Fuller et al.*, 1999). As a result, there is a possibility that CO can be used as a surrogate for soot concentrations if the physical basis for the link between these two atmospheric components is well understood.

There is an obvious link between CO and soot since both are produced in abundance during inefficient combustion processes. The formation of soot depends on the carbon/oxygen ratio in the hydrogen-air mixture during combustion. The combustion stoichiometry is (*Seinfeld and Pandis*, 1998)



where C_s is the soot formed and the ratio of carbon to oxygen is $m/2a$. The C/O ratio is critical for determining the amount of soot formed, i.e. if there is sufficient oxygen to tie up all available carbon as CO, then no soot will form. With less and less oxygen, more soot is formed. Thus, one would expect the relationship between CO and σ_a to be related to altitude, fuel composition, and combustion efficiency.

In the following sections, the measurement techniques and sampling site will be discussed, followed by an analysis of five, continuously high pollution days that represent typical conditions in a urban area. The presentation is closed with some preliminary conclusions and recommendations for additional studies.

MEASUREMENT AND ANALYSIS METHODOLOGY

The experimental site was located within the Mexico City Ajusco Ecological Reserve (19° 15' N, 99° 11' W), in the southwest corner of the Mexico City basin, at an elevation 440 m above the average city level of 2240m. This site provided measurements in the residue of the city's mixed layer at night and early morning, and in the polluted mixed layer that enveloped the site during the day. The field campaign extended from 4 to 18 November 1997, a period that is normally near the end of this region's rainy season.

Continuous measurements at a sampling rate of 1 Hz were made of carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO, NO_x) and ozone (O₃). The total scatter and hemispheric back scatter coefficient of aerosols were measured at three wavelengths (450, 550, 700 nm) with a nephelometer and the absorption coefficient, σ_a , with a particle soot absorption photometer (PSAP, Radiance Research Corp.), after the particles were first passed through a 1 µm cut-size impactor and heated to insure a relative humidity less than 40%. The PSAP measurements were corrected for light scattering and other effects that bias the absorption measurements using the suggested factors of *Bond et al.* (1999). The optical coefficients were averaged at one minute intervals, and taken 24 hours a day. Visible and ultraviolet solar radiation

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were measured with hemispheric radiometers. Meteorological measurements (wind speed and direction, temperature and relative humidity) were also recorded. The equipment was installed in a building within the Reserve, with all gas and aerosol samples taken from air coming through a chimney that extended above the building by approximately two meters (a total of approximately 8m above the ground) and ventilated with a flowrate of approximately $90 \text{ l} \cdot \text{m}^{-1}$. The meteorological measurements were made at the same elevation as the top of the stack, about three meters to the north. All the measurements were processed into six minute averages that corresponded to the accumulation interval of the DMA.

The remainder of this paper focuses on the measurements made of CO , σ_a , and wind.

RESULTS AND DISCUSSION

Five days during the research period were selected for the evaluation of the $\text{CO} - \sigma_a$ relationship, November 14-18, 1997. These days were selected since they are days with high ozone levels representative of the typical high pollution days in Mexico City. Figure 1 illustrates the daily trends in CO , O_3 , and σ_a over this five day period.

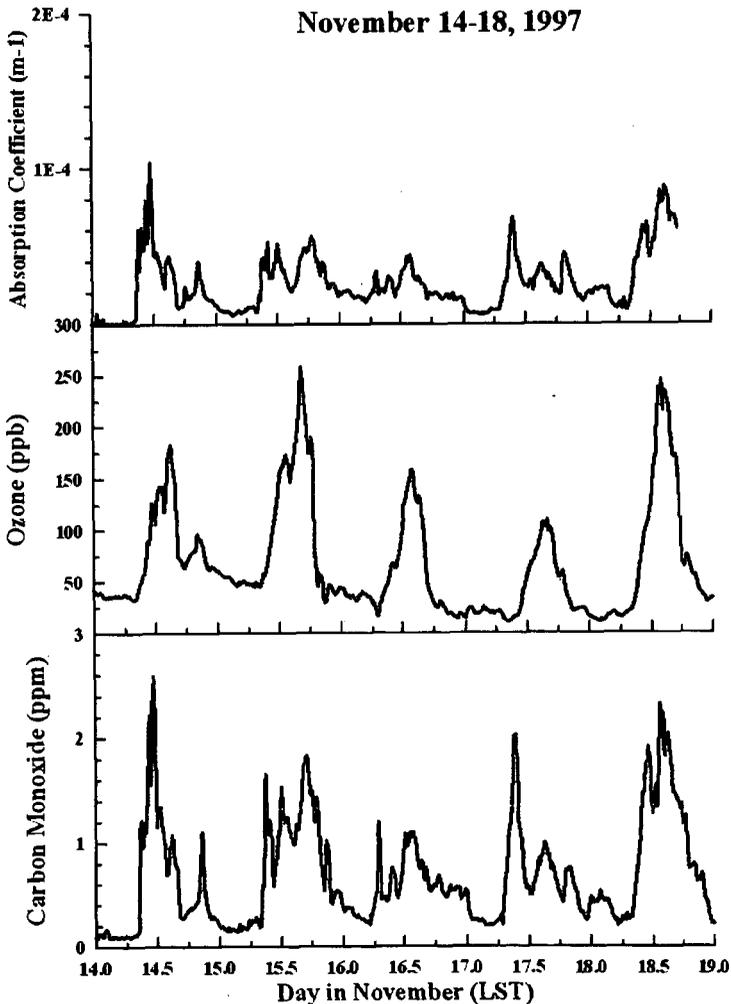


Figure 1

The initial rapid increase in CO occurs as the morning airflow shifts to a southwesterly direction and emissions from early morning traffic are transported up the hillside to the research site. As the sun rises and heats the Mexico City basin, the atmospheric mixed layer develops and grows to an altitude higher than the measurement site. Ozone increases with increasing actinic fluxes during the day. The relationship between CO and σ_a is clearly seen in Fig. 2 as the trends for one of the days, November 14, are displayed for the time period between 6:00 and 18:00 LST.

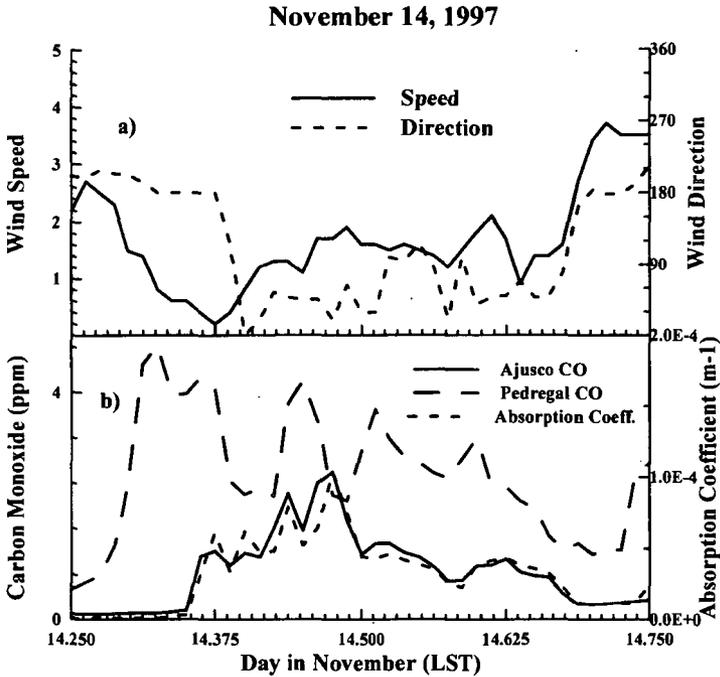


Figure 2

Figure 2b clearly shows that the σ_a changes with CO at the research site. Also presented in this figure is the CO measured upwind, in the city basin at one of the city's pollution monitoring sites (Pedregal). This particular research site is approximately two kilometers to the north of the Ajusco. When the winds are southerly at average speeds of 2 ms^{-1} (Fig. 2a), the CO measured at the Ajusco site represents the city level CO that has aged approximately one and a half hours. The CO normally decreased by about 50% from the city to the research site. This decrease occurred mostly as a result of dilution.

Figures 3 and 4 are scatter diagrams of σ_a Vs CO for all five days (Fig. 3) and four the 14, 16, and 17 of November only. The linear regression of σ_a as a function of CO, and Pearson correlation coefficient were computed and are shown on the two figures. These figures indicate a very good linear correspondence between σ_a and CO, reflected in statistically significant correlation coefficients, i.e. an indication that a first order polynomial fits the data well with high confidence levels. There is a certain degree of scatter, however, a group of points that appears to have a similar slope as the best fit line, but with an offset that could either be a decrease in σ_a or increase in CO. These data originate primarily from November 15 and 18, as seen in Fig. 4, where these days have been removed from the analysis. The slope and offset of the best-fit line, excluding these two days, is not significantly different and the correlation coefficient increases only slightly.

Further analysis of the relationship between σ_a and CO, with respect to meteorological conditions and other anthropogenic emissions, e.g. O_3 and NO_y , indicate that the linear regression coefficients of σ_a Vs CO remain remarkably constant regardless of local meteorology or other emission indicators.

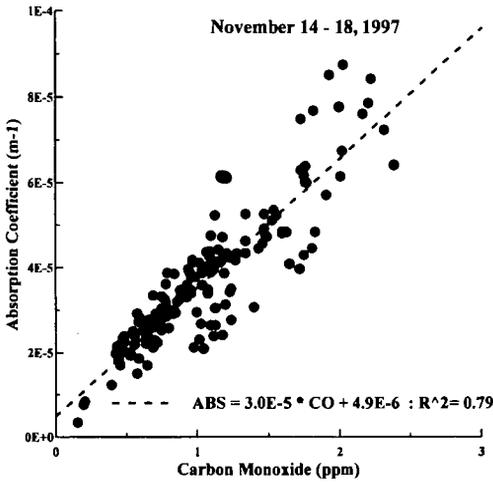


Figure 3

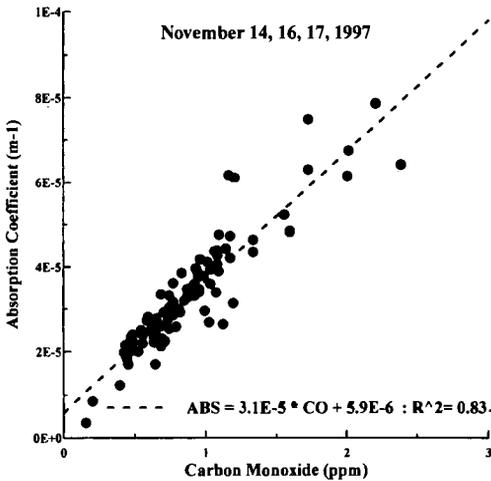


Figure 4

The positive offset, indicated by the non-zero intercept of the best-fit line, suggests that there is possibly some type of hysteresis that occurs on a daily basis, i.e. that there is a residual of soot aerosols that remain aloft when the mixed layer decays in the afternoon. When the five days were analyzed on an individual basis, although the slopes of the best-fit lines remained approximately 3×10^{-5} , the offsets ranged from $1 - 12 \times 10^{-6}$. This might be related to the previous days soot levels and maximum height of the mixed layer; however, additional evaluation of the measurements are needed before this can be better ascertained.

SUMMARY

As the amount of soot and CO produced by combustion is proportional to the type of fuel that is used and the amount of available oxygen, it is likely that the soot-CO relationship can vary from city to city. In addition, the current measurements were made several kilometers distant and 1-2 hours of aging downwind of the primary sources. Since the mixing and dilution processes are different for gases and aerosols, the CO- σ_a relationship may possibly depend upon the distance from emission sources, as well.

The ability to estimate soot from CO measurements is highly promising, however, because of the ease of measuring CO compared to soot, the abundance of past CO measurements that could be analyzed with this relationship, and the potential for better monitoring of soot in the future. Evaluation of this relationship continues at UNAM with a current focus on measuring CO and σ_a closer to emission sources in the city. The evaluation will concentrate on further refining the CO Vs σ_a relationship and understanding how other factors potentially affect this relationship.

The absorption coefficient is a useful parameter for assessing decreases in optical depth and the subsequent effect on radiative fluxes and impacts on photochemistry and climate change. The soot mass, however, is very important when evaluating the impact on health and heterogeneous processes. Hence, filter samples of aerosols are being analyzed to measure the soot mixing ratio. These will be used to estimate the specific absorption of Mexico City soot in order to convert absorption measurements to mixing ratios.

ACKNOWLEDGEMENTS

The experimental site was generously provided by J. Soberón and A. Hernández (Instituto de Ecología, UNAM). The authors thank Ing. Pedroza and his team at the Red Automática de Monitoreo Atmosférico (RAMA), who provided data from the monitoring network sites. Partial support for this study was provided by Academia Mexicana de Ciencias, the UNAM-CRAY program (SC007597) and Consejo Nacional de Ciencia y Tecnología de México (27528-T). The authors also thank Dr. John Ogren, NOAA Climate Modeling and Diagnostics Laboratory, for loan of the soot photometer system and helpful suggestions in interpreting the measurements from this instrument.

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Examination of Hydroxyl Polycyclic Aromatic Hydrocarbon Isomers Using Time of Flight Mass Spectrometry

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Key Words

Time of flight mass spectrometry
Polycyclic aromatic hydrocarbons
Photochemistry

Introduction

Determination of toxicity and health effects associated with particulate matter requires chemical speciation of the aerosol. Particulate matter formed by combustion processes contain a wide variety of polycyclic aromatic hydrocarbons (PAH) and their derivatives. PAH derivatives, such as nitro-PAHs, have significantly larger biological activity than unsubstituted PAHs. Exposure of the particulate matter to NO_x , SO_x , and photochemical atmospheric processes can produce substituted PAHs. Aromatic sulfonates have been studied as a contaminant in association with municipal waste water.[1] However, little is known about the possible effects of these hydrophilic aromatic sulfonates on the environment or about their degradation in the atmosphere.

Analytical tools for the qualitative and quantitative determination of highly water-soluble aromatic anions at the trace levels in aerosols have not been available. Currently, liquid chromatography is the most commonly used technique for detecting highly polar aromatics. However, liquid chromatographic methods require a large sample size and multiple runs [2][3].

Laser Desorption Ionization Time-of-Flight Mass Spectrometry (LDIMS) has proven to be an effective method for detection of trace levels of polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives [4][5] in airborne particulate matter. This paper discusses the use of LDIMS to examine two naphthalene sulfonate isomers (1-naphthol-4-sulfonic acid and 1-naphthol-3-sulfonic acid) and nitro-naphthanol isomers to study the structural information as well as possible photochemical reactions from the mass spectra.

Experimental

Two isomers: sodium salt of 1-naphthol-4-sulfonic acid (1,4-SNS) and sodium salt of 1-naphthol-3-sulfonic acid (1,3-SNS) were chosen for study. Both were purchased from TCI America (Portland, Oregon) and used without further purification. Each compound (10 mg) was dissolved in 1 ml methanol, and was mixed with 9 ml ethyl acetate. The solution was applied directly to the sample surface (20mm^2) of an aluminum probe and crystallized on the surface after normal air drying.

All the mass spectra were obtained using our custom built time-of-flight mass spectrometer. The sample probe was introduced into the instrument through a fast pump-down load-lock antechamber. Our previous papers provide a detailed description of the instrument [4].

A pulsed ultraviolet laser with the wavelength of 266nm was used for desorption and ionization. The 8 ns duration ionization pulses were produced by attenuating the fourth harmonic of a Spectra-Physics Quanta Ray DCR-3Nd:YAG laser. The laser energy was $\sim 0.8 \times 10^7 \text{W/cm}^2$ at the focus. Each mass spectrum is the sum of fifty-five laser shots at a 5 Hz repetition rate.

The ion source optics are composed of the repeller, the extractor and accelerator plates based on Wiley-McLaren design. Switching the polarity on the ion source plates can produce mass spectra of either positive or negative ions. In the positive ion mode, the potentials on each ion optics are: 7500v on the repeller, 2470v on the extractor, with the

accelerator and flight tube at ground potential. A microchannel plate (MCP) detector is set at the end of the 96 cm flight tube. A fast high-voltage transistor switch (HTS50-06 from Eurotek, Germany) is used to provide a 271 ns delay between the creation of the ions with the laser pulse and the application of the high voltage for extraction of the ions. The delayed extraction of the ions allowed time for prompt decay of metastable ions and yielded improved resolution.

Results and Discussion

The mass spectra of the two isomers given in Fig. 1 have several features in common. In negative mode (Fig. 1a and 1b), both isomers show a molecular peak with mass 246 and [M-Na]⁻ peak with mass 223. The [M-SO₃Na]⁻ anion with mass 143 is most intense because the carbon-sulfur bond is easily broken in the ionization process [6].

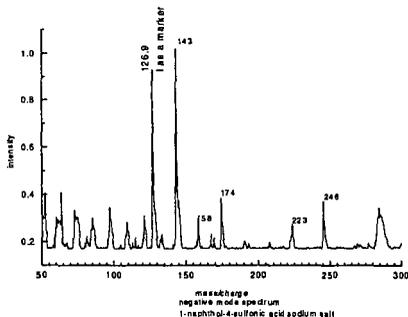


Fig. 1a

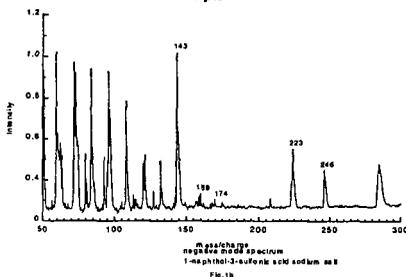
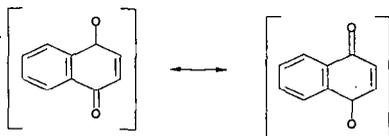
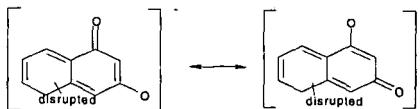


Fig. 1b

On the other hand, the two isomers did exhibit characteristic fragment ions in negative mode. The mass 158 anion is more stable in 1,4-SNS than in 1,3-SNS. The mass 158 anion is assigned as the naphthalene quinone anion, [M-SO₂Na-H]⁻, following a dissociation path similar to that reported by Binkley et al. [7]. The sulfonate anions can rearrange in the gas phase reaction and form phenoxide ions. The enhanced signal intensity for the 1,4 isomer is driven by the charge delocalization. The 1,3 isomer cannot delocalize the negative charge as effectively.

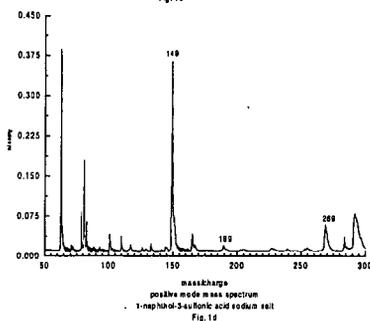
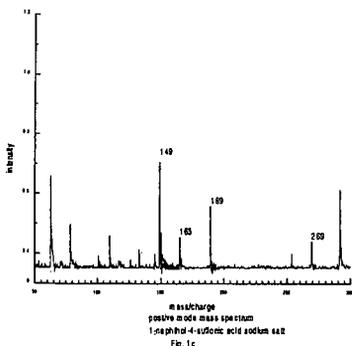


The 1,4-SNS forms quinone structure in which the negative charge is well distributed in the highly conjugated system



In 1,3-SNS the conjugate system is disrupted, therefore, the negative charge can not distribute as well as in 1,4-SNS. Therefore, the 158 anion is more stable in 1,4-SNS than in the 1,3-SNS.

Neither isomer forms a stable molecular positive ion, however diagnostic fragment ions are observed in Fig. 1c and 1d. Several sodium adduct ions are observed. The mass 269 peak, formed by association of Na^+ with the sulfonic acid salt, $[\text{M}+\text{Na}]^+$, is observed for both isomers. The Na^+ cation is the most intense peak due to the high vapor pressure of sodium and the low ionization potential.



The differences in the structure of the two isomers yields a difference in the positive ion spectra as well. The mass 189 cation is more intense in 1,4-SNS than in 1,3-SNS. The observation of Brykov et al. [8] that the 1,4 isomer can photochemically re-arrange in condensed phase or as a dimer pair to produce the 1,2 SNS isomer opens the possibility for a pathway that would produce the 189 cation. The 1,2 SNS isomer can form an epoxide adduct with Na^+ ions of mass 189.

Conclusion

In summary, the study of the 1,4-SNS and 1,3-SNS isomers provide new understanding of the fragmentation of the radical ions formed from hydrocarbon sulfates in gas phase. It demonstrates that slight change of molecular structure can cause differences in ion stability. The fragmentation pathways observed in mass spectrometry suggest that formation of naphthalene sulfonic acid in acidic sulfate aerosol droplets can lead to formation of naphthalene quinones by ultraviolet photochemistry.

Acknowledgment

This work was supported by the NIEHS Superfund Basic Research Grant P42ES-04699 and the California Air Resources Board.

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Chemical Composition of Fine Particles in the Tennessee Valley Region and Its Relationship to Stationary Sources

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To be Presented at the Symposium on Particulate Matter and Fossil-Fuel Combustion
ACS Division of Fuel Chemistry, San Francisco, CA, March 26-31, 2000

EXTENDED ABSTRACT

As the monitoring and regulatory implementation schedules for the revised particulate matter (PM) National Ambient Air Quality Standard (NAAQS) evolve, it is clear that the new annual NAAQS metric for fine particulate matter with aerodynamic diameter less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) will be difficult for many parts of the country to attain. The need to better understand the composition of fine particles ($\text{PM}_{2.5}$) and its temporal and spatial variability is broadly supported within regulatory, industrial and research communities. Realizing the potential consequences of the revised PM NAAQS, the Tennessee Valley Authority (TVA) and Tennessee Valley state and local regulatory organizations began operating the first comprehensive, regional prototype-FRM $\text{PM}_{2.5}$ monitoring network in the eastern U.S. on April 22, 1997^{1,2}. Every third-day $\text{PM}_{2.5}$ sampling was initiated at three core sampling stations in Nashville, Knoxville, and Lawrence County, TN. Five additional sites were added in Chattanooga and Memphis TN (August 1997), Decatur AL and Paducah KY (October 1997), and Huntsville, AL (June 1998).

The single-event particulate matter sampler models used in this effort included five prototype Partisol®-FRM Model 2000 (R&P Inc.) samplers, three prototype RAAS™ Model 2.5-100 (Graseby-Andersen) samplers, and one EPA-designated FRM $\text{PM}_{2.5}$ sampler, Model PQ200 (BGI Inc.). Each of these samplers draw air through a 10 micron (μm) size-selective inlet and remove particles greater than $2.5 \mu\text{m}$ with a WINS impactor. The $\text{PM}_{2.5}$ particles themselves were collected on Zefluor™ Teflon 46.2-mm filters with 2 mm pore size (Gelman Sciences, Inc.) through December 1998, thereafter on ID-stamped, Whatman filters with support rings. Initially, samples were collected for a 24-hour period every third-day; the sampling frequency was changed to every sixth-day on October 1, 1998.

Following gravimetric analysis (Mettler Microbalance), selected 24-hour samples were analyzed for elements Al through Pb using x-ray fluorescence (XRF) by EPA-approved Protocol 3. After XRF analysis, the samples were extracted ultrasonically and analyzed by the TVA's Support Services Group for ammonium by automated indophenol colorimetry and for sulfate and nitrate by ion chromatography. For selected sampling days at the network's core sites, samples of fine mass were collected on collocated samplers using quartz as the collection medium. These quartz filters were analyzed by the thermo-optical reflectance (TOR) technique³ for organic and elemental carbon. The filters were then extracted ultrasonically in water and analyzed for ammonium, sulfate, and nitrate as described above for Teflon filters. Data from the collocated Teflon & quartz samples were used to determine the average chemical composition of fine particles by season at the three core sites. Specific attention was given to seasonal variations in the fine particle chemical composition, and in composition differences between urban and rural sites.

During two additional periods, more intensive sampling was done at a mobile-source impacted site in Chattanooga, TN, about 3 km from the network site. Continuous measurements of mass (TEOM) and light scattering ($3\text{-}\lambda$ nephelometer) were made in early March, 1998, and repeated, with the addition of continuous elemental carbon measurements (aethalometer⁴), in September, 1998. The data from these measurements were used to examine diurnal and seasonal variations in mass and composition at this site. A new sampler (PC-BOSS⁵) designed to accurately measure both non-volatile and semi-volatile constituents of fine mass was tested at urban and rural sites to test the accuracy of the prototype FRMs. Our ongoing assessment of data from network and special studies allow us to provide preliminary answers to the following questions.

- *What are the fine particle mass concentrations in the South-central US and what are the implications relative to the NAAQS?* Fine particle annual mass concentrations in the Tennessee Valley range from 14 to 20 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). All seven urban/suburban sites exceeded the $15 \mu\text{g}/\text{m}^3$ level of the annual $\text{PM}_{2.5}$ standard. The rural Lawrence County TN site remained below the annual standard (Table). None of the stations exceeded the $65 \mu\text{g}/\text{m}^3$ level of the 24-hour $\text{PM}_{2.5}$ standard. Summer high-winter low seasonality is evident.

- *How well does the Federal FRM measure fine mass and what positive and negative biases does it have?* The current FRM PM_{2.5} mass measurements underestimate the contribution of volatile/semi-volatile nitrates and organic carbon species. Preliminary information from the summer of 1997 (PC-BOSS sampler) at our Lawrence County site indicates that the semi-volatile fraction is both highly variable and significant⁶. Since the organic fraction of fine particles appears to be highly suspect from a health effects standpoint, it is prudent to make periodic assessments of semi-volatile and non-volatile organic carbon fractions when particle composition measurements are made.

- *What is the composition of these fine particles and what do they imply for development of control strategies?* Based on composition measurements, both inorganic sulfate and carbonaceous compounds make up large fractions of PM_{2.5} mass (Figure). Sulfate provides the largest fraction (≈50%) in background air (Lawrence County) with organic carbon compounds making up next largest fraction (≈33%). For the urban stations the situation is largely reversed with the organic aerosol fraction being dominant (≈50%) followed by sulfate (≈30%). Control strategies designed to lower organic carbon (transportation and industrial sources) and sulfur dioxide emissions (fossil fuel combustion sources) will therefore be most effective in achieving compliance with the PM_{2.5} annual NAAQS.

- *What are the spatial, seasonal, and diurnal variations in these concentrations and what does this tell us about sources and fates?* Higher fractions of sulfate are found in fine particles at all sites in the summer months, compared to the remainder of the year. Diurnal variations show the effects of primary sources and meteorology, with higher concentrations of primary particles (e.g., elemental carbon) during the morning rush hour and higher concentrations of all constituents at the surface during periods in which a stable surface layer is present (poor vertical mixing).

- *What are the controllable fractions of fine mass and what are the sources of those potentially controllable fractions?* The largest fractions of fine mass are attributable to organic carbonaceous material and ammonium sulfates. The sulfate fraction can in theory be controlled by further reducing emissions of its gaseous precursor, SO₂, although non-linear gas-to-particle conversion processes appear to be reducing the “bang for the buck”. The organic fraction is largely uncharacterized and a high priority should be placed on characterizing what fraction of it is controllable by reducing man-made emissions of particulate organics and their gas-phase precursors.

Table Monthly Mean PM_{2.5} Mass Concentrations (µg/m³). TN Valley PM_{2.5} Network

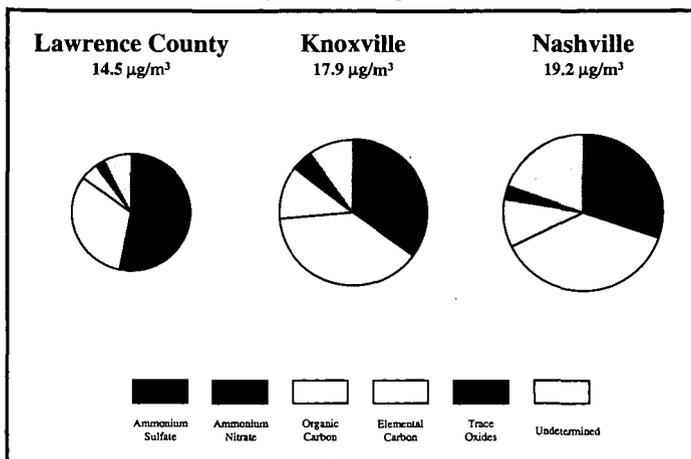
Month/Station	LC	KN	NS	CH	MP	DC	PD	HV	Mean
May-97	8.9	14.8	12.9						12.2
Jun-97	14.3	15.8	20.8						17.0
Jul-97	21.8	23.7	23.7						23.1
Aug-97	15.8	19.9	22.0	22.5					20.1
Sep-97	18.1	20.6	21.7	23.2	19.1				20.6
Oct-97	13.8	15.8	19.1	24.6	16.9	18.8	16.8		18.0
Nov-97	13.2	20.1	18.0	19.9	15.6				17.4
Dec-97	13.7	19.2	20.8	21.9	17.7	23.3	18.1		19.3
Jan-98	9.8	17.5	12.4	16.6	13.3		14.1		14.0
Feb-98	12.4	9.6	17.6	15.7	22.6		16.6		15.7
Mar-98	11.4	10.0	16.3	14.4	15.4	15.6	13.0		13.7
Apr-98	14.0	13.8	16.3	16.2	16.0	22.9	15.0		16.3
May-98	16.9	26.8	22.7	24.7	26.0	22.4	23.2		23.2
Jun-98	13.8	14.5	16.4	16.9	18.8	23.7	15.6		17.1
Jul-98	15.6	22.5	22.0	22.2	18.1	24.8	24.3	24.6	21.8
Aug-98	22.7	25.4	32.8	30.3	22.0	22.4	31.8	24.8	26.5
Sep-98	18.5	23.1	21.8	26.4	20.8		19.3	19.6	21.3
Oct-98	10.5	11.8	17.2	14.9	10.5		10.6	14.4	12.8
Nov-98	15.9	16.5	16.9	26.2	15.1		23.9	20.5	19.3
Dec-98	8.3	12.9	12.5	10.6	10.7		11.2	10.6	11.0
Jan-99	10.3	12.3	13.7	13.7	9.7		13.0	11.8	12.1
Feb-99	11.3	13.4	15.1	16.3	11.5		14.7	14.3	13.8
Mar-99	8.8		13.1	13.1	9.5		14.6	11.3	11.7
Apr-99	9.7		10.8	12.9			11.7	10.3	11.1
May-99	13.9			20.2			12.5	13.5	15.0
Jun-99	15.0			22.2			22.2	15.3	18.7
Station Mean	13.8	17.3	18.2	19.4	16.3	21.7	17.1	15.9	17.0

LC=Lawrence County TN, KN=Knoxville TN, NS=Nashville TN, CH=Chattanooga TN, MP=Memphis TN, DC=Decatur AL, PD=Paducah KY, HV=Huntsville AL.

Conclusions

TVA has measured fine particles ($PM_{2.5}$) in the Tennessee Valley region using prototype Federal Reference Method (FRM) samplers since April, 1997, and results indicate that compliance with the new NAAQS annual standard will be difficult. The chemical composition of fine particle samples has been estimated, and our results indicate that about 1/3 of the measured mass is sulfate, 1/3 is organic species, and the remainder is "other". The sulfate fraction is highest at rural sites and during summer months, with uniformly large fractions of organic aerosol in urban areas. Short-term variability of fine particle mass has been measured, and sampling performed which accounts for semi-volatile constituents of fine mass (nitrates, organics). Results show diurnal variability affecting exposure, and suggest that FRM measurements significantly underestimate organic constituents. Potentially controllable anthropogenic sources of fine particulate organics remain largely uncharacterized.

Figure $PM_{2.5}$ Composition



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SOURCING COAL COMBUSTION-DERIVED PAH IN THE ENVIRONMENT

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Keywords: Polycyclic aromatic hydrocarbons, coal combustion, source-apportionment.

ABSTRACT

To investigate the effects of domestic coal burning on the distribution and isotopic composition of environmental PAH, a series of soil samples were collected in a coal-burning village (Lochwinnoch) nearby Glasgow, UK. Analyses showed that, typically, PAHs in the Lochwinnoch samples were isotopically heavy having $\delta^{13}\text{C}$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. It was also noted, however, that alkylated PAHs would appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Therefore, to address the possibility that parent PAHs may survive in soils preferentially, two weathering experiments have commenced using a low temperature coal carbonisation tar from the Coalite process. Initial results have shown that after as little as 80 days weathering period, parent PAHs, particularly fluoranthene and pyrene, become more prominent than the alkylated species, suggesting that parent PAHs survive oxidation/weathering to a greater extent than their alkylated counterparts.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) in the environment arise from a number of potential natural and anthropogenic sources, with major contributions from coal utilisation⁽¹⁾, diesel exhaust emissions⁽²⁾ and biomass combustion – both accidental and intentional⁽³⁾. Although conventional analytical techniques are useful for the identification and quantification of PAH in environmental samples, they provide little information on the source of these pollutants. The potential of using compound-specific isotopic analysis for source-apportionment of environmental PAH has been demonstrated by O'Malley *et al.*^(4,5), Lichtfouse *et al.*⁽⁶⁾ and the authors⁽⁷⁻¹⁰⁾. O'Malley *et al.* indicated that PAH arising from woodburning and vehicle emissions exhibited significantly different isotopic signatures⁽⁴⁾ and the same authors have also reported the isotopic compositions of *n*-alkanes and PAH produced from combustion of C₃ and C₄ plant species⁽⁵⁾. Lichtfouse *et al.*⁽⁶⁾ have reported significant anthropogenic hydrocarbon inputs into soil using a combination of biomarker, $\delta^{13}\text{C}$ and ^{14}C analyses. The authors have found that the $^{13}\text{C}/^{12}\text{C}$ isotopic ratios for PAH derived from coal and wood pyrolysis and diesel particulates vary over a range by ca. 8 ‰ which could provide a basis for source apportionment in a number of environments⁽⁷⁾.

To establish a basis for applying gas chromatography - isotope ratio mass spectrometry ($\delta^{13}\text{C}$ GC-IRMS) to source PAHs from coal utilisation, stable isotopic ratios have been determined as a function of coal rank and process conditions⁽⁸⁻¹⁰⁾. The results have indicated that the primary control on the isotopic values of coal-derived PAHs is the extent of ring growth required to form PAHs during processing. Thus, for relatively mild conversion processes such as low temperature carbonisation where the major aromatics are alkyl substituted 2-3 ring PAHs, the isotopic signatures are similar to those of the parent coals (ca. -25 ‰). However, the $\delta^{13}\text{C}$ values for the PAHs become lighter in going to high temperature carbonisation, gasification and fluidised-bed combustion as the extent of ring condensation increases and confirming that the PAHs are not released as primary volatiles. To demonstrate the applicability of the technique to the analysis of environmental PAHs where major inputs from coals could be expected, samples collected in the vicinity of a low temperature carbonisation plant in the UK were analysed^(9,10). In addition to low temperature coal tar, significant inputs of PAHs from transport fuels, high temperature carbonisation and combustion sources (coal/biomass) were inferred from the isotopic ratios, taken in conjunction with the differences in alkyl substitution patterns.

In this paper we report findings on PAH formation in domestic (grate) combustion and resultant isotopic compositions. Furthermore, to trace PAH from domestic combustion, a series of soil samples have been collected in the area of Lochwinnoch, a village approximately 15 miles south west of Glasgow, UK, where a large proportion of the domestic properties still use coal combustion as a primary source of heating. To determine the fate of PAH following emission to the environment, an experiment has commenced using soil spiked with low

temperature coal carbonisation tar from the Coalite process^(9,10) to investigate the effect of biodegradation/weathering on PAH survival and their resultant isotopic compositions.

EXPERIMENTAL

Three domestic soot samples were selected for analysis. The first sample (domestic fire soot 1) emanates from a single coal-burning fire chimney and the sample supplied by a local chimney sweep also comes from a series of fires burning only coal. However, the second soot sample (domestic fire soot 2) is from a domestic fire on which both coal and wood have been burned. Soil samples were collected from various points in the village of Lochwinnoch, 15 miles south west of Glasgow, UK. Collection sites encompassed areas the village Main Street (sample LW5), the centre of a residential area of the village (sample LW6) and a sample collected from a heritage trail approximately 1 mile from the centre of the village (sample LW7).

Soil from open ground approximately 1 mile from Glasgow city centre was dried at 40 °C *in vacuo*, and the soil sample was then mixed with a predetermined quantity of low temperature coal tar (20 % w/w). The coal tar-coated soil was divided into sub-fractions that were placed where the original soil sample was collected. Each sub-fraction was packed in a roughly cylindrical area to a depth of approximately 2 cm and diameter of 6 cm (the beds for each sub-fraction were approximately 3 cm apart). The sub-fractions have been recovered after increasing periods of time. By the time the second sample was taken (80 days), grass growth was already evident over the coal tar coated soil.

All soil and soot samples were dried *in vacuo* at 40°C, soil samples ground to 75-212 µm particle size and all samples (including tar pre-coated soil) extracted by reflux in dichloromethane (DCM) for 10 hours. The DCM extracts (following solvent removal) were fractionated by open column alumina chromatography (fine grain activated neutral alumina) to yield neutral aromatic fractions for $\delta^{13}\text{C}$ GC-IRMS analysis as described previously^(7,8,10). Reported isotopic data represent the arithmetic means of at least two duplicate analyses and the estimated repeatability for individual hydrocarbons, based on an earlier study by Eakin *et al*⁽¹¹⁾ with the VG Isochrom II GC-IRMS system, is 0.2-0.4 %. The experimental error of the machine was between 0.5 and 1.0 ‰, with precision decreasing as the intensity of GC peaks, in relation to the unresolved background, decreased.

RESULTS AND DISCUSSION

Domestic Soot Samples

Figure 1 compares the gas chromatograms for the neutral aromatics extracted from the domestic soot samples. The isotopic compositions of extracted PAH for 2 of the samples are listed in Table 1. The sample provided by the chimney sweep emanates from coal fires as does soot sample number 1 (collected from a single chimney). However, domestic soot sample number 2 was obtained from the chimney of a domestic fire on which both coal and wood have been burned. The parent PAHs in sample 2 are much more dominant than in the other two samples (Figure 1) and their $\delta^{13}\text{C}$ values are in the region of -28 to -30 ‰. As can be seen from Table 1, the isotopic compositions of PAH extracted from soot sample number 1, where coal is known to be the sole contributor, lie in the region of -25 ‰. Since UK bituminous coals are known to exhibit bulk isotopic compositions in the region of -24 to -25 ‰^(9,10), this would suggest that PAH released are primary volatiles from coal devolatilisation. By considering these isotopic compositions and also taking account of the fact that wood burning gives PAHs with values below -30 ‰⁽⁷⁾, it can be suggested that, in this instance, the PAHs in domestic soot sample number 2 have been sourced from both coal and wood. The parent PAHs are more dominant in the soot provided by the chimney sweep than in the first domestic sample analysed, but alkylated PAHs are still major constituents (Figure 1). Comparison of the two coal-burning chimney samples suggests that the ratio of alkylated to parent PAHs varies considerably in soot from domestic fires and is clearly going to reflect the average devolatilisation temperature. The authors are now conducting tests under controlled conditions on both bituminous coals and smokeless fuels to further examine this phenomenon.

Lochwinnoch Soil Samples

Figure 2 shows the gas chromatograms for the neutral aromatics extracted from the Lochwinnoch soil samples investigated and Table 2 lists the $\delta^{13}\text{C}$ values of selected PAHs and the neutral aromatic yields for each of the samples. A full suite of samples have been analysed by GC, but the 3 samples selected for GC-IRMS exemplify the variations found in composition. Sample LW5 was collected from the village Main Street and, as well as the parent PAH peaks, a broad unresolved hump is also evident in the chromatogram. This is characteristic of the highly complex distribution of heavily substituted alkyl aromatics found in diesel particulates^(7,9,10). The

sample collected from a residential street (LW7) displays a similar distribution of parent PAH as the main street sample, but the broad shoulder arising from heavily substituted alkyl aromatics is much less prominent in the chromatogram (Figure 2), suggesting a lower input from diesel particulate. A sample was also collected from a heritage trail situated approximately one mile from the centre of the village (LW 6), which displays a different distribution of parent PAH to the other two samples. As can be seen from Table 2, the total concentration of neutral aromatics in the heritage trail sample (0.02 %) was also significantly lower than corresponding concentrations in the residential street sample (0.08 %) and the main street sample (0.2 %).

The $\delta^{13}\text{C}$ values for the parent PAH are generally quite similar for samples LW5 and LW7 and mainly occur in the range -24 to -26 ‰, consistent with the PAHs arising from domestic coal burning. However, alkylated aromatics are much less prominent in the residential street sample (LW7) than the soot samples obtained thus far from coal fires (cf. Figures 1 and 2). The slightly heavier values (ca. -24 ‰) for the lower molecular mass PAH in the main street sample (LW5) could be indicative of biodegradation/weathering having occurred to a greater extent in relation to LW7. The distribution of parent PAHs in the Heritage Trail sample (LW6) is significantly different to that for the other two samples. Further, the higher molecular mass PAHs and phenanthrene/anthracene are isotopically light (-29 to -30.5 ‰) suggesting an input from sources other than coal and diesel. The location of the Heritage Trail sample in conjunction with the isotopically light PAH would suggest an input from biomass combustion.

Weathering experiment

The GC traces of the neutral aromatics from the initial low temperature tar and the tars recovered after the soil had been in the ground for 40 and 80 days are compared in Figure 3. After 40 days, the lower molecular mass constituents (alkylnaphthalenes) decreased to a considerable extent and, after 80 days, the proportions of parent PAHs remaining, notably fluoranthene and pyrene, are beginning to increase in relation to the complex distribution of alkylated aromatics whose peaks dominate the GC trace for the initial tar. Thus, these preliminary results appear to provide direct evidence that, even after a relatively short weathering period, the alkylated aromatics are beginning to be depleted preferentially in relation to the parent PAHs.

CONCLUSIONS

The PAHs in the Lochwinnoch village samples were isotopically heavy having $\delta^{13}\text{C}$ values close to -25 ‰ that are consistent with the PAHs emanating from coal burning. The sample collected from a trail outside the centre of the village exhibited a different distribution of PAH to those collected on the main street and residential area. However, alkylated PAHs appear to be more prominent in soot from coal fires than in the samples collected in Lochwinnoch where domestic combustion was determined to be the major source. Initial results from a weathering experiment show that after as little as 80 days, parent PAHs, particularly fluoranthene and pyrene, become more prominent than alkylated species, suggesting that these compounds may survive biodegradation to a greater extent than their alkylated counterparts.

ACKNOWLEDGEMENT

The authors thank the British Coal Utilisation Research Association (BCURA) for financial support.

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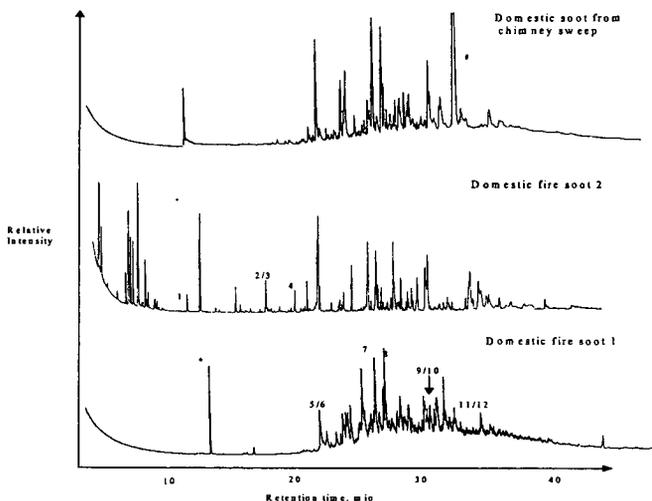


Figure 1 GC traces for the aromatics from the domestic soot samples
 Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; 14. Dibenz(a,h)anthracene; 15. Benzo(ghi)perylene; 16. Indeno(1,2,3)pyrene; * Internal standard; #plasticiser

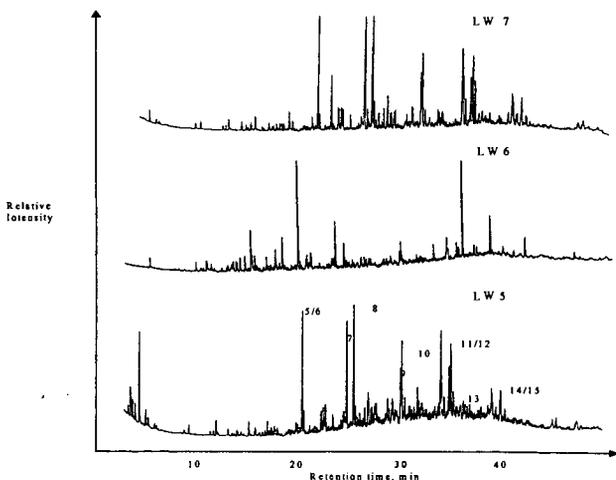


Figure 2 GC traces for aromatic fractions from Lochwinnoch samples
 Key 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benz(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; 14. Dibenz(a,h)anthracene; 15. Benzo(ghi)perylene; * Internal standard.

Table 1 Isotopic compositions of PAH extracted from domestic soot samples

PAH	Soot 1	Soot 2
Phenanthrene	-24.8	-29.0
Anthracene	-25.5	-28.9
Fluoranthene	-25.9	-30.6
Pyrene	-26.1	-28.9
Benzo(a)anthracene	-25.2	-29.5
Chrysene	-25.2	-29.4
Benzo(a)fluoranthene	-24.2	-29.4
Benzo(k)fluoranthene	-24.5	-29.5

Table 2 Neutral aromatic yields and isotopic compositions of PAH extracted from Lochwinnoch samples

PAH	Sample/Isotopic Composition (%)		
	LW 5	LW 6	LW 7
1. Naphthalene	-24.6	-	-
2. Acenaphthylene	-	-	-25.0
3. Acenaphthene	-	-	-25.0
4. Fluorene	-23.9	-25.1	-25.8
5. Phenanthrene	-23.7	-29.1	-25.6
6. Anthracene	-23.7	-29.1	-28.1
7. Fluoranthene	-24.7	-25.0	-25.1
8. Pyrene	-25.3	-25.2	-25.7
9. Benzo(a)anthracene	-24.7	-26.0	-26.0
10. Chrysene	-24.7	-26.0	-26.0
11. Benzo(a)fluoranthene	-25.2	-30.5	-25.7
12. Benzo(k)fluoranthene	-25.2	-30.5	-25.7
13. Benzo(a)pyrene	-25.3	-30.5	-26.8
Neutral aromatic yield (%)	0.21	0.02	0.08

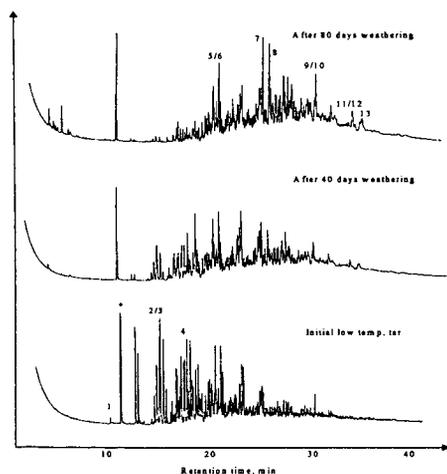


Figure 3 GC traces for aromatic fractions from the coal tar and soil extracts after 40 and 80 days
 Key 1. Naphthalene; 2. Acenaphthylene; 3. Acenaphthene; 4. Fluorene; 5. Phenanthrene; 6. Anthracene; 7. Fluoranthene; 8. Pyrene; 9. Benzo(a)anthracene; 10. Chrysene; 11. Benzo(b)fluoranthene; 12. Benzo(k)fluoranthene; 13. Benzo(a)pyrene; *Internal Standard.

AMBIENT FINE PARTICULATE MATTER (PM_{2.5}) SAMPLING AND ANALYSIS IN THE UPPER OHIO RIVER VALLEY

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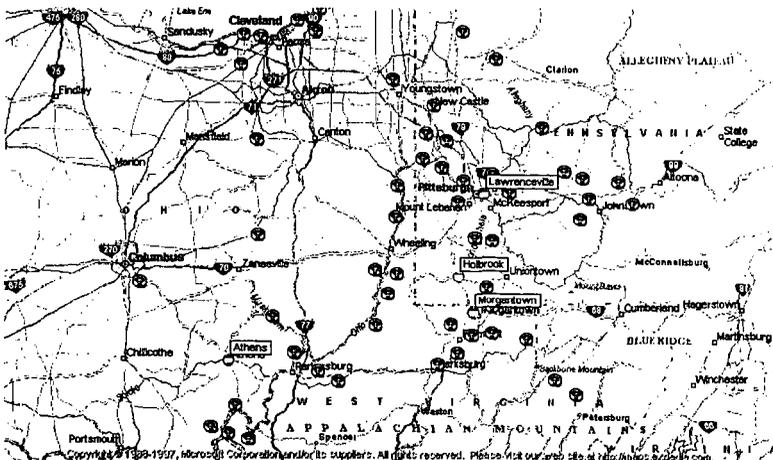
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INTRODUCTION

Ambient fine particulate matter (PM_{2.5}) originates from a wide variety of emission sources, both man-made and natural. The combustion of coal to generate electricity can produce primary PM_{2.5} (e.g., fly ash, carbon soot, associated trace metals), the gaseous precursors (e.g., SO₂ and NO_x) to the formation of secondary fine particles (e.g., ammonium sulfates and nitrates), and condensable species (e.g., H₂SO₄). However, there remain numerous uncertainties regarding the linkage between coal-fired boiler emissions and the visibility and health-related impacts that have been associated with ambient fine particulates. As part of its ambient fine particulate program, the DOE-Federal Energy Technology Center (DOE-FETC), in cooperation with key stakeholders including EPA, local and state environmental agencies, industry, and academia, established and is operating several PM_{2.5} speciation sites in the Upper Ohio River Valley (UORV).

The overall goal of the Upper Ohio River Valley Project (UORVP), is to investigate the nature and composition of fine particulate (PM_{2.5}) and its precursor gases in the Upper Ohio River Valley and provide a better understanding of the relationship between coal-based power system emissions and ambient air quality in the Upper Ohio River Valley region. This geographical area, encompassing southeastern Ohio, western Pennsylvania, and northwestern West Virginia, was chosen for this extensive fine particulate research because it mirrors an area in the eastern half of the continental United States that is not well characterized but has a high density of coal-fired electric utility, heavy industry (e.g., coke and steel making), light industry, and transportation emission sources. The UORV is also in the center of the ozone transport region, which provides a platform to study interstate pollution transport issues. This region, with its unique topography (hills and river valleys) as well as a good mix of urban and rural areas, has a high population of the elderly who are susceptible to health impacts of fine particulate as well as other related environmental issues (e.g., acid rain, Hg deposition, ozone).

Advanced Technology Systems, Inc. (ATS), with Desert Research Institute (DRI) as the subcontractor, was contracted by DOE-FETC in September 1998 to manage the UORVP. The map below shows the location of the sites.



Two urban and two rural monitoring sites are included in the UORVP. The four sites selected were all part of existing local and/or state air quality programs. One urban site is located in the Lawrenceville section of Pittsburgh, Pennsylvania. This site is an air quality monitoring station operated by the Allegheny County Health Department. A second urban site is collocated at a West Virginia Division of Environmental Protection (WVDEP) monitoring station at the Morgantown, West Virginia, Airport. One rural site is collocated with the Pennsylvania Department of Environmental Protection (PADEP) at a former NARSTO-Northeast site near Holbrook, Greene County, Pennsylvania. The other rural site is collocated at a site operated by the Ohio Environmental Protection Agency (OHEPA) and managed by the Ohio State Forestry Division in Gifford State Forest near Athens, Ohio.

EXPERIMENTAL

Testing and Analysis Plan

Table 1 provides the overall PM_{2.5} sampling and analysis plan requirements.

The UORVP is arranged to obtain a base level of intermittent samples every sixth day at all the four sites. This will allow for estimates of monthly, seasonal, and annual averages. To investigate the differences between months of high production of secondary particulates from atmospheric reactions, one month in the summer will be used for sampling every day, with PM_{2.5} material obtained on a 6-hour schedule to evaluate episodal and diurnal variations in sample composition. Sampling for particulate (ammonium) nitrate and gaseous nitrogen species, as well as ammonia, will provide data to investigate the apparent low nitrate levels found in eastern PM_{2.5} catches.

For comparison with summer conditions, a one-month daily sampling period was performed in February 1999 and another is projected for mid-winter 2000. To provide for comparability with stations to be set up as part of the national PM_{2.5} monitoring network, the basic sampling is being conducted using PM_{2.5} FRM sequential filter-based samplers. In addition, PM₁₀ sequential samplers were installed at one urban and one rural site. The UORVP sampling protocol will allow for a comparison of the PM₁₀ and PM_{2.5} mass and chemistry, but the emphasis of the project is on the PM_{2.5} component.

The measurement of several gases that are relevant to characterizing photochemistry, or are precursors for particle formation, was also implemented. These include ozone and its precursors (NO_x, HNO₃, and NH₃) as well as sulfur dioxide (SO₂). The observations will be completed with the acquisition of surface meteorological data at all sites, including wind speed and direction, temperature, relative humidity, precipitation, and UV radiation and insolation.

ATS contracted DRI and LabCor to analyze the collected samples following the guidance presented in Table 1.

RESULTS AND DISCUSSION

For brevity reasons, only a sample of the results obtained during the month of June 1999 are shown in Table 2. The continuous trace depicts thirty-minute average ambient air particulate loadings obtained with a PM_{2.5} tapered element oscillating microbalance (TEOM) with measurement initiating after midnight of May 31. Besides showing emission trends that peak around midday, the data shows that although the average loading is around 10 to 20 µg/scm, levels as high as 75 µg/scm are evident. The bars shown at intervals represent 24-hour averages for the TEOM (bottom bar) compared to discrete filter 24-hour integrated mass loadings (top bar). Please note that when the values agree closely, the bars are fused into one as indicated by the average values from June 29. These data provide a snapshot of how well the TEOMs and the discrete filter samplers are performing.

CONCLUSIONS

The goal of this project is to obtain and document reliable and quality data pertaining to ambient fine particulate along the Upper Ohio River Valley. The data obtained should:

- Provide generalized idea of types of PM_{2.5} sources.
- Provide input on the impact of sampling artifacts such as condensation/volatilization on FRM performance.
- Provide various correlations (day/night, urban/rural, etc).

- Provide information on PM_{2.5} concentrations/compositions for a part of the country not previously characterized.
- Provide a data base for others to use for:
 - Health studies
 - Source/Receptor analysis
 - Management System Development and
- Provide a platform for further scientific research.

The sample data discussed above confirms that reliable data that can be duplicated by two different sampling techniques is being obtained. Further data reduction, analysis, correlation and interpretation are on going and will be presented at the conference.

ACKNOWLEDGEMENTS

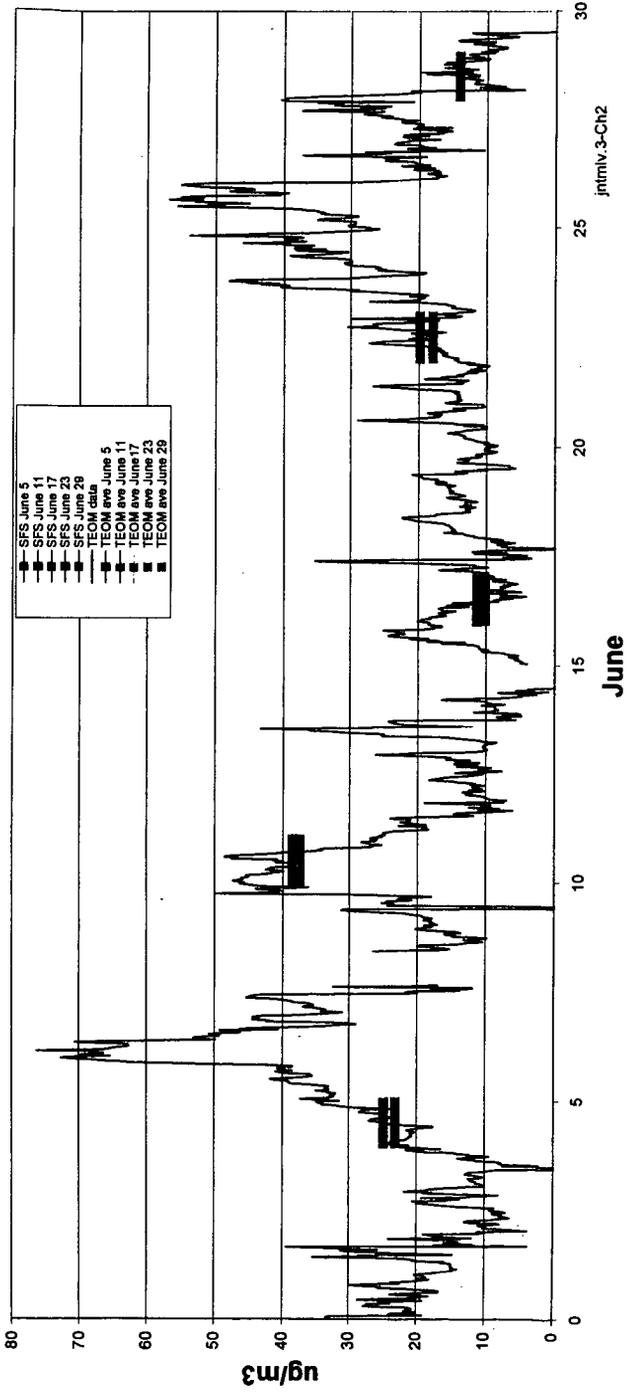
We wish to acknowledge DOE-FETC funding on Contract No. DE-AC26-98FT40456 and Dcsert Research Institute, University of Ohio at Athens, and LabCor as subcontractors.

Table 1 - PM_{2.5} SAMPLING AND ANALYSIS

SAMPLER	DENUDER	CHANNEL NO.	FILTER MATERIALS		ANALYSIS	
			Front	Back	Front	Back
SPS-PM2.5	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SASS #72	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SPS-PM10	(none)	A	Teflon*	Quartz	Mass (Gravimetry), Elements (XRF)	Carbon (TOR)
		B	Quartz	Cellulose/NaCl	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	NO _x ; (IQ)
SGS-TP	Nitric Acid (none)	A	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
		B	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
SASS #74	Nitric Acid (none)	A	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
		B	Quartz	Cellulose/NaCl	NO _x ; (IQ)	NO _x ; (IQ)
SGS-PM2.5	Ammonia (none)	A	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
		B	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
SASS #75	Ammonia (none)	A	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
		B	Quartz	Cellulose/Citric Acid	NH ₄ ⁺ ; (AG)	NH ₄ ⁺ ; (AG)
FRM (R&EP) ^a	(none)	-	Teflon*	(none)	Mass (Gravimetry), Elements (XRF)	-
FRM (R&EP) ^b	(none)	-	Quartz	(none)	Carbon (TOR); O ₃ ; NO _x ; SO ₂ ^a ; (IC); NH ₄ ⁺ ; (AG); Na ⁺ ; K ⁺ ; (AA)	-
Portable PM2.5	(none)	-	Polycarbonate	(none)	COSEM	-

XRF = X-Ray Fluorescence, TOR = Thermal/Optical Reflectance, IC = Ion Chromatography, AC = Automated Cobinometry, AA = Atomic Absorption, COSEM = Computer Controlled Scanning Electron Microscopy

TABLE 2: Lawrenceville-TEOM PM2.5 & SFS PM2.5



RAPID, MEASUREMENT-BASED SOURCE APPORTIONMENT OF AIR PARTICULATE MATTER

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KEYWORDS: air particulate matter characterization, source apportionment, thermal desorption GC/MS.

INTRODUCTION

There are two basic approaches to the quantitative apportionment of air particulate matter (PM) source contributions at a given receptor site and point in time. The first approach is based on a detailed inventory of the contributing local and long range sources and their expected PM emission activities (at the selected point in time minus the calculated transport time), combined with the use of atmospheric dispersion models capable of calculating the probability that particulate matter emitted by a given source will be transported to the selected receptor site at that particular point in time. The second approach is based on detailed physical and chemical characterization of one or more PM samples collected at the selected receptor site and time point, combined with the use of quantitative receptor models capable of apportioning these characteristics to potential local and long range sources with the aid of a library of known source patterns.

As pointed out in many textbooks [1], both approaches should be combined whenever feasible. In practice, however, most PM source apportionment efforts cannot draw upon reliable source emission and activity inventories and are also severely constrained by the high cost and time requirements of comprehensive PM characterization efforts. As a result, our present knowledge about the relative contributions of local and long range PM sources to air quality problems within many North American airsheds, let alone airsheds in other areas of the world, provides an inadequate basis for effective regulatory measures aimed at cost-effective protection of health and environment. Consequently, there is a need for the development of rapid, reliable and cost-effective PM characterization and apportionment techniques.

Currently used characterization methods for PM receptor samples are typically based upon inorganic analysis of 24-hr filter samples by means of x-ray fluorescence (XRF), proton-induced x-ray emission (PIXE), scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX), or neutron activation analysis (NAA) methods. Over the past decade organic PM characterization methods involving solvent extraction of 24-hr filter samples followed by combined gas chromatography and mass spectrometry (SX-GC/MS) have demonstrated their power in providing hundreds of potential source marker compounds, particularly for a wide range of petroleum- and biomass-type materials combustion and processing sources which fail to produce characteristic inorganic markers or patterns. Quantitation of organic as well as inorganic measurements is typically achieved on the basis of mass balance techniques involving careful weighing of moisture-equilibrated filters (before and after exposure) and expressing chemical parameters in percentage of total sample mass.

Over the past few years, the advantages of novel PM sampling and analysis methods requiring only 1- to 2-hr long sampling periods, thereby producing time-resolved circadian PM profiles revealing characteristic anthropogenic activity and/or meteorology cycles as well as episodic events, were demonstrated for selected organic PM marker components by some of the present authors [2] using thermal desorption (TD) GC/MS techniques. Equally fast sampling approaches to inorganic PM characterization by means of SEM-EDAX and PIXE were demonstrated by Anderson et al. [3]. Although use of these novel, rapid sampling methods can greatly speed up source attribution, quantitative source apportionment still requires laborious filter weighing operations. Moreover, in areas with new or unusual sources and fuels, existing source profiles are often inadequate, thus requiring lengthy, costly and socio-politically sensitive source sampling and characterization operations.

A novel, rapid PM characterization strategy is presented. The procedures outlined can drastically reduce the time and effort required for exploratory source apportionment studies and are based on a combination of: (1) rapid TD-GC/MS of 2-hr PM samples; (2) differential source plume profiling of complex sources or source clusters; and (3) real-time, size-distributed particle concentration measurements.

EXPERIMENTAL

PM samples for TD-GC/MS analysis were collected on 19 mm dia. quartz fiber (QF) filters in a 16.7 l/min flow of air passing through an isokinetic (dichotomous sampler type) ambient air sampling tower equipped with a 10 micrometer cut-off impactor. QF filters were cleaned by preheating in a high temperature furnace and stored in particle-free containers, as described by Sheya et al. [4]. QF slivers of approximately 2 mm wide were reproducibly cut from the particle-laden filters and inserted into carefully cleaned borosilicate glass sample tubes and quickly inserted in to the hot (250 C) injection port of a GC system (HP 5890A) equipped with a 10 m long, 320 micrometer i.d. GC column coated with an 0.25 micrometer layer of DB1 and connected to a desk-top quadrupole mass spectrometer (HP MSD5972). When rapid heating of the QF slivers to higher temperatures is desired, e.g. for pyrolysis studies, the pyrex tubes can be lined with ferromagnetic foils of precisely known inductive heating behavior and a well-defined end point temperature corresponding to the Curie-point temperature of the selected alloy.

GC/MS data were analyzed using the HP ChemStation program and NBS mass spectral library. Multivariate statistical analysis of relative peak intensity data, as well as the corresponding size-distributed particle count and meteorology data where applicable, was performed by means of principal component analysis (PCA) using the NCSS version 7.0 software package, followed by Varimax rotation of the PCA loadings and scores to highlight the more highly orthogonalized components in PCA space. Where appropriate, the scores of the first four Varimax factors were plotted in the form of time-resolved "skyline" plots using standard plot programs.

Size-distributed particle concentration measurements were performed with a Climet Model CI 208C 8-channel particle analyzer with specially built computer interface. Total particle volumes in each size range were calculated assuming distribution-corrected average particle sizes and spherical particle shapes.

RESULTS AND DISCUSSION

Figure 1 shows the close agreement between TD-GC/MS and SX-GC/MS analysis profiles of PM samples obtained from the same Hi-Vol quartz fiber filter. In studies currently underway in our laboratory of the nearly 100 compound peaks routinely monitored in the GC/MS profiles approximately 90 % are readily identifiable in both profiles, with the intensities of most of these showing strong correlations. Clear differences are seen in the broad multimodal "humps" underlying both profiles. These humps, generally referred to as the unresolved complex matter (UCM), are highly characteristic of the GC/MS profiles of both solvent and thermal extracts from PM receptor samples and are also seen in most combustion source samples. Apparently, the physicochemical differences between both extraction methods result in somewhat different relative UCM fraction yields. Presumably, for the SX-GC/MS method these relative UCM fraction yields will also be affected by the choice of the solvent whereas the relative UCM yields of the TD-GC/MS technique may well vary as a function of desorption conditions. Thus far, the observed differences appear to be quantitative rather than qualitative and, thus, should be amenable to routine standardization and calibration procedures.

The type of information obtainable from time-resolved circadian TD-GC/MS profiles is illustrated by the skyline plots shown in figure 2. Rather than to show an arbitrary selection of the many different single compound profiles produced by this technique each skyline plot in figure 2 shows a linear combination ("factor") of highly correlated compound profiles, thought to represent a particular PM 10 source, or combination of related sources. To further illustrate the validity of the factor analysis approach to source detection, also commonly used to reduce and interpret inorganic PM10 compound data [5], the same type of factor loading patterns producing the factor score profiles shown in figure 2 (representing a series of PM10 samples collected at the international bridge in Hidalgo, at the USA/Mexico border in December 1995) was found in two other sets of samples obtained at the border in different locations and at different time periods in December. As expected, combustion sources known to produce significant organic PM emissions are dominant. However, the prominent (5 sigma) "urban dust" event observed in the evening of December 6th is largely characterized by inorganic, re-entrained city dust components but can still be observed thanks to several characteristic organic markers [6].

Since weighing of 2-hr filter samples would not only be very time-consuming but is also impractical in view of the more than 10x lower average sample quantities (compared to conventional 24-hr samples), a different approach needs to be found to calibrate each sample with regard to differences in sample size as a basis for quantitative compound analysis by TD-GC/MS. This is achieved by the use of multichannel (size-distributed) particle counting in parallel with the collection of each 2-hr filter sample, thus allowing us to calculate the number of particles collected by the filter in each size category. As shown in figure 3, the four upper and the four lower channels of an 8-channel optical particle counter (OPC) track each other closely with regard to relative changes in calculated total particle counts. Between these two sets of channels, however, significant quantitative as well as qualitative differences can be observed. On several occasions we have been able to correlate calculated total particle volumes (assuming spherical particle shapes for the purpose of convenience) with PM mass measurement data obtained with nearby situated Beta-gauge instruments. An example of the close agreement achievable using a simple, single shape plus density correction coefficient is shown in figure 4. Both weighing and size-distributed counting techniques have their potential strengths and weaknesses as book-keeping ("balancing") methods for PM samples and their components, as non-correctable losses and gains in particle numbers as well as in total particle mass can occur on the filter during and after collection. A detailed discussion of these pros and cons falls outside the page limitations of these preprints but some relevant data will be presented in the talk. It should be noted that each particle size-distribution profile is a vector unto itself. Consequently, substitution of particle count vectors for mass numbers in source apportionment methods such as the widely used chemical mass balance (CMB) model, requires some adaptation of the algorithms to higher dimensional outputs, e.g. by substituting partial least squares or canonical correlation analysis methods for the conventional multilinear regression method.

Finally, we need to examine the possibility of by-passing the conventional source sampling and characterization methods, requiring the use of elaborate equilibrium chambers permitting direct stack, flue or tailpipe sampling of individual sources. Although these methods are likely to remain indispensable for large comprehensive source characterization studies, conceptually the main difference with ambient source plume samples taken in close proximity to the source is the inevitable dilution with ambient air containing background PM. However, more than likely the source is using plenty of intake air with background PM (which may or may not be altered during its passage). This intake air background can usually be ignored in the source profile because of the very high concentrations of emitted particulates. However, these high concentrations, often accompanied by above ambient temperatures and particle flow velocities, come at a high cost since the concentration, size distribution and composition of the sampled particles may be affected by various non-equilibrium processes.

When obtaining ambient plume samples in close proximity to the source the advantages of more highly representative particle equilibria are now being traded off for the disadvantages of higher dilution and additional contamination with background PM. Thus, it will largely depend on the sensitivity and specificity of the analytical methods used to obtain the needed PM source profiles whether this trade-off is acceptable or not. As shown by the factor analysis examples in figure 2 the large numbers of highly specific variables in GC/MS based methods enables successful linear deconvolution of complex mixture profiles into their chemical components. Based on hands-on experience we expect relatively few problems in subtracting background contributions from targeted source profiles as soon as the contribution of the targeted source, or source cluster, accounts for more than 20-30 % of the total PM signal.

In order to verify both the ambient equilibrium conditions of the source PM components, the nature and concentration of background PM components and the rate of dilution it will be advantageous to obtain control samples and size-distributed particle count measurements directly upwind of the source (or source cluster) as well as further downwind inside the plume. Of course, the proposed approach will not work well with source (cluster) plumes which are too high above ground to be sampled conveniently at a reasonable distance from the source (cluster) and will also be strongly dependent upon favorable weather conditions.

Figure 5 provides a purely conceptual example of the combined use of differential source plume profiling and size-distributed particle volume balancing as a way of determining the quantitative relationship between the intensities of observed chemical source markers (or marker pattern) in receptor samples and the volume fraction of collected particulate matter explained by the source or source cluster to which the marker(s) or pattern can be attributed.

CONCLUSIONS

Direct TD-GC/MS analysis of 1- to 2-hr QF filter samples provides a rapid approach to characterization and identification of organic PM components in receptor as well as source samples.

Size-distributed particle concentration measurements, obtained in parallel with PM filter sampling, are presented as an in-situ, real-time calibration alternative to conventional filter weighing procedures.

Differential profiling of ambient source plume samples, in conjunction with size-distributed particle concentration measurement, is proposed as a low cost, minimally intrusive method of obtaining characteristic PM emission profiles of complex or inaccessible sources or source clusters.

ACKNOWLEDGMENTS

The expert technical assistance of Christian Kasteler as well as the generous help and advice of Drs. W. Jarman and B. Simoneit are gratefully acknowledged. The research reported here was supported by the Southwest Center for Environmental Research and Policy (SCERP; Project No.: AQ95-10) with the sponsorship of EPA and the State of Utah.

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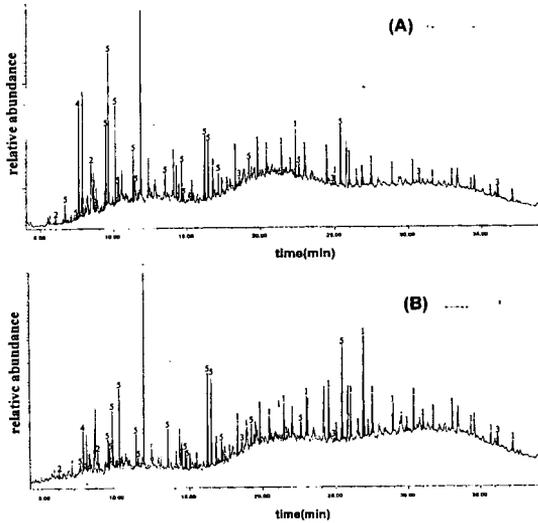


Figure 1. Comparison of solvent extracted (A) and thermally extracted (B) PM constituents. Peak labels: (1) alkanes; (2) N-containing compounds; (3) aromatics and PAH; (4) aliphatic alcohols and phenols; and (5) other O-containing compounds.

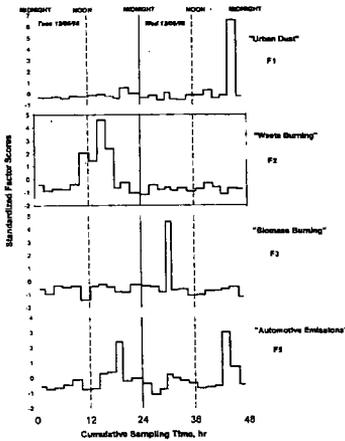


Figure 2. Time-resolved plot of four Varimax-rotated factor scores for the Hidalgo (TX) PM data set. All interpretations are tentative until confirmed by area-specific source sampling. Since factor scores are standardized a score of "3" can be regarded as a "3 σ event" in statistical terms, and so on. Note the characteristic periodic traffic peak pattern of F5 events and, the episodic character of major F1 and F2 events.

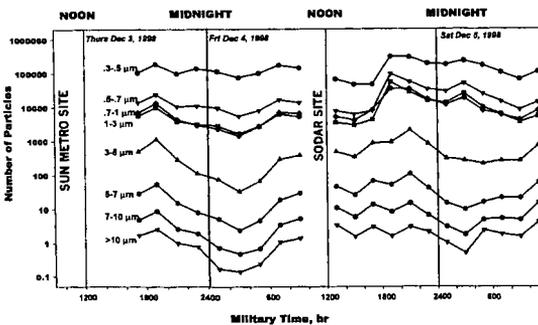


Figure 3. Averaged (2-hr averages of 4 min. intervals) 8-channel particle count at 2 El Paso (TX) sites. Note the "natural" division between the lower and higher size classes.

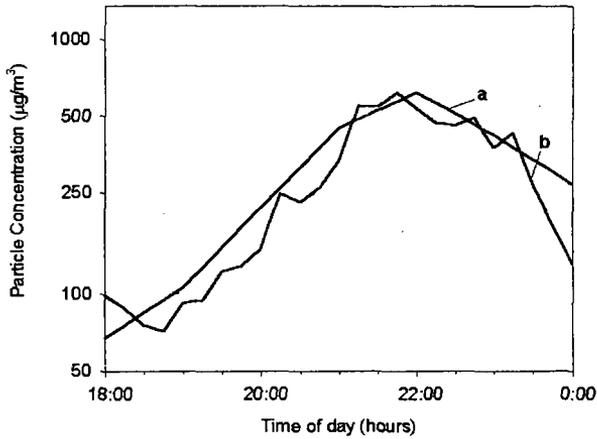
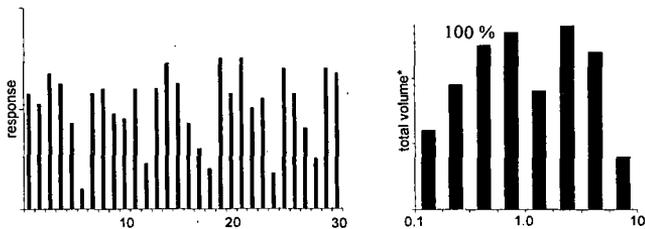


Figure 4. Use of beta attenuation monitor particle density measurements to calibrate particle density values calculated from multichannel particle count data at the Calexico site in December 1992.

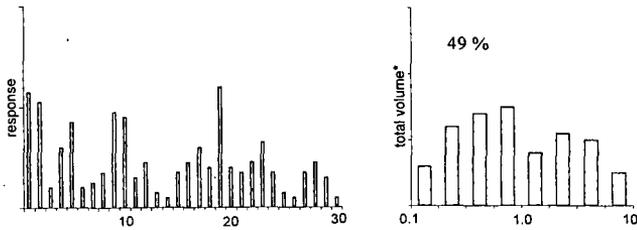
A. SOURCE PROXIMITY GRADIENT PROFILES (downwind)

c.g. Spectroscopic Data

Size / Volume Data



B. AMBIENT BACKGROUND PROFILES (upwind)



C. BACKGROUND-SUBTRACTED SOURCE PROFILES (A minus B)

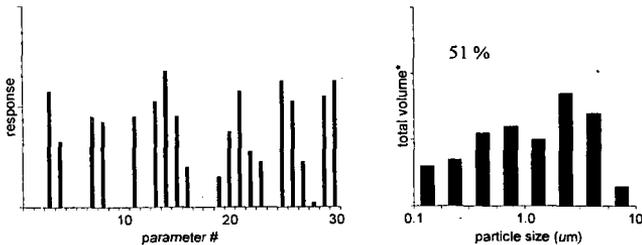


Figure 5. Conceptual illustration of the proposed Differential Source sampling approach aimed at producing characteristic, background-subtracted source profiles and the accompanying size-distributed particle data.

COMPOSITION OF THE ATMOSPHERIC AEROSOL AT THE POINT OF OBSERVATION

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KEYWORDS: Particulate matter measurements, PM_{2.5}, aerosol equilibria

INTRODUCTION

It is difficult to avoid altering particulate matter suspended in the atmosphere with most particulate matter measurement techniques. We address the extent to which methods based on the separation of the particulate and gas phases adulterate the particulate phase in suspension at the point of sampling with respect to particles up to and including 2.5 μm in aerodynamic diameter (PM_{2.5}). Specifically, we consider mass alteration during sampling and subsequent sample processing due to the volatility of ammonium nitrate and organic matter, and due to the adsorption of organic compounds on quartz fiber filters.

Here we present results from sampling the ambient aerosol during July 1999 at Fort Meade, MD (39.083°N, 76.750°W), a non-urban site in the Baltimore-Washington corridor. Additional sampling will take place during the (ideally) seasonally representative months of January 2000, April 2000, July 2000, and January 2001 as part of the Maryland Aerosol Research and Characterization (MARCH-Atlantic) study, a multi-year project designed to facilitate improved understanding of atmospheric fine particulate matter. Specific objectives of the study are (1) to characterize the changes in composition of PM_{2.5} as a function of time, (2) to identify the most likely sources of PM_{2.5} to the region, (3) to investigate potential biases in various PM_{2.5} measurement techniques, and (4) to provide useful information to the State of Maryland and EPA concerning PM measurements and regulations.

We add to the growing body of studies that have investigated potential sampling biases in filter based methods for particulate phase nitrates (e.g. Zhang and McMurry, 1992; Hering and Cass, 1999) and organics (e.g. Tang et al., 1994; Turpin et al., 1994; Gundel et al., 1995; Eatough et al., 1996). We compare the 24-hour TEOM PM_{2.5} mass concentration with those measured by a collocated filter sampler, and examine how the PM_{2.5} composition varied as a function of PM_{2.5} mass concentration during July 1999. We also compare inorganic aerosol composition measurements to expectations based on aerosol thermodynamic equilibrium calculations.

EXPERIMENTAL

In July 1999, 24-hour filter samples for PM_{2.5} concentration and composition along with gas phase HNO₃, NH₃ and hourly measurements of SO₂, CO and PM_{2.5} were added to an existing state air quality monitoring site at Fort Meade, MD. The existing measurements consisted of 24-hour Federal Reference Method (FRM) for PM_{2.5}, 1-hour O₃, NO, NO_x, and surface and aloft meteorology

This study employed two Sequential Filter Samplers (SFSs) and two Sequential Gas Samplers (SGSs) programmed to sample for 24 hours through filter packs that are replaced manually every third day. Detailed descriptions of these samplers can be found in Chow et al. (1996) and references therein. In brief, each sampler has two channels, each containing a filter pack containing one or two sampling filters through which a pump draws air at a rate of 20 L/min.

SFS-1 is used to determine PM_{2.5} mass and chemical composition. The sampling stream to both channels of SFS-1 is preceded by a PM_{2.5} size-selective inlet and nitric acid denuder. A Teflon filter is used on one channel to determine mass and elemental concentrations via gravimetry and x-ray fluorescence, respectively, after equilibration at 21.5 \pm 1.5 °C and 35 \pm 5% relative humidity. The second channel contains a quartz filter followed by a sodium chloride impregnated cellulose filter. A section of the quartz filter is extracted and used to determine the concentration of water-soluble ions: sodium and potassium by atomic absorption spectroscopy; chloride, sulfate, and non-volatilized nitrate by ion chromatography; and ammonium by automated colorimetry. The sodium chloride impregnated cellulose filter is used to determine the

amount of particulate nitrate that evaporates off the front quartz filter. SFS-2 is used to determine the amount of organic (OC) and elemental (EC) carbon in $PM_{2.5}$. SFS-2 is equipped with sampling cartridges containing two quartz filters in series on one channel, and a Teflon filter followed by a quartz back-up filter on the second channel. A section of each quartz filter is analyzed by thermal optical reflectance (TOR) for organic and elemental carbon.

Gas phase nitric acid is sampled using SGS-1. Channel one contains a quartz filter followed by a sodium chloride impregnated cellulose filter. Channel two contains a nitric acid denuder upstream of the two filters. A section of every filter is extracted and analyzed for nitrate by ion chromatography. The ambient gas phase nitric acid concentration is determined from the difference between the total nitrate collected on the channel 1 filters minus the total nitrate collected on the channel 2 filters. A second SGS, SGS-2, is used to measure gas phase ammonia concentrations. One channel contains a quartz filter followed by a citric acid impregnated cellulose filter. The second channel contains an ammonia denuder upstream of the two filters. A section of each filter is extracted and analyzed for ammonium using automated colorimetry. The ambient gas phase ammonia concentration is determined from the difference between the total ammonium collected on the channel 1 filters minus the total ammonium collected on the channel 2 filters. The SFSs and SGSs were operated at ambient temperature.

The SFS and SGS filter packs are shipped cooled and sealed between a central laboratory and the sampling site approximately once each week. Filters are sealed and kept cold immediately after removal from the sampler. Each sampler contains a filter pack open to the atmosphere that is changed out every 3rd day. It serves as a dynamic blank, the variance of which determines the lower quantifiable limit for the respective observables.

Continuous measurements of $PM_{2.5}$ mass using a TEOM[®] Series 1400a (Patashnick and Rupprecht, 1991) equipped with a $PM_{2.5}$ inlet have been obtained at the site for all months after July 1999. The TEOM's sample stream of 3 L/min is preheated to 50°C prior to entering the sampling chamber.

RESULTS

The average 24-hour $PM_{2.5}$ concentration measured during July 1999 from SFS-1 was $20.6 \mu\text{g}/\text{m}^3$, with a range of 5.5 to $37.1 \mu\text{g}/\text{m}^3$. The 24-hour TEOM mass concentration averaged $3.5 \pm 1.2 \mu\text{g}/\text{m}^3$ higher (95% confidence interval, paired t-test) than the collocated SFS sampler. Measurements from the two samplers were tightly correlated with $R = 0.98$. On average, sulfate, ammonium, nitrate, organic carbon, elemental carbon, and crustal material composed 38%, 13%, 2%, 36%, 7%, 4% of $PM_{2.5}$ in July 1999 at Fort Meade, respectively. Substantial differences in the composition of $PM_{2.5}$ were observed between days with high and low $PM_{2.5}$ concentrations. On the days with the highest $PM_{2.5}$ concentrations ($>30 \mu\text{g}/\text{m}^3$, 8 days) in July 1999, the fraction in sulfate + ammonium averaged 59% ($19.6 \mu\text{g}/\text{m}^3$) of the total mass, while the fraction in carbonaceous material ($1.4 \times \text{OC} + \text{EC}$) averaged 27% ($8.9 \mu\text{g}/\text{m}^3$). The averages changed to 37% ($2.8 \mu\text{g}/\text{m}^3$) and 67% ($4.9 \mu\text{g}/\text{m}^3$), respectively, on the days with the lowest $PM_{2.5}$ concentrations ($<11 \mu\text{g}/\text{m}^3$, 7 days). Figure 1 displays how the composition of $PM_{2.5}$ varied with $PM_{2.5}$ concentration. It is apparent from Figures 1d and 1e that changes in the $PM_{2.5}$ concentration is driven largely by sulfate and ammonium rather than carbonaceous material.

The amount of nitrate collected on the backup NaCl impregnated cellulose filter in SFS-1 was approximately 9 times larger than the amount collected on the front quartz filter (Figure 2). Thus, evaporative losses of particle phase nitrate from quartz filters can result in a large underestimation of particulate nitrate in the eastern US in the summer. We assume that the nitrate collected on the backup filter represents the amount of ammonium nitrate that evaporated off the front quartz filter, which ranged from -1% to 9% (0.1 to $1.1 \mu\text{g}/\text{m}^3$) and averaged ~2% ($0.36 \mu\text{g}/\text{m}^3$) of the total $PM_{2.5}$ mass measured on the Teflon filter of SFS-1. If the Teflon filter is subject to the same evaporative losses of ammonium nitrate as the quartz filter, the $PM_{2.5}$ mass measurement may be underestimating the true ambient $PM_{2.5}$ concentration by 1 to 9% on any given day.

Potential biases associated with the organic particulate material may be larger. Each channel on SFS-2 employed the use of a quartz fiber back-up filter. One backup filter was preceded by a Teflon filter, while the other was preceded by a quartz filter. Figure 3 shows the amount of organic carbonaceous material that was detected on the backup filters, relative to what was measured on the front quartz filter of SFS-1. The amount of organic carbon measured on the backup filter behind the Teflon averaged over 50% of what was measured on the front quartz filter, while the backup filter behind quartz averaged ~30% of the OC measured on the front quartz filter. These amounts are on the order of 10% of the total $PM_{2.5}$ mass, indicating sampling biases associated with organic particulate material can be substantial in the eastern US in the summer. The material detected on the backup filters likely comes from two sources: 1) OC that evaporates off the front filters, which results in a negative sampling bias for OC and $PM_{2.5}$, and 2) gas phase organic compounds that adsorb on quartz filters, which contributes to a positive sampling bias for OC and the reconstructed mass. However, the relative contributions from each of these possibilities are highly uncertain. An additional source of uncertainty in the

determination of the concentration of organic particulate material resides in the multiplier of 1.4 used to estimate the average molecular weight of organic particulate matter (what actually resides on the filter) per carbon weight (what the TOR technique measures). The concentrations of organic particulate material reported here (as in Figure 1) were calculated by TOR analysis of the front quartz filters of SFS-2, without corrections from a backup filter.

We use the SCAPE2 (Kim et al., 1993) inorganic aerosol equilibrium model to compare the observed gas-particle partitioning of ammonia-ammonium and nitric acid-nitrate to calculations based on thermodynamic equilibrium. The SCAPE2 model requires inputs of observed temperature, relative humidity, total nitrate (gas + particulate phases), total ammonium, sulfate, sodium, chloride, potassium, and magnesium. The last four species are not significant in the data presented here. The model then calculates the gas phase concentrations of ammonia and nitric acid as well as the particulate phase concentrations of ammonium and nitrate at thermodynamic equilibrium. Figure 4 compares the SCAPE2 calculated and observed concentrations of the four species. The agreement between the equilibrium calculations and observations is excellent for the dominant phase species ($R \geq 0.99$ for gas phase nitric acid and particulate ammonium). The correlations for the minor phase species are not as strong. However, the differences between the SCAPE2 calculated and observed concentrations are not statistically significant at the 95% confidence level, except in the case of ammonia where the observed concentration is $0.11 \pm 0.07 \mu\text{g}/\text{m}^3$ larger (95% confidence interval) than the calculated concentration.

CONCLUSIONS

Based on measurements and theoretical evaluation of aerosol observations made in July 1999 at a non-urban site in the Baltimore-Washington Corridor, 24-hour $\text{PM}_{2.5}$ mass concentration measurements appear to underestimate the highest 20th percentile concentration of "dry" suspended particles by approximately 10%. This bias appears to be a function of losses of particulate ammonium nitrate and organics from the filters during sampling. Additional research is required to determine the sign and magnitude of the potential error in sampling organics.

Evaporative loss of particulate nitrate from filters during sampling can represent a large fraction of the total particulate nitrate. However, particulate nitrate appears to be only a small fraction of the total $\text{PM}_{2.5}$ in the Mid-Atlantic US in the summer. The observed partitioning of nitrate and ammonium between the particulate and gas phases is well reproduced by thermodynamic equilibrium theory.

Although the carbonaceous material accounts for approximately 20 to 70% of the $\text{PM}_{2.5}$ mass from the highest to the lowest mass concentration days, ammonium sulfate is the dominant constituent of the $\text{PM}_{2.5}$ on the higher mass concentration days.

Comparison of diurnal mass measurements of $\text{PM}_{2.5}$ using a TEOM instrument with a collocated 24-hour $\text{PM}_{2.5}$ filter sampler correlate with a small positive bias in the TEOM average over the filter sampler measurements.

ACKNOWLEDGEMENTS

This work was supported in part by Baltimore Gas and Electric Company and Potomac Electric Power Company (TC9183). We also acknowledge additional support from Maryland Industrial Partnerships (MIPS Award 2304). The authors thank Dick Wies and Fran Pluciennik at Maryland Department of the Environment for use of the Fort Meade sampling site and associated air quality and meteorological data.

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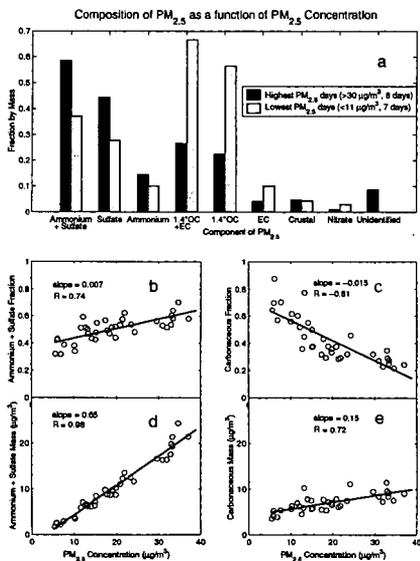


Figure 1. (a) Composition of PM_{2.5} on the days with the highest (>30 µg/m³, 8 days) and lowest (<11 µg/m³, 7 days) PM_{2.5} mass concentrations in July 1999 at Fort Meade, MD. The unidentified fraction represents the difference between PM_{2.5} measured on the Teflon filter of SFS-1 and the sum of sulfate + ammonium + 1.4*OC + EC + crustal + nitrate + volatilized ammonium nitrate. The crustal component is taken as 2.14*Si + 1.89*Al + 1.43*Fe + 1.67*Ti + 1.4*Ca + 1.2*K from x-ray fluorescence analysis. (b) The relationship between the fraction of PM_{2.5} in sulfate + ammonium and PM_{2.5} concentration. (c) The relationship between the fraction in carbonaceous material and PM_{2.5} concentration. (d) The relationship between the ammonium + sulfate mass and PM_{2.5} concentration. (e) The relationship between the carbonaceous mass and PM_{2.5} concentration. The carbonaceous material is determined from the front quartz filter of SFS-2, without corrections from a backup filter and is taken as 1.4*OC + EC.

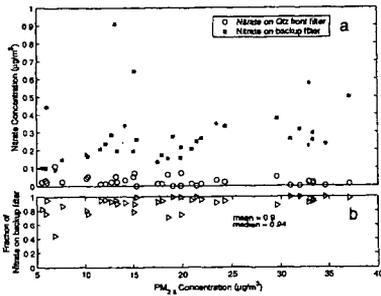


Figure 2. (a) The amount of nitrate collected on the front quartz filter and the backup sodium chloride impregnated cellulose backup filter in SFS-1 as a function of $PM_{2.5}$ concentration. (b) The fraction of nitrate collected on the backup filter ([nitrate on backup filter]/[nitrate on front filter + nitrate on backup filter]) versus $PM_{2.5}$ concentration.

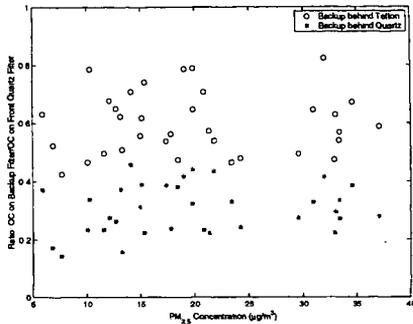


Figure 3. The amount of OC collected on each quartz backup filter in SFS-2 divided by the amount of OC measured on the front quartz filter of SFS-2 as a function of $PM_{2.5}$ concentration.

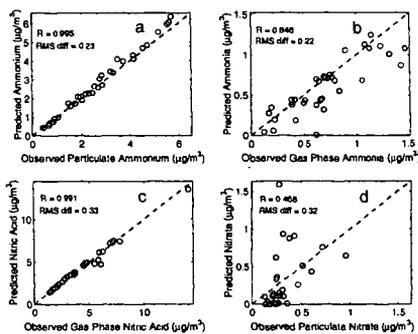


Figure 4. Comparison of the concentrations of inorganic $PM_{2.5}$ components calculated by the SCAPE2 aerosol equilibrium model to those observed for (a) particulate ammonium, (b) gas phase ammonia, (c) gas phase nitric acid, and (d) particulate nitrate. The dashed line is the 1:1 line. Observed particulate nitrate is taken as the sum of nitrate measured on the front quartz and backup sodium chloride impregnated cellulose filters of SFS-1. Observed particulate ammonium includes the ammonium that is assumed to have evaporated off the front quartz filter of SFS-1 in the form of ammonium nitrate, which is determined from the amount of nitrate collected on the backup sodium chloride impregnated cellulose filter.

PM_{2.5} SAMPLING AND CHARACTERIZATION PROGRAM IN LIBRARY, PA

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KEYWORDS: fine particulate matter, PM_{2.5}, ambient air sampling

INTRODUCTION

Particles with a mean aerodynamic diameter of ca. 45 μm or less, known as total suspended particulate (TSP), have been of concern to the health community since the 1950s. In July 1997, the EPA proposed its most restrictive ambient air standard for particle matter. This standard applies to particles with a mean aerodynamic diameter of 2.5 μm or less (PM_{2.5}). It sets an annual limit for PM_{2.5} of 15 $\mu\text{g}/\text{m}^3$, averaged over three years, and a 24 h limit of 65 $\mu\text{g}/\text{m}^3$ (98th percentile, averaged over three years). In supporting documentation for the recommendation to implement this new standard, EPA stated that SO₂ (a precursor to the formation of secondary sulfate particles) is a key source of PM_{2.5}, and of concern to human health. EPA also stated that the SO₂ is predominantly generated by the combustion of fossil fuels, especially coal. Another class of compounds which EPA stated to be a major component of PM_{2.5} and also of concern to human health is nitrates derived from NO_x generated in the combustion of fossil fuels. In addition to regulations based on alleged health effects, in an effort to regulate PM_{2.5}, EPA also proposed draft regional haze regulations that focus on the impact of PM_{2.5} on visibility impairment in Class I ("pristine") areas of the United States. The scientific bases for these standards are now under review.

CONSOL R&D began a sampling program in January 1997 in Library, PA (thirteen miles south of Pittsburgh, PA) to measure the concentration of PM_{2.5} particles collected from the air and to characterize the components of the collected samples. This paper describes the sampling methods, data collected, and conclusions drawn from this program.

At the time CONSOL began its sampling program, no federal reference method (FRM) had been established for the collection of fine particles 2.5 μm or smaller. At CONSOL, the initial samples were collected using cyclone samplers. CONSOL R&D has a great deal of experience using cyclones for the collection of particles from stationary source stack sampling work.

In July 1997, EPA published an FRM for PM_{2.5} collection; the method requires the use of impactors, not cyclones. CONSOL added a Graseby-Andersen FRM single channel sampler to the on-site PM_{2.5} sample collection effort being performed with the cyclones. Later, a Graseby-Andersen sequential PM_{2.5} sampler was employed. Collection with both the cyclones and the Graseby-Andersen samplers continued until January 1999, at which time the use of the cyclones was discontinued. The samplers were collocated (within four feet of each other). Weather data also were collected on the CONSOL Library, PA, site beginning June 1998.

EXPERIMENTAL

Prior to 1997, the procedures used to acquire samples with cyclone samplers were those used primarily for sampling of stack gases.¹ The cyclones used for this work provide a particle size cut (with a mean diameter of 2.5 μm , D₅₀) within the range of 0.1-10 μm .³ Two types of filter material were used, Teflon™ and quartz. Quartz filters are difficult to weigh because they fluctuate in weight with changes in humidity. However, they were used for selected samples to eliminate carbon background, which would interfere in the anticipated carbon analyses. Procedures for sample collection and determination of PM_{2.5} concentration with the FRM samplers is detailed in the Code of Federal Regulations 40 Part 50 Appendix L. The FRM specifies the use of Teflon™ filters. Field blanks were acquired; field blank weights are one to two orders of magnitude smaller than sample weights.

Collected samples were weighed and randomly selected samples were analyzed for sulfate, nitrate, chloride, and ammonium by ion chromatography (IC). Quartz filters were reserved for carbon analyses.

RESULTS AND DISCUSSION

Comparison of Cyclone to FRM Sampler Collected Filter Samples

Two cyclones were collocated with the single-channel Graseby-Andersen FRM sampler for thirteen months. $PM_{2.5}$ concentrations were calculated from the mass of particles collected on the filters and the air flow rate through the filters. Figure 1 shows good correlations ($R^2 = 0.967$ and $R^2 = 0.942$) between the $PM_{2.5}$ concentrations measured in the same 24 h period using the two sample collection devices. The slopes of the two lines on Figure 1 are 0.96 and 1.07 for cyclones 1 and 2, respectively.

Seasonal and Daily Variations

$PM_{2.5}$ concentrations for all samples collected outdoors in the period of January 1997 through August 1999 are shown in Figure 2. Some variations with the seasons can be observed. The $PM_{2.5}$ concentration in ambient air averages $20.0 \mu\text{g}/\text{m}^3$ throughout the two and one half plus years of the outdoor sampling program, excluding high ozone days. Ozone action days (designated as open points) were declared by the Pennsylvania Department of Environmental Protection (DEP). The average $PM_{2.5}$ concentration for high ozone days was $42.3 \mu\text{g}/\text{m}^3$. $PM_{2.5}$ concentrations were examined for variations according to day of the week (Table 1). Because of the large standard deviations, little variation is observed. The range of $PM_{2.5}$ concentrations is roughly equivalent regardless of the day of the week.

Variations in $PM_{2.5}$ Concentration with Weather Data and Ozone Concentration

Total $PM_{2.5}$ concentration was examined as a function of weather data (temperature, barometric pressure, rainfall, and humidity). A trend with weather data is evident only in the relationship of $PM_{2.5}$ and temperature. $PM_{2.5}$ concentration is higher on days when the temperature exceeds 80°F . The $PM_{2.5}$ concentration distribution shifts to higher values for samples acquired at $\geq 80^\circ\text{F}$ (Figure 3).

$PM_{2.5}$ concentrations are plotted as a function of ozone concentrations acquired by the Pennsylvania State DEP at a location 17 miles southeast of Library, PA (Charleroi, PA). $PM_{2.5}$ concentrations increase with increasing ozone concentration (Figure 4); this is consistent with the work of Chu and Cox². It cannot be definitively determined from these data whether the higher $PM_{2.5}$ concentration levels are a result of higher temperature, the higher ozone concentrations, or other confounding effects.

$PM_{2.5}$ Composition

Sixty-four filter samples collected from January 1997 through August 1998 were analyzed for sulfate, nitrate, ammonium, and chloride. The average composition for particles collected on non-ozone action days is: 32 wt % sulfate, 11 wt % ammonia, 7.5 wt % nitrate, 3.0 wt % chloride and 46 wt % organic and inorganic carbon and mineral matter. The average composition for samples collected on ozone action days is: 48 wt % sulfate, 14 wt % ammonia, 1.5 wt % nitrate, 2.2 wt % chloride, and 34 wt % carbon and mineral matter (Table 2).

The concentration of sulfate ($\mu\text{g}/\text{m}^3$) in the $PM_{2.5}$ collected on non-ozone days was in the range of 0.8 to $16.0 \mu\text{g}/\text{m}^3$. On ozone action days, the range of $PM_{2.5}$ sulfate concentrations was 7.4 to $35.5 \mu\text{g}/\text{m}^3$. There is a general increase in sulfate and ammonia concentration in the summer months and an apparent decline in concentration of nitrates. The highest chloride concentrations were found in particles collected in June and July.

Sulfates and nitrates exist in the atmosphere as aerosols. When reacted with ammonia, they form fine particles that can precipitate. Thus, the form of the sulfates and nitrates in the particles is likely to be ammonium salts. Several ammonium salts are possible (ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, ammonium bisulfate, $(\text{NH}_4)\text{HSO}_4$ and ammonium nitrate, NH_4NO_3). In addition, chlorides would likely be found as ammonium chloride (NH_4Cl). The correlation between the concentration ($\mu\text{mole}/\text{m}^3$) of ammonium and the concentration ($\mu\text{mole}/\text{m}^3$) of sulfate in the $PM_{2.5}$ collected on all days is good ($R^2 = 0.94$). The ammonium and sulfate mole ratios may provide a clue to which ammonium sulfate salt predominates in the particulate matter. Two assumptions were made in the data analysis; they are: 1) all Cl^- and NO_3^- are present as ammonium salts, and 2) all SO_4^{2-} is present as an ammonium salt. The mole ratios of NH_4^+ (residual) to SO_4^{2-} , after accounting for the Cl^- and NO_3^- , range from -0.2 to 2.0. The average value is 1.3. Thirty-nine percent of the filter samples have an $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio of 1.6 to 2.0 and 47% have a ratio of 1.0 to 1.5. From the limited number of samples and the limited data analysis, it is likely that both ammonium sulfate and ammonium bisulfate are present in the particulate matter.

CONCLUSIONS

A fine particle matter ambient air sampling program has been conducted on the CONSOL R&D sit in Library, PA, (south of Pittsburgh, PA) for almost three years. Particles with an aerodynamic mean diameter of 2.5 μm or less ($\text{PM}_{2.5}$) were collected using two types of sampling equipment, cyclones, and impactors. The two kinds of sampling equipment when collocated were found to collect the same mass of particles in the same time. The collected samples were analyzed using several methods. In conjunction with the particulate matter collection, weather data also were obtained for a portion of the sampling program duration. Total $\text{PM}_{2.5}$ concentration was found to vary slightly with season and vary little with day of the week, changing significantly (greater than one standard deviation from the mean of the non-ozone days) only on days of high ambient air ozone concentrations and temperatures greater than 80 °F. The magnitude of the effect of either of these linked variables on the concentration of $\text{PM}_{2.5}$ cannot be determined from the data presented here. However, because the effect is strong, the importance of including these and other confounding variables in $\text{PM}_{2.5}$ ambient air studies and $\text{PM}_{2.5}$ related health effect studies is indicated. The average $\text{PM}_{2.5}$ ambient air concentration for all days in which samples were acquired is 20.0 $\mu\text{g}/\text{m}^3$. On non-ozone action days, the average $\text{PM}_{2.5}$ concentration is 17.8 $\mu\text{g}/\text{m}^3$. Neither of these concentrations would meet the proposed EPA limit of 15 $\mu\text{g}/\text{m}^3$. The concentration of sulfate found (on average) for all days (33%) is approximately that found by EPA (34.1%) in $\text{PM}_{2.5}$ acquired in the eastern U.S.³ Further studies, which include compositional analyses of many more samples collected from sites around the eastern U.S., are required to confirm this result. A good correlation was found between the ammonium and sulfate concentrations in the particles indicating the possibility that the sulfate is resident in the particles as ammonium salts.

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Table 1. $\text{PM}_{2.5}$ Concentration Ranges, Averages, and Standard Deviations for Non-Ozone Action Days, Sorted by Day of the Week

	Number of Samples	Range		Avg	Std Deviation
		Low	High		
Monday	25	8.0	48.9	18.6	11.7
Tuesday	48	2.4	38.5	14.2	8.5
Wednesday	41	10.1	51.3	19.2	7.9
Thursday	75	2.3	46.9	18.6	8.1
Friday	12	5.9	28.4	17.2	6.5
Saturday	25	7.2	33.5	15.5	8.1
Sunday	26	6.2	34.7	18.6	8.4

Table 2. Average Concentration (wt %) of Components in $\text{PM}_{2.5}$ Samples

Component, wt %	All Samples (a)		Non-Ozone Action Days (b)		Ozone Action Days (c)	
	average	σ	average	σ	average	σ
Sulfate	33	13	32	12	48	7.9
Ammonium	11	3.2	11	3.3	14	2.0
Nitrate	7.0	19	7.5	20	1.5	1.3
Chloride	2.9	3.9	3.0	4.0	2.2	1.1
Balance (d)	46		46		34	

a) Total of all samples analyzed: 63

b) Total of non-ozone action day samples analyzed: 54

c) Total of ozone action day samples analyzed: 9

d) Includes Inorganic and Organic Carbon and Minerals

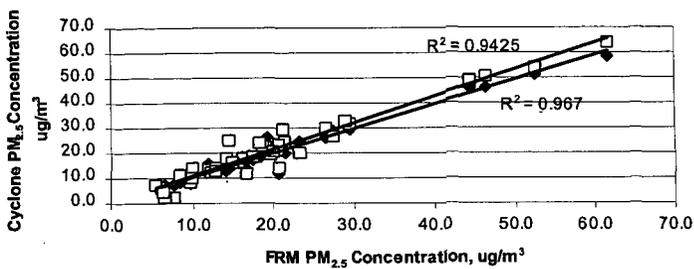


Figure 1. Comparison of PM_{2.5} Concentration Measured in Cyclones 1 (solid points) and 2 (open points) with the Single-Channel FRM Sampler.

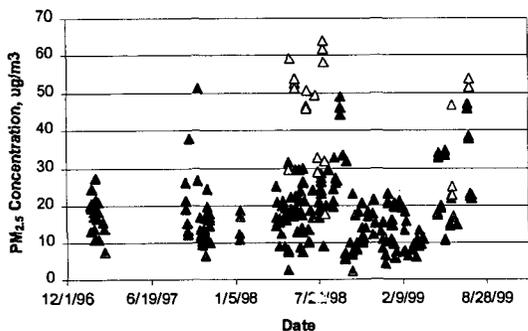


Figure 2. PM_{2.5} Concentration - CONSOL R&D Library, PA 1/27/97 - 7/30/99 (Open Points are Ozone Action Days).

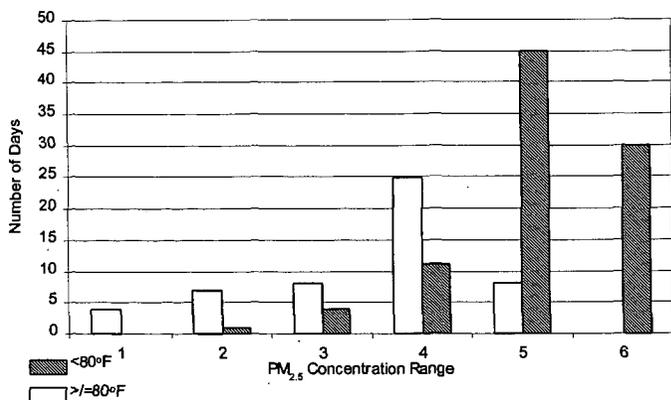


Figure 3. Change of PM_{2.5} Concentration Distributions with Different Outside Daily High Temperature Ranges.
 (PM_{2.5} Concentration Ranges (µg/m³): 1 = 50*; 2 = 40-50; 3 = 30-40; 4 = 20-30; 5 = 10-20; 6 = 0-10)

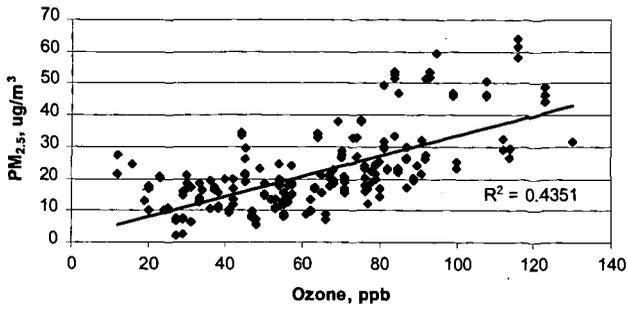


Figure 4. PM_{2.5} Concentration Measured in Library, PA vs. Ozone Concentration Measured in Charleroi, PA

PM2.5 EMISSION CHARACTERIZATION FOR STATIONARY SOURCE GAS COMBUSTION

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ABSTRACT

Reliable PM2.5 source apportionment will require accurate inventories of speciated emissions from stationary sources. Although gas combustion is typically thought of as a "clean" process, the enormous quantities of gas burned in boilers, process heaters, and engines could make even small emissions concentrations significant. This study shows that current methods for measuring emission factors and speciation profiles from gas fired sources may have significant artifacts leading to overestimation of emissions. Chemically speciated results using an improved test protocol for natural gas- and refinery gas-fired boilers and process heaters are presented.

INTRODUCTION

New ambient air standards for particles 2.5 μm or less in diameter, referred to collectively as PM2.5, will motivate regulators to identify and control emission sources contributing to ambient PM2.5. Sulfates, nitrates, and carbon (elemental and organic) dominate PM2.5 composition in most urban and many non-urban areas; ammonium and elements also are present^{1,2}. Combustion devices are believed to be the most significant source of PM2.5.

The majority of primary emissions from combustion is often found in the PM2.5 or smaller size range, especially for devices equipped with particulate emission control equipment and for clean burning fuels such as gas. The predominant gaseous precursors of secondary particulate sulfates and nitrates are: sulfur dioxide (SO_2) and sulfur trioxide (SO_3); oxides of nitrogen (NO and NO_2 , the sum of which is designated NO_x); and ammonia (NH_3). Secondary organic aerosols formed from volatile organic carbon compounds also may be very significant in some areas, especially during the summertime when photochemical activity is high³.

Methods for identifying sources of ambient PM2.5 employ modeling approaches, which range from simple to complex. The chemical "fingerprint" of a source's emissions can be used to apportion the contribution of regional sources to local ambient PM2.5 using chemical mass balance models, one example of such methods. These relate the chemical speciation profile of ambient air samples to sources based on speciation profiles for all sources in the modeled area. Reliable results require complete speciation profiles for every source⁴.

The quality of source emissions data which presently exist is often questionable because of: a lack of data for different process configurations to account for site-specific differences; data based on measurements using older, less sensitive or selective techniques; and/or incomplete profiles. Thus, there is a need for new source emission data for specific sources and locations using the latest measurement technologies to provide more reliable source apportionment results^{2,5}.

GAS-FIRED COMBUSTION SOURCES

Combustion of gaseous fuels in steam boilers, process heaters, gas turbines and stationary reciprocating internal combustion engines accounts for a major fraction of fossil fuel combustion in the U.S. Most if not all petroleum refinery boilers and process heaters in the U.S. are gas fired. Petroleum refining is the most energy-intensive of the major energy-consuming industries in the U.S., consuming 3.3 Quads of energy in 1994⁶. The majority of this was accounted for by combustion of gaseous fuels. There is widespread use of reciprocating engines and steam generators in exploration and production activities. Many refineries are situated in or near areas where ambient PM2.5 levels are predicted to exceed the new NAAQS.

Based on 1982 data gathered in southern California, petroleum industry equipment is believed to be a minor source of carbonaceous aerosols in ambient fine particulate matter⁷. Organic compounds may be present in emissions from gas-fired sources as products of incomplete combustion. Organic aerosols in the atmosphere result from semivolatile organic compounds ($>\text{C}_{20}$) present in the source combustion products and atmospheric reaction of volatile organic compounds ($>\text{C}_7$) to form heavier, condensable organics⁸. Tests for "air toxics" conducted over the past ten years provide a partial database of volatile and semivolatile organic compound emissions for several classes of petroleum industry sources. Recent pilot-scale tests indicate that the yield of selected organic compounds from gas combustion is extremely low under operating conditions representative of good operating practice normally found throughout the industry⁹. Emissions of BTX (the sum of benzene, toluene and xylene), formaldehyde, and PAH (the sum of 16 polycyclic

aromatic hydrocarbons) derived from pilot scale tests of a single refinery heater burner and field tests of petroleum industry boilers and process heaters reveals a range of emissions typically near or below detection limits, even when the most sensitive test methods available are used. Compared to boilers and process heaters, stationary reciprocating internal combustion engines (RICE) have relatively high average PAH emission factors – on the order of 0.1 lb per million Btu of gas fired. PAH emissions from asphalt blowing are slightly lower than stationary RICE. PAH emission factors for refinery boilers, process heaters, gas turbines, and coke calciners are approximately an order of magnitude lower. While these types of data may provide a clue to sources of ambient aerosol precursors, the tests usually looked only for specific compounds deemed toxic or carcinogenic, ignoring many other organic compounds such as fuel fragments that may contribute to ambient organic aerosols.

Tests of industrial gas-fired boilers and gas turbines in which particulate emissions measurements included both the filterable and condensable particles show that the condensable fraction is significant, sometimes exceeding the filterable fraction¹⁰. The contribution of the condensable fraction is even more pronounced for oil-fired sources. For example, tests of distillate oil-fired industrial boilers showed condensable particulate matter amounted to several times the filterable particulate. A comparison of fine organic carbon emissions from an oil-fired industrial boiler showed total condensable organic aerosol was 7 to 16 times higher than the filterable organic fraction.

SOURCE CHARACTERIZATION TEST METHODS

Source characterization approaches for particulate matter fall into two general categories: source-level sampling and ambient-level sampling. The general sampling and analytical principles for characterizing particulate mass, size, and composition are similar for the two types of measurements, but the specific approaches differ due to the differences in gas temperature, pollutant concentrations and background gas composition. In the context of regulatory enforcement, source-level sampling is currently the accepted approach for total suspended particulate and PM10 measurements for stationary sources, while ambient level sampling using dilution is the accepted approach for mobile source particulate emission measurements.

Source-Level Sampling

The most common approaches to source-level sampling for particulate employ an in-stack filter or a filter external to the stack and heated to a constant temperature (e.g., EPA Method 17 or Method 5).¹¹ Heating the filter avoids condensation of moisture and/or acid aerosols, depending on the temperature selected. These methods define primary particles that are filterable at the filter temperature.

Condensable particulate is frequently defined as the amount of material collected in a series of impingers in an ice bath downstream of an in-stack filter and includes both fine particles which pass through the filter and vapors which condense at the temperature of the gas leaving the impingers (typically 60-70°F).^{12, 13} Impinger methods for condensable particulate are subject to substantial artifacts¹⁴ that do not occur in atmospheric processes, especially when ammonia, sulfates and/or chlorides are present in the exhaust, and thus may not provide an accurate measure of primary condensable particles.

PM10 and PM2.5 are commonly measured using in-stack cyclones or cascade impactors^{13, 15}, or occasionally using heated out-of-stack cyclones.¹⁶ While these methods may provide regulatory agencies a means of enforcing emission limits defined using the same methods on a specific type of source, they may not be generally applicable to all source types and may be biased high or low due to interferences and artifacts. Further, the methods may allow subtraction of sulfate or chloride captured in the impingers as a matter of policy, which may not be appropriate when conducting source apportionment studies for PM2.5.

Source-level measurement methods also exist for secondary particle precursors. NO_x and SO₂ emissions can be characterized using continuous gas analyzer systems. SO₂ can be measured by high-temperature filtration of the sample to remove solid particles, followed by cooling to a temperature below the H₂SO₄ dew point (but above the moisture dew point) and subsequent filtration to remove condensed acid mist¹⁷. Gaseous ammonia can be trapped in sulfuric acid impingers and subsequently analyzed by ion chromatography, although the sample must be filtered at stack temperature to avoid biases due to formation or decomposition of solid/liquid ammonium compounds. Gas-phase organic compounds usually are measured by using a sorbent trap, which strips organics from the gas onto the sorbent. The sorbent is subsequently analyzed by thermal desorption of the organic compounds into a gas chromatograph/mass spectrometer system for quantification and speciation.

Dilution Sampling

Ambient-level sampling for source characterization involves diluting the exhaust gas and subsequently sampling and analyzing the diluted gas using ambient air methods. This has at least one major advantage over source-level sampling in that results are directly comparable to ambient air measurements. If the dilution is performed in a manner which simulates conditions in the exhaust plume, then particles which form in the plume are represented in the sample. Ambient air methods are similar in general principle to source-level measurements for combustion devices, but somewhat simpler because provisions in source-level methods to eliminate problems caused by the high gas temperature, high moisture content, higher pollutant concentrations and interfering major

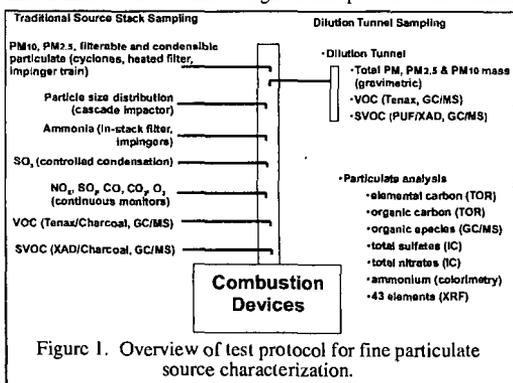
and minor gases are not necessary. Because of the comparatively low temperature of ambient air and diluted source samples, a greater range of sampling media such as Nylon and Teflon membrane filters can be used. This simplifies and extends the range of chemical speciation measurements.

Dynamic dilution samplers for stationary source studies draw a hot exhaust gas sample continuously into a chamber where it is mixed with a continuous flow of conditioned ambient air or pure inert gas. The diluted sample is then drawn through multiple filters, sorbents or denuders, which strip particles and/or selected gases from the sample. These are then taken to an analytical laboratory for analysis.

Hildemann et al.¹⁸ introduced a dilution sampler designed specifically for characterizing organic aerosols at very low concentrations. The key features of this system were: 1) it did not contain any plastic or rubber materials that could leach organics into the system or prevent thorough decontamination of the system; 2) it allowed for a relatively large sample size to facilitate detailed chemical analysis of organic compounds; 3) it allowed for dilution and cooling of the sample fully to ambient temperature; 4) the dimensions and the flow rates in the system were selected to minimize particle and vapor losses onto the walls; and 5) it provided for long sample residence times. Dilution ratios of at least 40:1 were used to assure adequate mixing between the sample stream and the dilution air, in addition to cooling the sample to essentially ambient temperature. An analysis of aerosol condensation, coagulation and nucleation rates in samples with low particle concentrations revealed that diffusion of condensing organic vapors to particle surfaces is relatively slow; hence, the design incorporates an additional residence time chamber providing a total of approximately 80-90 seconds residence time to facilitate condensation of low concentration aerosols. The design has been used by Hildemann and others¹⁹ to generate detailed organic aerosol speciation data for several types of sources.

TEST APPROACH

Tests were performed on a gas-fired boiler and a gas-fired process heater in refineries. Both units were fired on refinery process gas. Both in-stack and dilution tunnel methods were included in the test matrix (Figure 1). The dilution tunnel used in these tests follows the Hildemann design discussed above. The diluted sample was passed through various collection media as illustrated in the figure. Volatile organic compounds were collected on Tenax sorbent, and analyzed by gas chromatographic separation and flame ionization detection of individual hydrocarbons for peak quantification, and/or combined mass spectrometric/Fourier transform infrared detection for peak identification. Semivolatile organic compounds were collected on quartz filters followed by



polyurethane foam (XAD-4 sorbent, which were extracted and analyzed by electron impact gas chromatography/mass spectrometry, using Fourier transform infrared detection, mass selective detection, and multiple ion detection for compound identification and quantification. Elements were determined on Teflon membrane filters by energy dispersive X-ray fluorescence. Ions were determined on quartz filters by ion chromatography. Organic and elemental carbon were determined on quartz filters by thermal optical reflectance.

Source-level sampling for total particulate, PM₁₀, PM_{2.5} and condensable particulate was performed concurrently and co-located with dilution tunnel sampling, providing a direct comparison between the results obtained with the two approaches. PM_{2.5} precursor measurements during the gas-fired unit tests included SO₂, NO_x and volatile organic compounds. In a separate test of a fluid catalytic cracking unit not reported here, particle size distribution was measured using *in situ* cascade impactors and PM_{2.5} precursor measurements also included SO₂ and NH₃.

The tests demonstrated that the dilution tunnel approach could be successfully applied to stationary industrial sources. One of the practical challenges to the tests was limited space on the stack sampling platform for placement of the dilution tunnel and ancillary equipment. These sites were selected in part due to the relatively generous sampling platforms available (a half-circle platform with two sample ports at the boiler site, and a full-circle platform with four sampling ports at the process heater site). However, there are many gas-fired sites where such generous access is not available since stack sampling of gas-fired sources is not universally required. Because of the limited space on the boiler site's platform, the dilution tunnel tests and in-stack method tests could not be performed concurrently; instead, they were performed on different days. Process operating data indicated similar process conditions during all tests. Better access was available at the process heater site, so these tests were performed concurrently. Each test run at both sites was six hours in duration, with a total of three runs for each measurement. In addition to stack samples, a single ambient air sample was collected near the combustion air inlets at each site for comparison.

PRELIMINARY COMPARISON OF IN-STOCK AND DILUTION TUNNEL RESULTS

The amount of filterable particulate collected using the in-stack methods was essentially near or below the overall method detection limit (Figure 2). However, condensable particulate matter (CPM) as defined by EPA Method 202 was measured at much higher levels. Analysis of the impinger contents from the boiler test suggests a large fraction of the measured CPM can be accounted for in sulfates and chlorides (Figure 3); however, the mass of sulfates based on the impingers is much greater than that based on the dilution tunnel filters. It is believed the impinger results may be biased high due to dissolved SO_2 in the impingers. Due to differences in the fuel gas sulfur content, SO_2 concentration at the boiler site was approximately 8 ppm, while SO_2 at the process heater site was less than 0.3 ppm. The sulfate concentration in the impinger contents and CPM mass also was higher for the boiler than for the process heater site. Total PM2.5 mass obtained with the dilution tunnel was much lower than the total filterable matter plus CPM mass obtained with the in-stack methods. The dilution tunnel should capture all of the filterable matter plus any aerosols that condense under simulated plume conditions. The striking difference between the dilution tunnel and in-stack method results and the observations noted above suggest that EPA Method 202 results are significantly biased. The values of total particulate agree qualitatively with results reported by EPA in its emission factor database for natural gas combustion in external combustion devices. However, assuming the EPA results were obtained using the same methods, a similar bias may be present in those data.

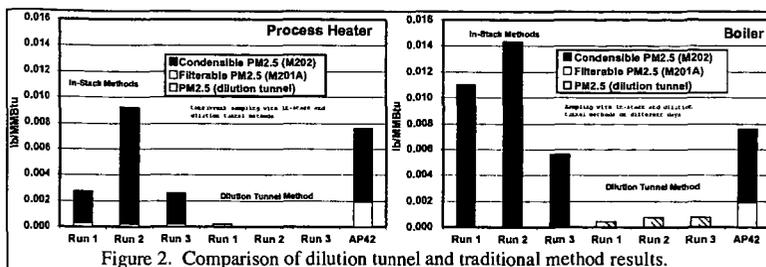


Figure 2. Comparison of dilution tunnel and traditional method results.

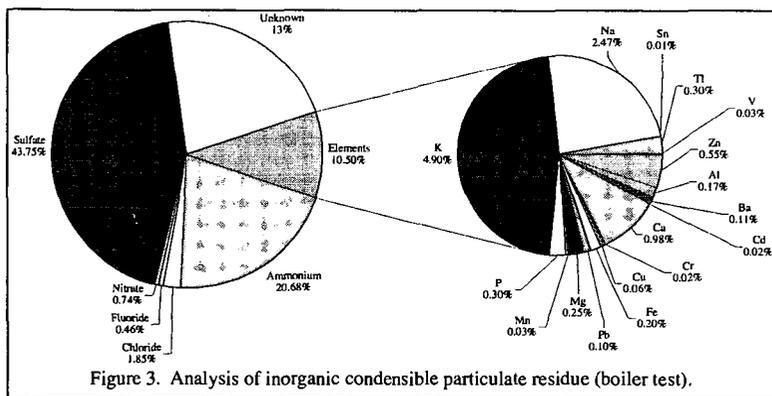


Figure 3. Analysis of inorganic condensable particulate residue (boiler test).

SUMMARY

The sampling methodology described in this paper should result in an improved characterization of source contributions to ambient PM_{2.5}, especially for sources with low particulate concentrations. The test results suggest that traditional source testing methods may significantly overestimate particulate emissions, especially the ultrafine condensable particle fraction. This may be due to analytical method artifacts associated with application of methods designed for much higher particle concentrations. Since particle condensation mechanisms are dependent on both vapor concentration and temperature, dilution tunnel methods provide conditions that more closely represent true atmospheric condensation conditions compared to impinger condensation methods.

ACKNOWLEDGEMENT

The authors wish to acknowledge the contributions of the test personnel, especially Robert Zimmerman and Stephanie Wien of GE-EER, and the staff of the host facilities who graciously allowed us access to the units for testing. The authors gratefully acknowledge the American Petroleum Institute, the U. S. Department of Energy, and the Gas Research Institute for co-funding this work.

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PARTICULATE IMPACTS ON VISIBILITY AT THE GRAND CANYON FROM NORTHWESTERN MEXICO

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KEYWORDS: Sulfate from Mexico, Visibility, Grand Canyon

ABSTRACT

Project MOHAVE was a large study to investigate the causes of visibility impairment in the Grand Canyon National Park region. An episode with regionally elevated sulfate gave the highest concentrations of sulfate measured at Meadview just west of the Grand Canyon on September 1 and 2, 1992. The elevated sulfate concentrations extended south into northwestern Mexico. Based on wind profiler data, emissions from the power plant in the vicinity of Meadview, MPP, could not have been responsible for the regionally observed sulfur oxides. A CMB model developed during Project MOHAVE was used to apportion sulfur oxides at Meadview and other sampling sites throughout the study region for August 31 - September 2, 1992. The results indicate that the contribution of MPP to sulfate at Meadview was typical. However, transport of SO_x from northwestern Mexico was elevated throughout much of the region during this time period. This led to the large increase in sulfate concentrations at Meadview on September 1 and 2. In addition to this major episode, the results obtained with the CMB model indicate that particulate emissions originating from northwestern Mexico are frequently present during the summer at the Grand Canyon. These results indicate that Mexico can be a significant source of visibility reducing particles at the Grand Canyon.

BACKGROUND AND METHODS USED

Project MOHAVE¹ was a joint partnership research program between the U.S. Environmental Protection Agency, the National Park Service and Southern California Edison. An objective of the program was to establish the relative contribution of emissions from the Mohave Power Project, MPP, to visibility degradation in the Grand Canyon region.

Chemical mass balance receptor based apportionment techniques have been used to estimate the point sources and regional contributors to SO_x (SO_2 plus particulate sulfate) and fine particulate sulfate present in the study region^{2,3}. Source profiles of SO_x from the four coal-fired generating station closest to the Grand Canyon National Park and from the various regional sources which can impact the Grand Canyon have been developed using spherical aluminosilicate (SAS) particles present in coal-fired power plant emissions^{3,4}, fine particulate Se, As, Pb, and Br, and light absorption by fine particles^{3,4}. These source profiles allow the CMB discrimination among the various point and regional sources of SO_x in the southwestern United States^{2,3}.

Details of the identification of the various regional sources and the establishment of the source profiles used in the CMB analysis have been given^{3,4}. The profiles of emissions from the coal-fired generating stations nearest the Grand Canyon [Mohave Power Project (MPP), Navajo Generating Station and Reid Gardner Generating Station were established from both ambient and stack data^{3,4}. The eight regional sources present in the Grand Canyon region during the July-August 1992 summer intensive^{2,3} are summarized below. In addition, the profile of emissions from the coal-fired generating stations in Arizona to the southeast of the Grand Canyon was determined from the ambient data.

The identified regional sources³ and their probable geographical origins^{2,3} include:

- SJ: Air masses from the San Joaquin Valley, CA area.
- LA: Air masses transported from the South Coast Air Basin and the San Diego, CA area.
- BC: Air masses for this source region originate from northcentral and northwestern Mexico.
- AZ: Characterized by air masses from the area generally south of the Grand Canyon.
- SE: Characterized by air masses from southeast of the Grand Canyon and Petrified Forest National Parks.
- NW: Days when the sampled air mass at a given site originated from the region north and west of the Grand Canyon established the NW region source profiles. The data were characterized by three distinctly different source regions. These included the profiles for NW1, a region which includes emission from coal-fired power plants (probably in northern Nevada) as evidenced by the elevated SAS/SO₂ ratio, a NW2 local region characterized by a high F_{Total}/SO_x ratio, and a LV profile in which SAS particles and F_{Total} are absent and which meteorological data suggest includes emissions from the Las Vegas urban area 100 km west of the MV sampling site, Figure 1.

The application of a hybrid CMB model² developed using regional profiles to the Project MOHAVE data accounted for all of the source profile species concentrations and for all of the SO₂ and sulfate. An episode of particular interest occurred at the end of the Project MOHAVE summer intensive. The concentrations of sulfate measured by IMPROVE at Meadview on September 1 and 2, 1992 were the highest concentrations reported at this site in six years of monitoring. During this period, the concentrations of SO₂ at Meadview were also high and about three times the sulfate concentrations. Some investigators have assumed this elevated SO₂ indicated that both SO₂ and sulfate at Meadview were dominated by emissions from the nearby Mohave Power Project, MPP. However, the concentrations of sulfate and SO₂ were also comparably high at all stations south of MPP⁶. We have used a combination of meteorological and CMB analyses to investigate the probable source of this regionally observed SO₂ and sulfate. The meteorological data indicate that MPP could not have been the dominant source of the SO₂ and sulfate present throughout the region during this episode⁶. The results indicate that the contribution of MPP to sulfate at Meadview was no higher than, but comparable to, that seen during the July - August 1992 Project MOHAVE Summer Intensive^{2,3,6}. However, transport of SO_x from the Baja California CMB source area was elevated throughout the region during this time period. This lead to the large increase in sulfate concentrations at Meadview on September 1 and 2.

THE SEPTEMBER 1 & 2 EPISODE

The Hybrid CMB model used to apportion sulfur oxides at Meadview and Hopi Point during the Project MOHAVE Summer Intensive period² was applied to IMPROVE data from the Meadview (MV), Las Vegas Wash (LVW), Cottonwood Cove (CC), Dolan Springs (DS), Essex (ES), Yucca (YU), Parker (PA), Wickenburg (WB) and Painted Desert (PD) sampling sites, Figure 2. These regionally distributed sites were all included in the CMB analysis because the IMPROVE data indicated they were all associated with a marked increase in SO₂ and sulfate on September 1 and 2. For most sites, the sulfate concentrations were higher than those measured during the Project MOHAVE 12 July through 30 August Summer Intensive. The source profiles previously developed as part of the CMB model^{2,3} were used without change. The paradigms previously used for the estimation of SO₂ and sulfate deposition and conversion, and for the regional and Meadview area specific transport times were also used without change². Details of this episode CMB analysis have been given⁶.

The CMB analysis results for sulfur oxide emission sources present in the study region for 2 September are given in Figure 2. As indicated, emissions from both LA and BC were generally present throughout the period at all sites. The impact from BC was greater than from LA for both SO₂ and sulfate. During the episode the highest concentrations of impacts from BC were found at Parker, Essex and Yucca. The highest impacts from LA were found at Essex and Yucca. High impacts for SO₂ (but not sulfate) from MPP were found at Cottonwood Cove, Dolan Springs, Las Vegas Wash and Meadview. Significant impacts from LV were found at Las Vegas Wash and Meadview. The site-to-site and day-to-day changes in sulfate and SO₂ are consistent with a southerly flow resulting in generally decreasing SO_x concentrations, but an increasing sulfate to SO_x ratio for the SO_x from the BC and LA source areas throughout the region. The sulfate impacts at Meadview from all sources for each sampling day are given in Table 1. The highest concentrations of sulfate from MPP were 0.69 µg/m³ at Dolan Spring on 1 September and 0.55 µg/m³ at Meadview on 2 September. All other estimated MPP sulfate impacts were

less than $0.4 \mu\text{g}/\text{m}^3$. In contrast, the highest estimated sulfate impact at Meadview from any source was $1.8 \mu\text{g}/\text{m}^3$ from BC on September 2.

RESULTS FROM THE PROJECT MOHAVE SUMMER INTENSIVE

The results obtained during the episode described above were consistent with the importance of the BC source in the Grand Canyon region during the Project MOHAVE Summer Intensive². These results are illustrated by the data in Figure 3 where are given the total sulfate present at the sampling site at Hopi Point in the Grand Canyon and the sulfate attributed to the BC source region during each day of the Project MOHAVE Summer Intensive. As indicated, sulfate from the BC region were frequently present at Hopi Point. When emissions from this source region were present, they often accounted for the majority of the sulfate. While concentrations as high as the $1.8 \mu\text{g sulfate}/\text{m}^3$ at Meadview on September 2 were not seen at Hopi Point during the summer intensive, concentrations from 0.5 to $1.5 \mu\text{g sulfate}/\text{m}^3$ were frequently seen. The BC region accounted for an average of 42% of the sulfate present at Hopi point during the Project MOHAVE summer intensive². Correlation of the CMB results with measured light extinction at Meadview indicated that light extinction due to anthropogenic emissions from the BC region, per unit of sulfate present from the source, was comparable to that for anthropogenic emissions from most other sources, but only about half that for emissions from the LA source region.⁷ However, the LA source region only accounted for 5% of the sulfate present at Hopi Point.² Thus, combination of the CMB and light extinction data obtained during Project MOHAVE suggest that emissions from northwestern Mexico were the dominant anthropogenic source of visibility impairing particulate material at Hopi Point in the Grand Canyon during Project MOHAVE.

ACKNOWLEDGMENTS

Support for this work was provided by Southern California Edison to participate in Project MOHAVE. However, the results, findings, and conclusions expressed in this paper are solely those of its authors and are not necessarily endorsed by the management and sponsors of Project MOHAVE.

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Table 1. Meadview Sulfate Source Apportionment, 31 August - 2 September 1992, $\mu\text{g}/\text{m}^3$.

Date	MPP	LV	LA	BC	Sulfate	
					Not Fit.	% ($\mu\text{g}/\text{m}^3$)
31 Aug	0.3	0.3	0.2	1.1	4.2	(0.1)
1 Sep	0.3	1.4	0.4	0.9	8.4	(0.2)
2 Sep	0.6	0.8	0.6	1.8	14.8	(0.6)

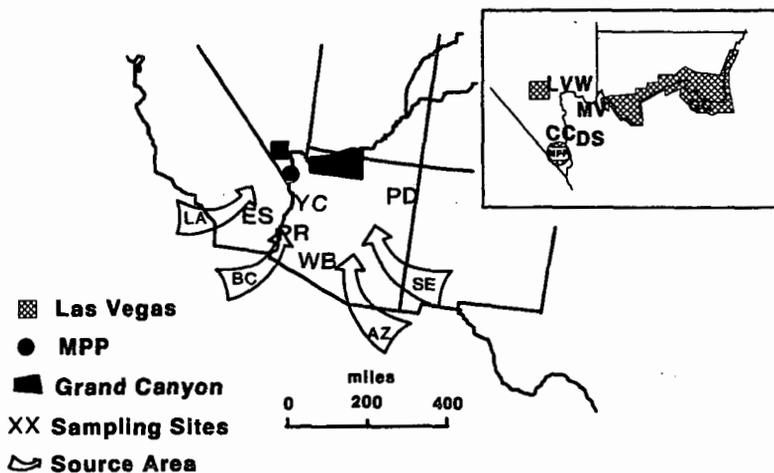


Figure 1. Location of the various sampling sites included in the CMB analysis for 31 August - 2 September 1992, and the expected origins of emissions from the sources included in the analysis; MPP, Las Vegas, LA, BC, AZ and SE.

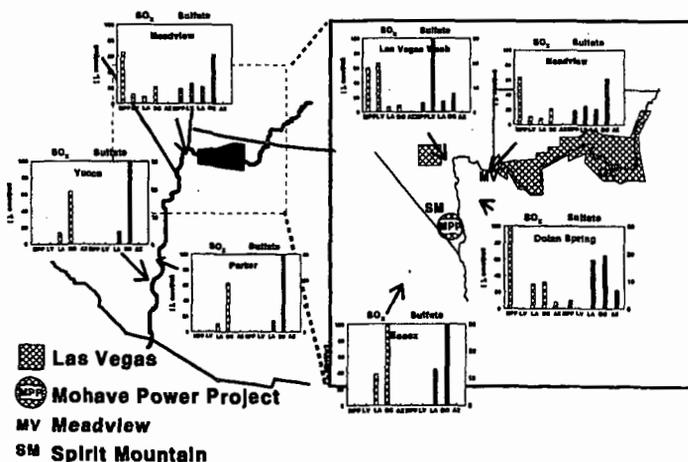


Figure 2. Results of the CMB analysis for SO_2 and sulfate (nmol/m^3) on 2 September 1992 at the sampling sites identified in Figure 1 for the sources identified in Figure 1.

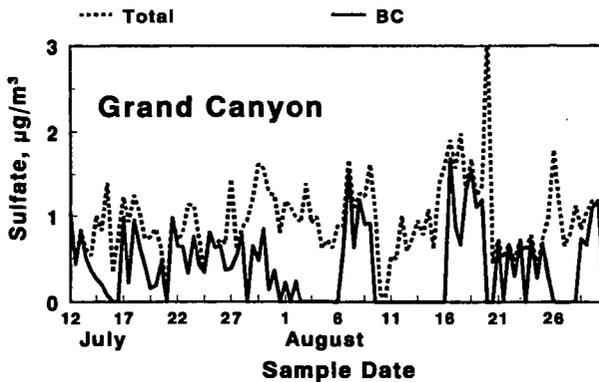


Figure 3. Total and BC sulfate at GC. Northern Mexico is often a major contributor to sulfate at the Grand Canyon.

PM_{2.5} SEMI-VOLATILE MATERIAL: PHILADELPHIA AND ATLANTA SUPERSITE RESULTS

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KEYWORDS: Fine particle sampling, semi-volatile organic material, ambient monitoring

ABSTRACT

Ammonium nitrate and semi-volatile organic material are significant components of fine particulate material in most urban atmospheres which are not properly identified during sampling with single filter samplers because of the loss of these materials from the collected particles during sampling. The composition of fine particulate material at the Philadelphia NARSTO and Atlanta Supersite studies was measured with two PC-BOSS diffusion denuder samplers and with a RAMS continuous monitor. Samples collected with the PC-BOSS were analyzed for sulfate, nitrate (including ammonium nitrate lost from collected particles during sampling), soot, organic material (including semi-volatile organic material lost from particles during sampling), crustal material, and mass. Significant amounts of semi-volatile organic material were present in the particles throughout both studies and semi-volatile organic material was not well measured with single filter samplers such as the a TEOM monitor or the PM_{2.5} FRM.

BACKGROUND

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased mortality and morbidity from respiratory and cardiopulmonary disease^{1,2}. These effects are observed with exposure to concentrations substantially below the U.S. PM₁₀ ambient air quality standard. The observed exacerbation of health problems is believed to be associated more closely with exposure to fine particles than coarse particles. As a result, the U.S. Environmental Protection Agency has promulgated³ revised standards for PM, which establishes new annual and 24-hour fine particle standards with PM_{2.5} as the indicator. This recognition of fine and coarse particles as different classes of PM pollutants is an advance in the understanding and control of PM. However, ambient fine particulate matter is not a single pollutant, but a mixture of many chemical species. Major components include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic metals); organic material; elemental carbon (or soot); crustal components; and water. Stable species such as trace and crustal elements, and sulfate can be accurately measured by available technology. However, monitoring technologies for organic carbon, nitrate and particulate water are not as well established.

The collection of particulate matter containing ammonium nitrate on a filter results in displacement of the equilibrium, $\text{NH}_4\text{NO}_3 \cdot x\text{H}_2\text{O}(s) = \text{HNO}_3(g) + \text{NH}_3(g) + x\text{H}_2\text{O}(g)$, with the extent of loss of ammonium nitrate from particles being a function of sampling time, filter face velocity, composition of the fine particles being sampled, temperature, humidity and other factors. However, in the eastern United States there tends to be little nitrate in fine particles because of the high acidity of the aerosol.

A second fine particulate component for which significant losses during sampling on a filter have been documented is semi-volatile organic material. Preliminary studies in eastern sites have indicated that an average of about one-half of fine particulate organic material is lost due to the stripping of semi-volatile organic compounds from the particles during sampling. The hypothesis of the studies reported here is that fine particulate mass will be significantly under-determined in eastern urban environments using the proposed PM_{2.5} Federal Reference Method (FRM) because of the loss of semi-volatile material from the particles during sampling. It is postulated that fine particulate mass, including the semi-volatile fine particulate species, is an appropriate surrogate for the components of fine particles which have been associated with observed mortality and morbidity effects in epidemiological studies. Under-determination of these semi-volatile species will tend to over emphasize the importance of non-volatile fine particulate components such as sulfate. In addition, the need is recognized for both real-time and week-long sampling methods which accurately measure PM_{2.5}, including the volatile constituents ammonium nitrate and semi-volatile organic material. The studies reported here used a PC-BOSS diffusion denuder sampler for the determination and characterization of fine particulate

mass, including semi-volatile organic and nitrate species which can be lost from fine particles during sampling with a filter, and a RAMS for the continuous measurement of fine particles.

EXPERIMENTAL

Samples were collected at the NARSTO summer 1999 sampling site at the Baxter Water Treatment Plant in Philadelphia PA during July, and at the EPA Supersite program at the Georgia Power facility in Atlanta GA during August. The two diffusion denuder samplers intercompared in these two studies were:

1. PC-BOSS

The combination of the technology used in the BIG BOSS sampling system⁴ and the Harvard particle concentrator has resulted in the Particle Concentrator-Brigham Young University Organic Sample System⁵. The system has been optimized to meet the following criteria; 1. Removal of at least 75% of the gas phase material before the sampled aerosol is passed through the diffusion denuder. 2. Efficiency >99% for the removal of SO₂, HNO₃, and gas phase semi-volatile organic material in the minor flow. 3. Determination of particulate mass, carbonaceous material and nitrate with a diffusion denuder sampler.

The inlet to the sampler is a Bendix cyclone with a particle cut of 2.3 μm aerodynamic diameter at an inlet flow of 150 L/min. The cyclone is followed by a virtual impactor particle concentrator. The particle concentrator separates most of the gas phase material into the major flow and leaves particles larger than the cut point (about 0.1 μm) along with a significantly reduced fraction of the gas phase material in the minor flow. The minor flow (25% of the total 150 L/min flow) containing concentrated particles enters the BOSS diffusion denuder^{4,6}. The denuder is comprised of 17 (4.5 x 58 cm) strips of Schleicher and Schuell charcoal impregnated filter paper which are separated at the long edges by 2-mm glass rods. This gives a diffusion denuder with both high efficiency and high capacity. The denuder is followed by two parallel filter packs. The filter pack containing a 47 mm quartz filter (Pallflex, pre-fired) followed by a 47 mm charcoal impregnated filter (3M EMPORE Carbon) is used to determine fine particulate nitrate and carbonaceous material, including semi-volatile organic material lost from the particles during sampling. The second filter pack contains 47 mm Teflon (Gelman Teflo) and nylon (Gelman Nylasorb) filters to determine mass, acidity, ammonium ion, sulfate and nitrate, including any nitrate lost from particles during sampling.

2. RAMS

The RAMS (Real-time Ambient Mass Sampler) is based on the modification of a TEOM monitor to allow for the determination of fine particle mass, including the volatile species⁵. Gas phase compounds which can be absorbed by a charcoal impregnated filter (CIF) are removed by a series of denuders and a Nafion dryer. The resulting airstream is then sampled by a TEOM monitor with a "sandwich" filter containing an R&P TX40 and an S&S CIF filter to collect particles and any ammonium sulfate or semi-volatile organic material lost from the particles during sampling. An active blank system with a filter at the inlet is used to correct for any inefficiency in the denuder and dryer for the removal of gas phase material.

RESULTS

The RAMS blank corrected data are illustrated in Figure 1 for both Philadelphia and Atlanta. Also shown in Figure 1 are conventional TEOM monitor data for the same time periods. As indicated, the concentrations of PM_{2.5} measured by the RAMS is generally either equal to or greater than that measured by the TEOM monitor. The time periods when greater PM_{2.5} mass is measured by the RAMS are those when measurable concentrations of semi-volatile material (dominated by semi-volatile organic material) are measured by the RAMS, but not the TEOM monitor.

The results obtained for the continuous determination of PM_{2.5} with the RAMS have been validated by comparison with results obtained from the PC-BOSS integrated samples to determine the mass of fine particulate material retained on a filter⁵ and the semi-volatile organic material and ammonium nitrate lost from the filter during sampling with a PC-BOSS⁵. Results obtained with RAMS and PC-BOSS denuder sampler show that PM_{2.5} mass, including semi-volatile fine particulate nitrate and organic species can be continuously and accurately monitored with the RAMS. The linear regression of RAMS vs PC-BOSS results give a slope of 1.02±06 (n=7) for the Philadelphia data and comparable results for Atlanta. The average composition of the fine particles collected during the time period shown in Figure 1 at Philadelphia is shown in

Figure 2. As indicated, an average of 35% of the $PM_{2.5}$ was lost from particles during sampling at Philadelphia. These species were not measured by either the TEOM monitor or a single filter sampler. The results obtained at Atlanta were similar, Figure 1.

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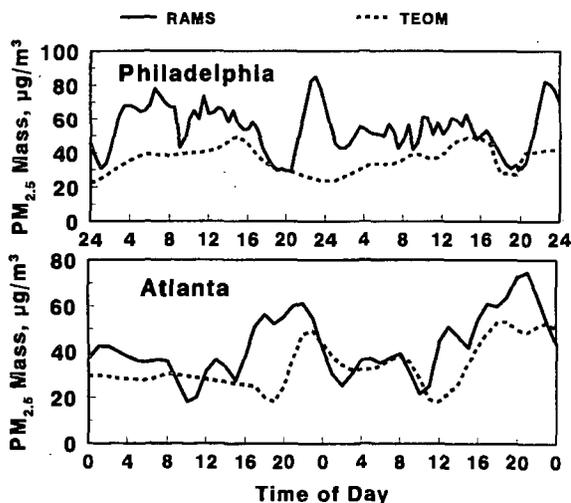


Figure 1. Comparison of 2 h running average of RAMS and TEOM monitor data at Philadelphia. The higher mass measurements with the RAMS is due to the determination of semi-volatile fine particulate material.

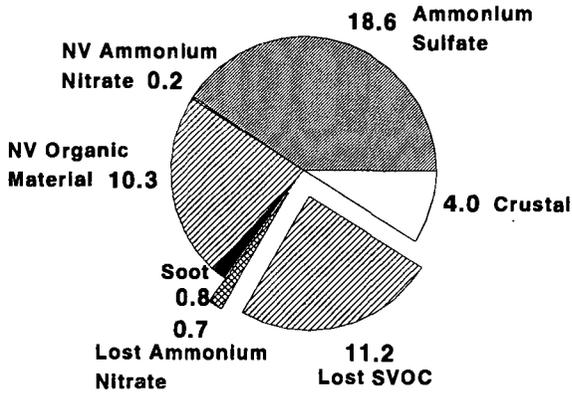


Figure 2. Composition of Philadelphia PM_{2.5}. The ammonium nitrate and SVOC lost from particles during sampling are collected by the RAMS, but not a TEOM monitor.

CHARACTERIZATION OF FINE PARTICULATE MATTER IN OHIO

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ABSTRACT

As a result of recent changes in the air quality standards for particulate matter, an exhaustive study was undertaken to measure PM_{2.5} in Ohio. The ambient results reported here are from an ongoing field experiment in Ohio that began in January of 1999. The ambient monitoring is part of a comprehensive health based study evaluating the impact of air pollution on pediatric health in Ohio. This is among the first of its kind in Ohio, with continuous ambient air monitoring at several sites to characterize fine particulate matter concentrations within the region using Tapered Elemental Oscillating Microbalance (TEOM) samplers. Two locations in Columbus, Ohio were chosen, one in the urban corridor and the other in a suburban location. A third location in rural Athens, Ohio was also established. In addition to the continuous monitors, filtered samples were gathered for chemical analysis of the particulate matter using an x-ray fluorescence spectrometer and an ion-chromatography unit. A spatial homogeneity in the mass concentration time-series data was noted. Sulfate was the largest component of the PM_{2.5} comprising approximately 40% of the total mass

INTRODUCTION

In 1997, the United States Environmental Protection Agency (EPA) implemented new National Ambient Air Quality Standards (NAAQSs) for ozone (O₃) and particulate matter (PM). These standards were based on multi-year scientific assessments that linked health effects to present air pollution levels. The standards, which tighten the requirements for attainment, will have significant economic and social impact for Ohio. For example, under the PM_{2.5} standard, estimates have indicated that 26 counties in Ohio will be in non-attainment. In comparison, one county in Ohio does not currently meet the NAAQSs for PM₁₀.

There is limited data on PM_{2.5} concentrations and its constituents in Ohio. The few historical studies (1,2,3) that have been conducted were health-based studies centered on areas with historically high levels of air pollutants, such as Steubenville, Ohio. This paper presents findings from an ambient PM_{2.5} monitoring campaign that is part of a large on-going health based study in Columbus and Athens, Ohio.

The field experiment, which began in February of 1999, consists of three longitudinal studies involving a rural location (Athens, Ohio), and two urban settings (both within Columbus, Ohio). Two contrasting sites in Columbus were established -- one urban (south central side of Columbus), and one suburban (New Albany, OH). Columbus, like numerous other metropolitan areas in the state and across the nation, has historically met the NAAQS for ozone and PM₁₀ but has the potential for non-attainment under the new PM_{2.5}, and O₃ standards. The rural site (Athens Ohio) was chosen due to its proximity to the background site established by Ohio EPA for PM₁₀ and recently PM_{2.5}. Athens is also being utilized as a background site for the Upper Ohio River Project (4), a comprehensive PM fine and precursor gas monitoring program centered in Pittsburgh that was initiated in early 1999.

MATERIALS AND METHODS

Data is collected simultaneously from three monitoring sites that typify urban, rural, and a downwind suburban location. These sites will aid in the characterization of fine particulate spatially and temporally. PM_{2.5} measurements are obtained with TEOM series 1400a monitors manufactured by Ruprecht and Patashnick Co. The TEOM is a real time gravimetric instrument that draws ambient air through a filter at a constant flow rate and measures PM concentrations continuously. The TEOMs are equipped with automatic cartridge collection units (ACU) fitted with 47 mm filter packs. Samples are collected on Teflon filters. At each site, seven hour (8:30 a.m. -3:30 p.m.) samples are collected Monday thru Friday. The outdoor monitoring regime is tied to simultaneous indoor and personal

monitoring conducted as part of the health based study. Particle mass is determined using an electronic microbalance. The Teflon filters are equilibrated prior to weighing under controlled conditions (22.5 ± 2.5 C and $35 \pm 5\%$ relative humidity). The filters are then subjected to elemental analysis by energy dispersive x-ray fluorescence (XRF). This non-destructive technique is capable of identifying and quantifying elements in the periodic table from atomic number 9 (fluorine) to atomic number 92 (uranium). The samples are then analyzed for water soluble ions by ion chromatography. The water soluble species measured include five anions (fluoride, chloride, nitrate, phosphate, and sulfate) and five cations (sodium, ammonium, potassium, magnesium, and calcium). Meteorological parameters such as temperature, wind speed, wind direction, relative humidity, and precipitation are also measured hourly at each site.

RESULTS/DISCUSSION

The first phase of this project is currently being analyzed. Detailed statistical analysis will be presented at the Particulate Matter and Fossil-Fuel Combustion Symposium - 2000 American Chemical Society Meeting in San Francisco, March 26-31, 2000. Site characterization of the $PM_{2.5}$ and its constituents both temporally and spatially will be evaluated. In addition, the influences of meteorological parameters on total mass and chemical constituents of the $PM_{2.5}$ will be examined.

Daily averaged TEOM data for February through the middle of May are contrasted in Figure 1 for the three sites -- New Albany (suburban, Columbus), Koebel (central urban, Columbus) and East (rural, Athens). What is striking about the preliminary analysis is the uniformity in the data between the sites. New Albany and East (which are approximately 80 miles apart) show very similar temporal profiles over the entire sampling period. Koebel (central urban location) which experienced higher concentrations, potentially influenced by local sources, also had similar temporal patterns. This uniformity is further demonstrated in Figure 2 which presents the diurnal changes in $PM_{2.5}$ for June 2nd thru the 6th. Again all three sites show similar patterns in the concentration profile. Table 1 lists the results of the daily averaged $PM_{2.5}$ concentrations for February and March. As expected Koebel (urban) had a slightly higher average concentration followed by New Albany (suburban) and East (rural). Preliminary analysis by ion chromatography on the filter samples for February and March at East indicates that SO_4^{2-} is the primary water-soluble fraction, comprising on average 40% of the total $PM_{2.5}$ mass.

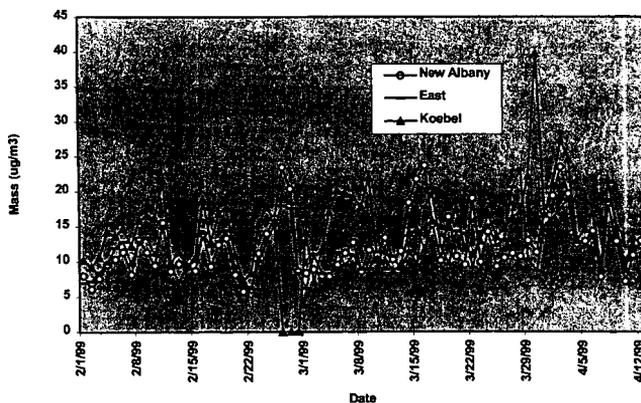


FIGURE 1. Daily average variations in $PM_{2.5}$ concentrations (TEOM) for Koebel (urban Columbus), New Albany (suburban Columbus), and Athens (rural).

CONCLUSIONS

Detailed analysis of the data is currently ongoing. However, preliminary review of the data indicates spatial homogeneity in the $PM_{2.5}$ concentration. This uniformity is experienced in

the daily average concentrations and in the diurnal patterns experienced at each site. SO_4^{2-} was found to comprise 40% of the $\text{PM}_{2.5}$ concentration at the rural site.

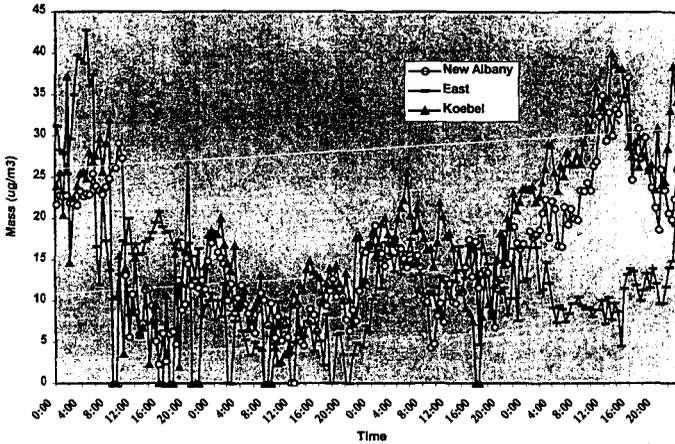


FIGURE 2. 30-minute average variations in $\text{PM}_{2.5}$ concentrations: June 2-6, 1999 for Koebel (urban Columbus), New Albany (suburban Columbus), and Athens (rural).

Table 1. Summary of the Daily Averaged $\text{PM}_{2.5}$ and Sulfate Concentrations for February and March 1999*

Site	Total Mass mean \pm SD	SO_4^{2-} mean \pm SD
New Albany (suburban)	11.8 \pm 4.1	
Koebel (urban)	14.7 \pm 5.1	
East (rural)	11.6 \pm 3.6	4.7 \pm 2.2

* Filter samples are collected five days per week (Monday thru Friday). Concentrations expressed as $\mu\text{g}/\text{m}^3$.

ACKNOWLEDGMENTS

The authors would like to acknowledge Peg Conley, Stacey Friel, Nick Michailides, Mayra Alvarado, and Case Garrison who are involved with collection, validation, and analysis of the $\text{PM}_{2.5}$ data. The efforts of Randy Hock and Paul Koval for evaluation and identification of site locations, and their interest and insight is also acknowledged. This ongoing project is funded by the Ohio Environmental Protection Agency.

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ENVIRONMENTAL IMPACT OF HEAVY METALS CONTAINED IN FLY ASH EMITTED FROM THE THAI LIGNITE-FIRED POWER PLANT

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ABSTRACT - In this work, the highly hazardous heavy metals (HM) are the focus of an assessment of the environmental impact of the Mae Moh Power Plant (Northern Thailand) fired with Thai lignites. The synergetic environmental impacts associated with the high sulfur content in the fuel (average value of 3.3% and maximum up to 7.0%) and the presence of a large number of heavy metals (As, Ba, Ce, Co, Cr, Cs, Ni, U, Rb, Sr, Th, etc) in the fly ash have been assumed in the model. Using data on the fly ash emission and HM content in the fly ash, the amount of heavy metals emitted from the lignite-fired boilers of the Mae Moh Power Plant was predicted. Calculation of the approximate rates of HM depositions was then conducted and the predicted values were compared with the corresponding element contents in regional soils. For various scenarios of power plant operation conditions and affected area, the environmental impact of heavy metals on that area was estimated. The results show the dangerous tendency of the HM accumulation in soil organic matter under certain conditions.

KEYWORDS: Environmental impact, heavy metals, Thai lignite-fired boilers.

INTRODUCTION

The power production sector of the Thai economy is the strongest emitter of suspended particulate matter (SPM) into environment. Annually, more than 1 Mton, or 80 % of the total SPM emission (referred to as fly ash), is discharged into the atmosphere from solid fuel-fired units, whereas the share of the SO_x emission from power generation accounts for 60 - 65 %. The contribution share of other pollutants (NO_x, CO₂, CO) formed in utility and industrial boilers is much lower (Chungpaibulpatana et al., 1997).

At present, Thai lignite is the major solid fuel used for power generation in Thailand, and this tendency will remain during the next 10-15 years. Lignite, like any other coal, structurally consists of aromatic rings connected by bridges of carbon, sulfur, nitrogen, and other heteroatoms. Coals also contain "grains" of mineral matter, basically consisting of aluminosilicates (or clays), sulfides, carbonates, oxides (usually quartz) and chlorides. Besides, heavy metals (HM) are incorporated into the coal structure as either organometallic compounds or inorganic materials, closely associated with the fuel matter. During combustion the mineral compounds are converted to oxides. Fly ash from conventional combustion boilers consists of conventionally seven oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O and K₂O) as well as traces of HM. When fluidized-bed combustion is used, some other compounds (for example, MgCO₃ and CaSO₄) are contained in fly ash leaving the stacks of the power plant.

Almost all chemical elements have been found in various types of coals (including lignites). As for fly ash, the content of various elements in it may vary in the range from the parts per trillion level (ppt) to more than 50 wt. %. The content of heavy metals (HM) for different solid fuels varies from less than 0.5 ppm (for Cd, Hg) up to several thousands ppm (for Ba, Zn) as indicated by Tillman, 1994.

In this work, the highly hazardous HM were the focus of an assessment of environmental impact of the Mae Moh Power Plant fired with Thai lignites.

MATERIALS AND METHODS

Presently, the Mae Moh Power Plant consumes almost all of the lignite used for power generation in Thailand and represents, in effect, the only source of HM emission from the power sector in the country. After the year 2010, Thai lignites will be gradually replaced with imported higher quality coals, which are planned to be fired in new power producing utilities (Chungpaibulpatana et al., 1997).

Thai lignite can be classified as a high sulfur, low-rank coal. Moreover, as time goes by, the fuel quality is being deteriorated. The lignite supplied to the Mae Moh Power Plant from different mines is currently characterized by a low content of carbon (20 - 35 %), a medium moisture content (26 - 35 %), a variable ash content (17 - 41 %), and a high sulfur content (1.7 - 3 %). The nitrogen content varies from 0.8 to 1.25 %, the oxygen content from 7 to 10.7 %, and hydrogen content from 1.8 to 3.2 %. The lignite's lower heating value is estimated to be 10.4 MJ/kg (averaged).

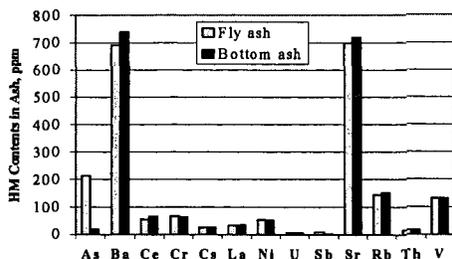


Fig.1. Variability of heavy metals measured in fly and bottom ash of Thai lignite

The most important data used to approach the objectives in our work were found in a paper devoted to determining the X-ray fluorescence analysis of fly and bottom ash (Fig.1) collected from units of the Mae Moh Power Plant (Ratanasthien et al., 1993). As may be seen in Fig.1, data referred to bottom ash confirm that the HM contents are of the same order as ones for fly ash, except for arsenic.

To estimate the emission of ash, we first estimated the total amount of ash (per annum) formed from fuel combustion in steam boilers installed at the power plant. Meanwhile, the SPM emission is associated with ash particles that enter the atmosphere with flue gas, i.e. those that pass through the ash removal equipment arranged downstream from the boilers and remain in the (waste) flue gas. The relevant data (Chungpaibulpatana et al., 1997) for the period of 1990 – 2030 are given in Fig. 2.

At present, the SPM emission is rather high and can be estimated to be about 1/3 of the total ash emission, indicating a low efficiency of ash collecting units used at the power plant. Since new power plants aimed at firing imported coals will be equipped with highly efficient ash collecting devices, the SPM emission is mostly associated with firing lignite, and the data can be used in our work (as given in Fig. 2) for estimating the HM emission from the power plant.

The Mae Moh Fuel-Power Complex (including the power plant) is located in Northern Thailand. The area is bound between 15°N to 20.5°N and 97.5°E to 101.5°E. The climate characteristics of the region (Climatological Division, 1994) and also the vegetation and soil properties of Northern Thailand were used for calculation of pollutants deposition rates and comparison with natural HM content in different soil/ecosystem combinations.

In the case of Thai lignite firing, the synergetic environmental impacts are associated with the presence in the fuel of high quantity of sulfur (1.7 – 3.0 %, in some samples up to 7.0 %) and large number of heavy metals (As, Ba, Ce, Co, Cr, Cs, Ni, U, Rb, Sr, Th, etc). Upon deposition, the synergetic environmental impacts of sulfur and HM are related to the acceleration of biogeochemical migration of most HM under acid conditions. The acidification of tropical soils due to sulfur acidity loading will undoubtedly facilitate the accumulation of many heavy metals in food chains in both terrestrial and aquatic ecosystems (Bashkin & Park, 1998).

The general concept of atmospheric transport and deposition computational method is that the concentration of any substance in air is calculated from its emissions, subsequently transported by (averaged) wind flow and dispersed over the area of interest due to atmospheric turbulence. Basically, the removal of the substances from the atmosphere by wet and dry deposition and photochemical degradation is described in general model algorithms. Meantime, transportation and dispersion of HM in the atmosphere are assumed to be similar to as for other air pollution compounds, for instance, such as SO₂ and the smog compounds (Dutchak et al., 1998).

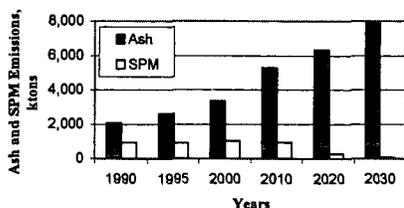


Fig.2. Emissions of ash and SPM (per annum) from the power sector in Thailand

The RAIN-ASIA computational model has been previously applied for the area in the North of Thailand scaled with the $1^{\circ} \times 1^{\circ}$ grid for different time/fuel scenarios based on sulfur deposition predicted data (World Bank, 1994). Some new results have been reconsidered recently using the updated input data (Kozlov&Towprayoon, 1998). Much more detailed studies were carried out by Doolgindachbaporn, 1995, and Ross et al., 1998, for the Mae Moh valley where the power plant is located. The resolutions were from 5 to 10 km cells. Differing in some details, these models indicate the area of most polluted zone as 134 – 179 km², averaged 159 km².

Due to lack of the comprehensive computational model for the HM depositions in the Mae Moh valley, we assume the following two assumptions in selecting the impacted area around the Mae Moh Power Plant:

1. The area of HM dispersion is assumed to be similar to that described in RAIN-ASIA for sulfur deposition, i.e., 20 $1^{\circ} \times 1^{\circ}$ Lola grid cells ranged between 16°N – 20°N and 98°E – 103°E. The total area is as much as 12321 km².
2. The area of HM dispersion is selected to be similar to that described by Doolgindachbaporn (1995) and Ross et al. (1998) for the Mae Moh valley only. The total area is (approximately) 159 km².

These assumptions allow us to estimate the boundary limits for depositions of heavy metals emitted from the Mae Moh Power Plant.

RESULTS AND DISCUSSION

In our study we will consider the toxic metals (according to US EPA classification), namely As, Ba, Cr, Ni and Sb, and also some others, whose emissions are expected to be high. The predicted values on HM emissions are represented in Table 1.

Obviously, HM emissions depend on both emission of SPM from the power plant and HM content in fly ash. The prevailing values of emissions were found for Barium and Strontium, the amounts of those by the year 2000 were estimated to be 716.22 and 726.6 tons/year, respectively.

The emissions of Vanadium, Rubidium, and Arsenic ranged between 120 and 220 tons per year. Relatively small emissions were found for Cesium, Chromium, Nickel, Cerium and Lanthanum (26 – 70 ton/year). The smallest values were found for Uranium, Thorium, and Antimony, they ranged from 5 to 9 tons per year.

However, the environmental impact of the HM depends not only on their emission. Mainly, it is associated with the deposition rates (which depend on the impacted area), relative increase in HM content in soil and some other factors. As mentioned above, two case studies (associated with different impacted areas assumed in computations) have been considered in our work to estimate the dispersion of HM over the area near the power plant.

In the first case study, the total amount of emitted HM was assumed to deposit proportionally to sulfur compounds dispersion over the (maximum) area of 12321 km². The selected year is referred to 1995. According to our assessment, if the impacted area were selected to be 12321 km², in the most polluted $1^{\circ} \times 1^{\circ}$ Lola grid cells, 100°E – 18°N, the deposition rates of HM would

Table 1. Predicted Values of HM Pollution from Power Generation in Thailand, tons

Element	1981	1986	1990	1995	2000	2010
As	29.394	84.561	201.285	196.599	221.094	204.054
Ba	95.22	273.93	652.05	636.87	716.22	661.02
Cr	9.177	26.4005	62.8425	61.3795	69.027	63.707
Ni	7.3554	21.1601	50.3685	49.1959	55.3254	51.0614
Sb	1.1868	3.4142	8.127	7.9378	8.9268	8.2388
Ce	7.4658	21.4777	51.1245	49.9343	56.1558	51.8278
Cs	3.588	10.322	24.57	23.998	26.988	24.908
La	4.5264	13.0216	30.996	30.2744	34.0464	31.4224
U	0.8570	2.46537	5.86845	5.73183	6.44598	5.94918
Rb	19.872	57.168	136.08	132.912	149.472	137.952
Sr	96.6	277.9	661.5	646.1	726.6	670.6
Th	2.3598	6.7887	16.1595	15.7833	17.7498	16.3818
V	18.078	52.007	123.795	120.913	135.978	125.498

have varied from 174 g/km²/year (U) up to 19665 g/km²/year (Sr). The intermediate values are shown for As (5984 g/km²/year), Cr (1868 g/km²/year) and Ni (1497 g/km²/year).

In the second case study the total amount of emitted HM was assumed to disperse evenly over the minimum area of 159 km². If the minimum impacted area were assumed to be 159 km², the values of HM deposition rates would vary from 40,500 g/km²/year (for U) to 4,064,200 g/km²/year (for Sr). The depositions of the most dangerous elements are shown to be equal to 1,236,450 g/km²/year for As, 386,100 g/km²/year for Cr and 309,000 g/km²/year for Ni. No doubt these values are of the great environmental concern for human and ecosystem health.

In spite of the very rough estimation, the predicted values of HM deposition rates are useful for comparison with their natural content in soils of North Thailand. Many considered heavy metals (Ba, Cr, Ni, Cs, La, V) are active biogeochemical migrants and they accumulate in the upper humus soil layer in much more significant amounts in comparison with their local or regional average values in soil and geological rocks, or clarks (Dobrovolsky, 1994). Accordingly, the annual HM deposition rates were compared with both values of HM content in upper humus layer and clarks. The average depth of heavy metal accumulation layer is assumed to be 20 cm.

Calculations have shown that even in the case of maximum area of impacted zone, 12321 km², the annual deposition rates of some heavy metals (As, Ni, Cs, La, V) are equal to 0.2 – 0.5 % of their clarks and achieve 13.5 % for Barium for the area of the most polluted LoLa grid cell of 18°N – 100°E. Nevertheless, many of these metals are biogeochemically active elements and their accumulation is much greater in the upper humus layer. The relative increase in this layer is significantly less and ranges between 0.005 – 0.05 % from corresponding values. Thus, the danger might be connected with As, which could accumulate in soils with annual rate of 0.5 % to the clark value and which is ecologically considered to be one of the most important pollutants.

A much more dangerous scenario can be calculated for the minimum impacted area, 159 km². In this case, even in humus layer the annual increase for biogeochemically active elements achieves 6.43 % for Ba being in range of 0.16 – 3.12 % for other HMs from their content in humus layer. Since the clark values are significantly less than those characterizing an accumulation in humus layer, the relative annual enrichments of HM content in soils are estimated to be between 3.48 % (for Rb) and 103.0 % (for As). These values are undoubtedly dangerous.

The situation is made worse by the synergistic influence of acidification loading from sulfur compounds, which is also dramatic in the region of interest. The increase in acidity of soils and surface waters is known to be accompanied by increasing the mobility of most heavy metals. It leads to possible accumulation of HM in food chains of both terrestrial and aquatic ecosystems.

Table 2 represents the accumulated amounts of HM in soil-biogeochemical fluxes in Tropical Wet Forest ecosystems surrounding the Mae Moh Fuel-Power Complex. The assumption was made that all amount of deposited HM might be accumulated in upper soil layers and could migrate with soil-biogeochemical fluxes of these trace elements. This is reasonable, taking into account high content of Ca and Mg in fly ash of Mae Moh Power Plant. One can see that in case of almost all trace metals (the exception is Sr), the 20 year exploitation of Power plant has led to significant accumulation of HM in the upper soil layers. The values of accumulation might vary from 1.8 ppm for U till 488.0 ppm for Ba. These values have to be added to the natural content of heavy metals in soils. The resulting values are higher than existing environmental quality criteria (limits) for HM contents in soils concerned As, Ba, Cr, Ni, and V (Radojevic and Bashkin,

Table 2. Accumulation of Some HM in Soils over the Minimum Impacted Area (159 km²) (during the period of 1981 – 1999)

Element	Natural content, ppm		Accumulation due to HM emission, ppm
	Upper humus layer	Clark	
As	-	5.0	62.0
Ba	432	0.6	488.0
Cr	197	5.8	19.4
Ni	84	3.2	15.5
Sb	-	1.0	2.51
Cs	20	1.8	7.6
La	80	2.0	9.5
U	-	1	1.8
Rb	-	100	41.9
Sr	-	300	203.5
V	212	3.2	38.1

1999). Furthermore, in many cases the content of HM is higher than the requirements for the remediation, even for commercial or industrial land use.

CONCLUSIONS

1. The emissions and environmental effects of heavy metals from the lignite-burned Mae Moh Power Plant (Northern Thailand) were estimated for the 30-years period from early 80's to year 2010. With increase in power production late in 90's and early in the next century, the major values of emissions were found for Barium and Strontium (more than 650 tons per year). The emissions of Vanadium, Rubidium, and Arsenic ranged between 120 and 220 tons per year. Relatively small emissions were calculated for Cesium, Chromium, Nickel, Cerium and Lanthanum (26 - 70 ton/year). The minimum values were shown for Uranium, Thorium and Antimony, ranging from 5 to 9 tons/year.
2. If the impacted area were considered as minimum one (159 km²), the values of HM deposition rates might be varied in the range from 0.04 (for U) to 4.1 (for Sr) ton/km²/year. The deposition rates, ton/km²/year, of the most dangerous elements were roughly estimated be 1.2 for As, 0.4 for Cr and 0.3 for Ni. If the impacted area were treated as 12321 km², the deposition rates of heavy metals for the most polluted 1°x1° Lola grid cells (100°E - 18°N) in 1995 would have varied from 0.174 (for U) up to 19.7 kg/km²/year (for Sr). The intermediate values were found for As (6.0 kg/km²/year), Cr (1.9 kg/km²/year) and Ni (1.5 kg/km²/year).
3. The 20-years period of exploitation of the Mae Moh Power Plant has led to significant accumulation of HM in the upper soil layer and their migration with soil-biogeochemical fluxes in the Tropical Wet Forest ecosystems surrounding the plant. The values of HM accumulation were estimated to vary from 1.8 ppm (for U) to 488.0 ppm (for Ba). Being added to the natural content of heavy metals in soils, the resulting values for As, Ba, Cr, Ni, and V are higher than the environmental quality criteria (limits) for HM contents in soils. In many cases, the contents of HM exceed the respective requirements for the remediation, even for commercial or industrial land use.

ACKNOWLEDGEMENTS

The authors wish to express thanks to Drs P. Khummongkol, S. Towprayoon and M. Kozlov (King Mongkut's University of Technology, Thailand) for assistance in data collection and interpretation. The authors also would like to thank Drs. S. Chungpaibulpatana and B. Limeechokchai (Sirindhorn International Institute of Technology, Thammasat University, Thailand) for useful discussions.

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EFFICIENT AND CLEAN POWER PRODUCTION: MINIMIZING IMPACTS OF INORGANIC COMPONENTS IN COAL AND OTHER FUELS

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KEYWORDS: solid fuels, combustion, gasification, environmental issues

ABSTRACT

The inorganic components associated with coal and other solid fuels influence the design and operation of power systems. The problems associated with inorganic species include abrasion, corrosion, and erosion of system parts; slag flow in wet-bottom systems; fouling and slagging of heat-transfer surfaces; formation of fine particulate and vapor-phase species that are difficult to collect and can cause adverse environmental effects; plugging of gas-filtering systems; and disposal and utilization of ash residuals. The inorganic components associated with solid fuels consist of major, minor, and trace elements, which occur in a wide range of forms. For example, the association of inorganic components in coal depends on rank and depositional environment. Firing solid fuels for power production transforms the inorganic species to gases, liquids, and solids and carries them through the system with the bulk gas flow. The interaction and behavior of the inorganic gases, liquids, and solids in the system are dependent upon system design and operating conditions. Research and development over the past 20 years have provided key insights into the fundamental behavior of major, minor, and trace elements in combustion and gasification systems as well as associated pollution control systems, leading to improvements in the performance and design of conventional and advanced power systems.

INTRODUCTION

The current and future use of solid fuels such as coal, biomass, petroleum coke, municipal solid waste, and paper products is greatly dependent on solving problems related to the combustion behavior of the high-temperature, noncombustible inorganic fraction, or the ash-forming constituents. The abundance and forms of inorganic components associated with these fuels vary widely and can have significant impact on the economic and environmental performance of the power system. The inorganic components are the root cause of many operational and environmental problems in conventional and advanced power systems, which may include abrasion and erosion of equipment; ash deposition and corrosion on heat-transfer and refractory surfaces in boilers and gasifiers; poor slag flow in slagging combustors and gasifiers; emissions of acid rain-forming species; hazardous air pollutant emissions, including precursors to secondary particulate matter formation; and increased requirements for air pollution controls. The literature on ash-related issues is immense. Overviews of ash-related issues and compilations of work by many investigators can be found in the work of Benson (1, 2), Baxter and Desollar (3), Couch (4), Williamson and Wigley (5), Benson and others (6), Benson (7), Bryers and Vorres (8), and Raask (9, 10). Overviews of the environmental issues such as mercury, trace elements, and particulate matter have been summarized in two special issues (11, 12). In addition, a review of mercury transformation; behavior, and control was conducted recently (13).

Current and future trends in the use of solid fuels are being and will be driven by economic and environmental factors. Environmental factors have had significant impact on the type of coal utilized by the power industry. The Clean Air Act Amendments (CAAA) of 1990, Toxic Release Inventory (TRI), and an increased awareness of global warming have made a significant impact on the diversity of use of solid fuels in the future. The 1990 CAAA identified 189 hazardous air pollutants that are subject to control. Eleven trace elements including antimony, cadmium, lead, nickel, chromium, manganese, selenium, beryllium, cobalt, and mercury are among the 189 toxic substances. Currently, a significant effort is being conducted on mercury measurement and control for coal-fired utility boilers. The TRI now requires electric utility companies to report their annual releases of toxic chemicals. The TRI is a national compilation of releases of more than 600 chemicals designated as toxic by the Environmental Protection Agency (14). As a result of increased environmental pressure, many utilities have switched to low-sulfur coals for compliance with SO₂ regulations. In addition, the utilization of biomass-derived fuels appears to be on the rise because of concerns over global warming, which may in part be caused by an increase in CO₂ in the earth's atmosphere. The combustion of biomass does not increase the overall CO₂ inventory in the atmosphere. Finally,

deregulation of the utility industry is increasing incentives to fire the cheapest fuels available such as spot-market coals, petroleum coke, waste materials, and biomass.

INORGANIC COMPOSITION OF SOLID FUELS

Coal

The association and abundance of major, minor, and trace elements in coal is dependent upon coal rank and depositional environment. The inorganic components in lower-rank subbituminous and lignitic coals are associated with the organic and mineral portions of the coal matrix. The lower-rank coals contain high levels of oxygen, some of which are in the form of carboxylic acid groups that can act as sites for cations such as Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} , and Ba^{2+} . The inorganic components associated with bituminous and anthracite are primarily in the form of discrete minerals. The major mineral groups include quartz, clay minerals, pyrite, and carbonates. The abundance and association of minerals in coal have been reviewed and published in *Fundamentals of Coal Combustion for Clean and Efficient Use* (15). The sulfur oxide emissions from power plants are derived from organic sulfur and mineral forms such as pyrite, gypsum, barite, and others. Air toxic metals can be associated both with organic functional groups and with minerals in coal. Commonly, trace elements in coal are included in the list of 189 toxic substances called out by the 1990 CAAA, for example, antimony, cadmium, lead, nickel, chromium, manganese, selenium, beryllium, cobalt, and mercury. The associations of trace elements in coals are summarized by Swaine (16), Finkelman (17), and Benson and others (18).

Petroleum Coke

The inorganic components associated with petroleum coke materials have been summarized by Bryers (19). Petroleum contains a low level of ash-forming species ranging from 0.5 up to 2.5 wt%. The inorganic components consist mainly of nickel, vanadium, sulfur, silicon, aluminum, and minor amounts of iron, sodium, and potassium. The key elements S, V, Fe, and Ni are organically associated as porphyrin complexes.

Biomass

The inorganic composition of biomass fuels has been reviewed by Jenkins and others (20). The inorganic components associated with biomass coals include Si, Al, K, Na, S, Cl, P, Ca, Mg, and Fe. These elements occur at different levels in various types of biomass fuel, including agricultural products (manure, hulls, pits), wood, herbaceous materials (grasses, straws, leaves), and a wide range of waste materials (e.g., municipal solid waste, sewage sludge, and plastics). Most of the inorganic components in plants are associated with the organic matrix, as in some lignitic and subbituminous coals. Biomass-type fuels also cause slagging and fouling problems that are similar to those produced from low-rank coals (6, 21–23). For example, in low-rank coals, alkali and alkaline-earth elements interact and combine with silicates to form low-temperature melt phases that melt at temperatures as low as 700°C, as well as sulfate phases that can have melting points as low as 650°C. Baxter and others (24) reported the formation of sulfate-, silicate-, chloride-, and carbonate-type deposits when biomass-type fuels were fired.

Trace elements are also of concern in biomass utilization. In Austria, Oberberger (25) reported concerns regarding the levels of Mn, Cu, An, Co, Mo, Ni, Cr, Pb, V, and Hg. The ash produced from biomass combustion systems is used as fertilizer, and the levels of selected trace elements must be below regulatory limits. Researchers in Austria have developed a method to fractionate the heavy metals.

BEHAVIOR IN CONVERSION AND ENVIRONMENTAL CONTROL SYSTEMS

Major, minor, and trace inorganic components associated with fossil and biomass fuels undergo a complex series of chemical and physical transformations in combustion and conversion devices, air pollution control systems, and in the ecosystem (26). These transformations are illustrated in Figure 1. The primary factors that influence the fate of the inorganic species include:

- The important operating conditions within the conversion system, such as oxygen stoichiometries and gas composition in general, flame and subsequent flue gas temperatures, particle residence times, and heating and cooling rates.
- The chemical composition and physical characteristics of inorganic components in the fuel that influence their reactivity and volatility during combustion or gasification.

- The transformations of inorganic components occurring during combustion/gasification and gas cooling that result in the formation of various inorganic vapor, liquid, and solid phases, depending on fuel composition and conversion conditions. These transformations typically result in the formation of a bimodal (modes at ~ 0.1 and $\sim 12 \mu\text{m}$) particle-size distribution of ash particles over a wide range of chemical compositions. Some mineral species in fuels may remain in their original form through the conversion and environmental control system. Other elements such as mercury may be released in their vapor state and tend to remain in the gas phase as an emission.
- The state (vapor, liquid, and solid) and physical properties (size, density, viscosity, and surface tension) of the intermediate ash species as a function of temperature, atmosphere, and residence time. The more volatile elements—which include the alkali metals (Na and K) and certain trace elements such as As, Se, Pb, Cd, Sb, Hg, and others—are enriched in the smaller size fractions of ash and in the vapor-phase portion of the flue gas stream. This distribution directly impacts fate of the inorganic intermediate species in the conversion and environmental control system.
- Ash deposition, corrosion, and erosion on heat-transfer surfaces depending on gas composition; condensed melt phases; ash particle size; and aerodynamics/fluid dynamic behavior.
- The progressive accumulation of intermediate ash materials that decrease heat transfer and increase fireside temperatures in the system. The characteristics of the liquid-phase components in deposits, as determined by their chemical composition are critical to deposit strength and growth development.

The capture of the inorganic intermediate material in air pollution control devices is dependent upon the form of the material and the mode of collection. In electrostatic precipitation, the collection efficiency of the particles is related to the resistivity of the ash and the particle size. Collection of ash in a baghouse is related to the size of the ash particles and the cohesive properties of the ash dust cake. The ash dust cake can capture both particulate and gas-phase components. Scrubbers are designed to capture vapor-phase species such as SO_2 , utilizing CaO or other reagents. The speciation of the inorganic elements, system conditions, sorbent composition and size, and residence time all influence the reaction of vapor-phase inorganic materials with dry and wet sorbents.

Hot-gas cleanup systems for advanced combustion and gasification systems utilize metal and ceramic-type filters. These filters must remove the particulate material to levels that can be tolerated by a turbine or fuel cell. Ceramic candle filters that are just beginning to be used in full-scale demonstration projects experience failures from a combination of adverse factors, including cyclic thermal stress, ash deposition and surface blinding, and corrosion of ceramic materials by alkalis, chlorides, trace elements, and molten slag phases.

DIRECTIONS FOR THE FUTURE

Future high-performance power systems that utilize coal, biomass, and oil and petroleum coke feedstocks must consider all of the forgoing impacts of inorganic components on system performance and emissions. The key is to match fuel quality with system design and operating conditions. Environmental drivers such as global warming, hazardous air pollutants, regional haze, and particle matter will have a major influence on future fuel sources, power system design, and operating conditions. In order to minimize environmental impact, control cost, and improve efficiency, it will be necessary to identify synergistic relationships for a variety of fuel blends, such as coal and biomass, under a wide range of design and operating conditions.

A vision for power systems for the next century is being developed by the U.S. Department of Energy Office of Fossil Energy (27). The Vision 21 power system is designed to coproduce electricity, heat, transportation fuels, and chemicals with little or no air pollution, solid wastes, or carbon dioxide emissions. The system would be fuel-flexible, thereby allowing for firing of a single fuel or a combination of fuels consisting of coal, natural gas, petroleum coke, and biomass. The energy plant comprises several modules, including combustion/gasification, separation/conversion, gas cleanup, CO_2 sequestration, power, fuels/ products, and steam and cogeneration. This scenario of how next-generation power systems will evolve must account for the effects of the noncombustible or inorganic fractions of the fuel, which greatly impact conversion and environmental control system components.

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FIGURES

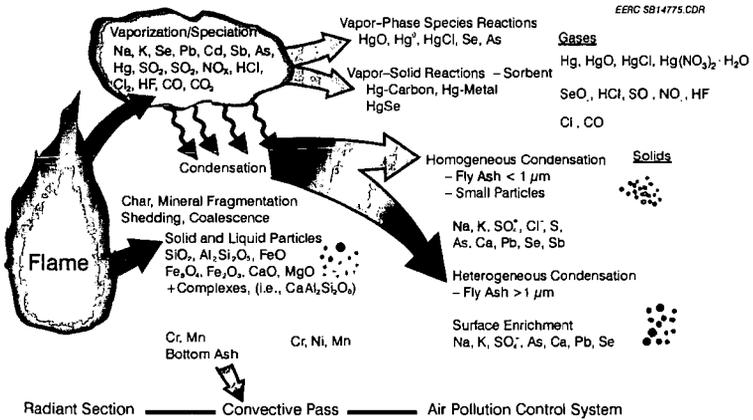


Figure 1. Examples of possible inorganic transformations during conversion.

TRENDS IN PREDICTING AND CONTROLLING EMISSIONS FROM COAL FIRED BOILERS

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ABSTRACT

The past decade has seen a dramatic increase in the use of computational fluid dynamics (CFD) in the solution of problems related to the design and operation of pulverized coal-fired utility boilers. Traditionally, there has been a major gap between the knowledge of coal scientists, who have over the past century made enormous progress in the characterization of coal and the processes it undergoes during combustion, and the application of that knowledge to the solution of practical problems. A well known practitioner often taunted the coal research community by saying, with some justification, that "the researcher's only contribution to the practitioner is to explain to him why he did what he did after he did it!" The advances in CFD and in computer visualization have made it possible to apply fundamental knowledge to the solution of real world problems and to translate the results to forms that are understandable and useable by the practitioners. A series of case studies will be presented on the application of fundamentals and CFD to characterize NO_x emissions, unburned carbon in fly ash, fly ash size and composition distribution, fouling and corrosion potential, and air toxics emissions, to illustrate the progress that has been made in the ability to solve real world problems with CFD. One can look forward to the day when computer simulations will guide the development and implementation of the next generation of clean and efficient coal-fired utility boilers.

INTRODUCTION

The challenges of meeting competitive and environmental targets can be guided by the use of computer simulations. This paper provides illustrations of how computer models are currently being used by the industry to solve some of the problems of trace element emissions. Although computer models for predicting furnace performance have been under development for some time, it is only recently that they have reached a state of maturity where industry is relying upon computer simulation to solve their problems.

A question that is becoming of greater interest in the U.S. is that of fine particles as the result of the recent promulgation of standards to control the ambient concentration of particles with diameters under 2.5 microns. The question here is how will the low-NO_x conditions influence the emissions of fine particles. Of greatest interest is the formation of the smaller particles in the sizes that penetrate the air pollution control devices (APCD) with relatively high efficiency, i.e., 0.1-1.0µm [Senior, et al., 1999a]. The transformation of mineral matter is dependent upon many factors including the size distribution of the coal, the combustion conditions, the forms of occurrence of the elements in the coal and the interaction of different elements.

The dominant constituents of coal mineral matter are iron, silicon, aluminum, the alkali and the alkaline earth elements. A schematic of how the minerals are distributed in coal, partially as included mineral matter, partially as atomically dispersed elements, and partially as extraneous mineral particles is shown in Figure 1. During combustion most of the mineral matter distributed in a coal particle is exposed on the surface as the surface of the char particles recede during oxidation. At the char surface, this mineral matter coalesces and forms one or more particles, usually in the 1 to 20 µm range, particles that will be captured with high efficiency by the APCD. However, a small amount, of the order of one percent of the ash in coal, will vaporize and subsequently recondense to form particles that are in the size range in which the penetration through the APCD is high.

The processes shown schematically in Figure 1 can be modeled. Figure 1 shows that part of the ash is vaporized and recondenses to form a submicron ash. Part of this vaporization occurs during devolatilization during which elements that are present in organometallic form, many of which are trace transition elements, are released. The refractory oxides (FeO, SiO₂, MgO, CaO) are vaporized by the reduction of the oxides to the more volatile suboxides or metals, the diffusion of the suboxides or metals to the particle boundary layer where they are reoxidized and condense to form a submicron aerosol [Quann and Sarofim, 1982]. The vapor pressure of the vaporizing suboxide or metal is determined at the higher temperatures by the equilibrium of the reaction between the refractory oxide (RO) and carbon monoxide (CO) inside the particle, or



The mass transfer from the surfaces of the mineral inclusions to the surface of the char particle determines the vaporization rate. The size of the submicron particles may be calculated from the mass vaporized using well-established theory on aerosol dynamics. In addition, as depicted schematically in Figure 1, the more volatile salts of the alkali metals and the volatile trace metals will vaporize. These will condense downstream of the combustion zone at points where the combustion products have cooled down to their condensation temperatures. They will deposit on the surfaces of existing particles, in a manner calculable from mass-transfer-limited condensation.

As mentioned previously, computational fluid dynamics (CFD) tools have been developed to the point where many practical problems of industrial interest can be solved. For coal-fired utility boilers, the problems are typically related to evaluating the viability of a modern retrofit, such as a low NO_x firing system, and evaluating the potential for adverse side effects such as increased levels of unburned carbon, additional deposition/fouling problems, and the potential for increased waterwall wastage. A case study will be presented here demonstrating how such CFD tools can be used to address a problem related to mineral matter transformations under low NO_x conditions. Because of the dependence of the vaporization of mineral constituents on temperature and local equivalence ratio, it is expected that staging for NO_x control will change the formation and emissions of fine particles. The temperature-oxidation history for individual particles provides the information needed for the calculations. Due to space limitations this paper will focus on presenting the transformation of mineral matter in ash to a sub-micron fume that transports air toxics.

METHOD

The development of a model for the vaporization ash was a two-phase process. Phase 1, the initial development of the model, is used to verify experimental data for single particle combustion. The second phase requires minor modifications such that multiple particles can be evaluated. Particle iterations such as this are common in advanced CFD codes used for modeling coal-fired boilers.

The development of the first phase of the model was necessary to verify this computational model with experimentally derived results. In this scenario, a particle temperature history was necessary for running the model. Since this data was not available from the experimental data, the information needed to be generated. This was done using coal properties and combustion conditions. This information was fed into a computer code, which calculates carbon burnout kinetics. These calculations provide the necessary information including particle size, temperature, and residence time. From this information, the vaporization of elemental ash inclusions can be determined.

The experimental results for ash vaporization were performed by Quann and have been documented in the literature (Quann and Sarofim, 1982). The model was run for 14 different coals used in the experimental analysis. Figures 2 and 3 summarize the results for the model cases as normalized against the vaporization determined by Quann. The code was used in calculating the vaporization for SiO_2 , Al_2O_3 , FeO , CaO , and MgO . However, due to space limitations the results are given only for SiO_2 and CaO .

As can be seen from Figures 2 and 3, the fourteen coals used in the model verification are referred to by their respective Penn State Coal Database number followed by the type, bituminous (B), subbituminous (SB), or lignite (L). It should also be noted that the vaporization when compared with Quann will vary depending on coal type and mineral inclusion size. Since the mineral inclusion size was not known for Quann's data, several cases were run. Agreement with Quann's data is observed for silica for the inclusion sizes of 10 to 20 μm , and for calcium for inclusion sizes of greater than 20 μm for the bituminous coals and less than 5 μm for the lignites. As will be discussed in the next section, coal 503-B will be used in actual multi-particle calculations. The values for the optimal inclusion sizes for each component for this coal are summarized in Table 1. The optimal inclusion size can be defined as those that are exactly verified with the Quann data.

RESULTS

The second phase of the vaporization had to be modified slightly to account for multiple particle iterations as performed in the CFD code. In addition, the code was run with and without the effects of CO_2 . In the comparison with the experimental results, the CO_2 was not an issue, but in an actual furnace case as will be shown, the CO_2 has a noticeable contribution.

The computational tools used in this study were developed by Reaction Engineering International (REI) to address a wide range of problems involved in the operation and design and of many combustion systems including utility boilers, pyrolysis furnaces, gas turbine combustors, rotary kilns, waste incinerators and smelting cyclones. The current models simulate both reacting and non-reacting flow of gases and particles, including gaseous diffusion flames, pulverized-coal flames, liquid sprays, coal slurries, injected sorbents, and other oxidation/reduction systems. Emphasis has been placed on simulating coal combustion and pollutant formation. This three dimensional, two phase reacting flow code (GLACIER) includes several capabilities necessary for accurate simulation of coal-fired boilers. These capabilities include turbulent particle transport with full coupling of particle and gas-phase mass and

momentum; coal reaction processes such as devolatilization, char oxidation and gas-particle interchange; NO_x formation/reduction chemistry; particle convection and radiation with absorption, emission and anisotropic scattering; full coupling of gas-particle energy exchange; and ash deposition. In addition, boiler-side waterwall and radiant panel surface temperatures can be predicted as part of the computation, given a backside (i.e., steam) temperature and surface resistance (from the deposit thickness and thermal conductivity, for example). As it applies to this paper, the vaporization model is actually a post-processor to be used in conjunction with the GLACIER software results.

The unit studied is a 500 MW opposed wall-fired boiler with twenty-four burners. Five wingwalls come in from the front wall. Prior to low-NO_x retrofit, the unit included Foster Wheeler's Intervane burners. During the retrofit, these burners were replaced by Foster Wheeler's Controlled-Flow/Split-Flame (CF/SF) burner. In addition, an advanced overfire air (AOFA) system was installed. This consists of an independent windbox for improved penetration/control of injection through eight directly opposed ports above each column of burners, and four underfire air ports at the level of the bottom burner row near the sidewalls.

As mentioned previously, the CO₂ was not an issue with the single particle model. However, under normal operating conditions, the CO₂ in the furnace plays a significant role. Figures 4 and 5 illustrate the cumulative vaporization for pre- and post-retrofit conditions accounting for effects due to CO₂ and neglecting the role of CO₂ respectively.

Since CO₂ is an issue which cannot be neglected it has been included in the current model for accurate calculation of the ash vaporization. Figures 6 and 7 illustrate the individual burner contribution to the total amount of ash vaporized. The symmetry plane has been identified, which is used in modeling the furnace in GLACIER. Also, the front and rear walls have been identified for both the pre- (Figure 6) and post-retrofit (Figure 7) cases.

DISCUSSION AND CONCLUSIONS

From these results it is evident that the modeling of ash vaporization is feasible. Additionally, it is apparent that the inclusion of CO₂ in the model is a necessary component. The presence of CO₂ ultimately suppresses the vaporization of ash as shown in Figures 4 and 5. Another aspect that is interesting to note is the variation in the vaporization between the front and rear wall. In the pre-retrofit case (Figure 6), the ash vaporization contribution from the front wall is 72 percent while the rear wall contributes only 28 percent. In the post-retrofit case, the contribution is more evenly distributed with 57 percent of the ash vaporized coming from the front wall and 43 percent from the rear. The next step in developing this vaporization model is to determine the particle size distribution of the vaporized ash.

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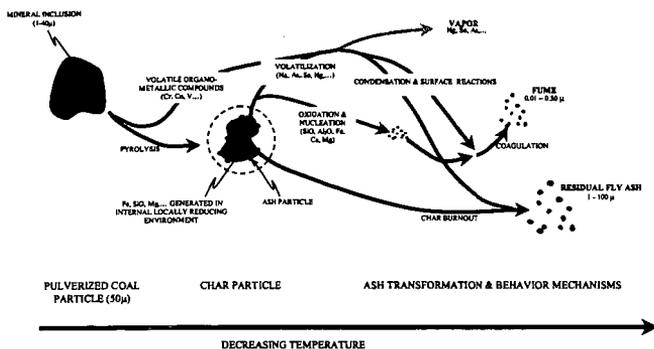


Figure 1: Schematic of Mineral Matter Transformation During Pulverized Coal Combustion.

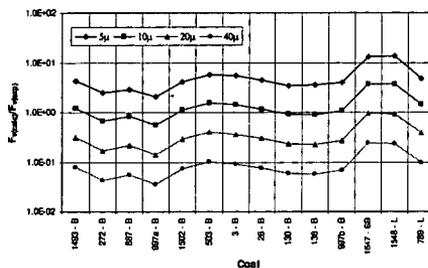


Figure 2: SiO_2 experimental results versus vaporization model.

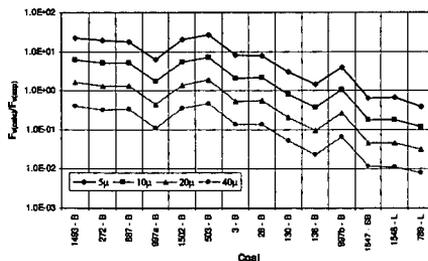


Figure 3: CaO experimental results versus vaporization model.

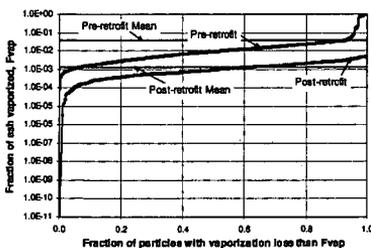


Figure 4: Cumulative vaporization for pre- and post-retrofit cases with CO_2 effect.

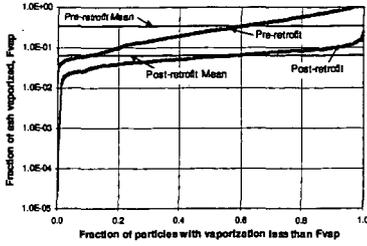


Figure 5: Cumulative vaporization for pre- and post-retrofit cases without CO₂ effect.

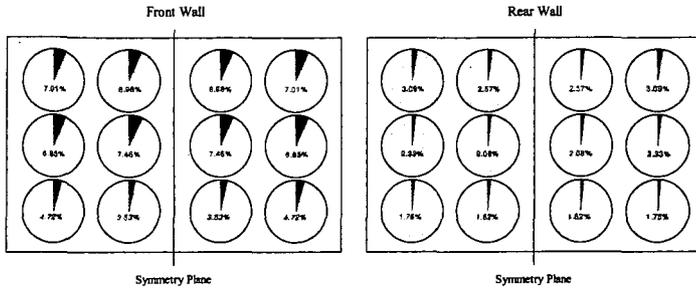


Figure 6: Pre-retrofit burner contribution to ash vaporization with CO₂ effects.

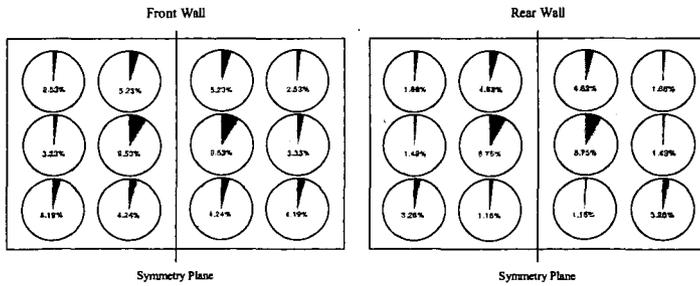


Figure 7: Post-retrofit burner contribution to ash vaporization with CO₂ effects.

Table 1: Optimal inclusion sizes for each ash component for coal 503-B.

Component	Optimal Inclusion Size (microns)
SiO ₂	13
Al ₂ O ₃	2
FeO	30
CaO	27
MgO	31

IGCC Technical Status, Trends and Future Improvements

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Presented at the American Chemical Society Meeting
San Francisco, CA

March 26-31, 2000

Introduction

Coal-based IGCC plants have been developed to commercial size over the past two decades. They have only been built as demonstration plants but are operating as commercial units. These units have now accumulated several years of operating experience and have shown that an IGCC plant can meet extremely stringent air emission standards while also achieving high plant efficiencies. The main barriers to the widespread adoption of IGCC technologies are: (1) demonstration of high availability, at least equal to existing pulverized coal (PC) plants; and (2) capital cost reduction to compete with state-of-the-art PC plants and natural gas-based combined cycles.

Current Status

Three coal-based, commercial-sized (but partially government-funded) IGCC demonstration plant projects are currently operating in the U.S and two in Europe, as summarized in Table 1. The following discussion provides a brief summary of the operational experience to date at these five sites.

Table 1. Coal-Based, Commercial-Size IGCC Plants

Project/Location	Gasification Technology	MW	Startup Date
Wabash River, Indiana, USA	Destec	262	10/95
Tampa Electric Company, Florida, USA	Texaco	250	9/96
Sierra Pacific Piñon Pine, Nevada, USA	KRW fluid bed	100	1/98
SEP/Demkolec, Buggenum, The Netherlands	Shell	253	Early 1994
ELCOGAS, Puertollano, Spain	Krupp-Uhde Prenflo	310	12/97 on coal

The three ongoing US IGCC projects are all based on different gasification technologies and illustrate different application opportunities. All three plants are based on General Electric 'F' gas turbines with turbine inlet temperatures of about 1260°C (2300°F) and equipped with multiple can combustors. The European IGCC projects are both based on Siemens gas turbines equipped with dual silo combustion chambers.

The Piñon Pine and ELCOGAS projects have seen limited operations to date, but both the GE 6FA at Piñon Pine and the Siemens V 94.3 at ELCOGAS have been running very well on natural gas at their design outputs. Although only extended multi-year operations can really test the durability of gas turbines in an IGCC application, the results to date from the projects with the GE F-class gas turbines are very encouraging.

Table 2 presents the major component and overall design performance of these plants, and compares these design values with the operational results achieved to date.

Both the Texaco gasifier at Tampa and the Destec gasifier at Wabash River have demonstrated that they can supply sufficient syngas to fully fuel their combustion turbines. At Tampa, fouling downstream of the gasifier and corrosion in the lower gas temperature range of 250–300°C have been the main causes of outages to date. The developers and plant operators are addressing these problems, but in the meantime the plant continues to perform well, albeit at lower than design efficiency. At Wabash River, the main remaining problem area seems to be the dry gas filter, where corrosion and blinding of the metallic candles continue to occur. The most recent operations at these sites are encouraging and show considerable progress, with both projects experiencing long runs and higher availability.

The SEP/Demkolec (Buggenum) project started operations in early 1994. The tight integration has led to some operational sensitivities and complexities, leading SEP to recommend only partial integration for future installations. This recommendation agrees with EPRI's general analysis of the merits of various degrees of integration, although the optimum performance/operability trade-off depends on the specific characteristics of the gas turbine and its compressor. The ASUs at Wabash and Tampa are supplied by their own compressors, so this problem does not arise.

The main problem encountered in the early years of operation at the Buggenum plant (also later encountered at Puertollano) has been combustion-induced vibrations and overheating in the gas turbine combustors. Design changes made in early 1997 have markedly improved the vibration problem, and since that time several long runs have been conducted, with an availability of over 80% in each quarter since the third quarter of 1997 (with the exception of the second quarters when the required annual inspection is conducted). In the third and fourth quarters of 1998, the Gasification Island was in continuous operation for over 2000 hours. The Shell gasifier has generally performed well and has achieved its design cold gas efficiency.

Table 2. Design and Actual Performance to Date of Major IGCC Projects*

Project	Wabash River	Tampa	Buggenum
Gas Turbine Output, MW	192 (192)	192 (192)	155 (155)
Steam Turbine Output, MW	105 (98)	121 (125)	128 (128)
Auxiliary Power Consumption, MW	35.4 (36)	63 (66)	31 (31)
Net Power Output, MW	261.6 (252)	250 (250)	252 (252)
Net Plant Heat Rate, kJ/kWh LHV Basis	9177 (8708)**	8739 (9244)***	8373 (8373)
Net Plant Efficiency, % LHV Basis	39.2 (41.2)**	41.2 (38.9)***	43.0 (43.0)
1998 IGCC Operating Hours	5139	5328	4939
1998 IGCC On-stream Factor, %	59	61	56
Total IGCC Operating Hours Through December 1998	10,393	10,010	13,768

* Performance is shown as design performance followed by actual to-date performance in parentheses

** Adjusted for HRSG feedwater heaters in service

*** Adjusted for gas/gas heat exchangers in service

The successful scale-up from the 225-tonnes/day gasifier at Houston (SCGP-1 operated 1987-91) to the 2000 tonnes/day unit at Buggenum has been amply demonstrated. The raw gas from a dry-coal-fed gasifier such as Shell has lower water content than the slurry-fed gasifiers of Texaco and Destec. Because of this, dew point corrosion in the lower temperature ranges is less likely to occur and, consequently, has not been a problem at Buggenum.

Both the Wabash River and Buggenum plants have met their overall IGCC design efficiencies. However, Tampa has experienced lower-than-design overall efficiency chiefly due to lower carbon conversion and removal of the gas/gas exchangers from service (to prevent fouling and corrosion).

In summary, these demonstration plants show that IGCC systems can provide power at higher efficiency than PC plants, with significantly lower air emissions and a more benign solid by-product. While the reliability/availability of these units has improved since they were first brought on line, they are not yet operating at commercially acceptable availability levels (only 56-61% in 1998). The developers and government sponsors of these demonstration projects understand this concern and are addressing it through continuing engineering efforts. Based on past experience in the development of new technologies, and assuming continued support by the various government and private parties involved, it is reasonable to expect that the remaining problems will be solved within the next five years.

Market Trends

A number of IGCC plants (many of 500 MW) will be commissioned over the next three years based on the use of petroleum residuals and located adjacent to large petroleum refineries. The shrinking market for high sulfur fuel oil and the impact of tightening fuel specifications and new environmental legislation is the impetus behind these projects. Most of these projects have multiple co-products, typically power, steam and hydrogen for the refinery plus sale of power to the grid or other nearby industrial customers. The projects in Europe are mostly based on heavy oil while the majority of the U.S. projects are based on low value petroleum coke. The experience gained from these projects should aid in reducing the capital cost of IGCC equipment and in providing greater confidence in the reliable operation of this technology.

IGCC plants can meet extremely strict environmental and emission standards and may be applicable to particular locations that have such requirements. If emissions including CO₂ were ever subject to externality charges or taxes this would make IGCC a more attractive technology. Several studies have shown that if CO₂ removal from fossil-based power plants is ever required for subsequent disposal, use or sequestration, that it would be much less costly to remove the CO₂ from syngas under pressure prior to combustion rather than removal from the huge volumes of stack gases after combustion at atmospheric pressure. The absorption process is driven by partial pressure and the size of vessels is much reduced under pressure.

Table 3. IGCC Plants based on Petroleum Residuals

Project/Location	Feedstock	Gasification Technology	MW /Steam/ Hydrogen	Startup Date
Shell- Pernis, Netherlands	Visbreaker tar	Shell	127/ Steam/H2	1/98
ISAB/Mission -Sicily, Italy	Asphalt	Texaco	500/Steam/H2	9/99
API/ABB/Texaco -Falconara, Italy	Visbroken Vacuum residue	Texaco	250/Steam	3/2000
SARAS/Enron	Heavy oils	Texaco	550/Steam	3/2000
Motiva/Texaco	Petroleum Coke	Texaco	200/Steam	3/2000
Total/EDF/Texaco-Normandy, France	Heavy oils	Texaco	365/Steam/H2	2003
Repsol/Iberdrola/Texaco - Bilbao, Spain				
Exxon Singapore	Ethylene cracker bottoms	Texaco	160/CO + H2	2002

Future Technical Improvements

The larger higher efficiency G and H gas turbines, with firing temperatures of ~1500°C (2732°F) are now entering commercial service based on natural gas. When applied to IGCC plants these turbines will provide further gains in efficiency and reductions in capital cost through economy of scale. The U.S. DOE through its Vision 21 initiative has a comprehensive R&D program with gasification as a key core technology.

Improvements in all aspects of the basic IGCC flowsheet are being addressed including ion transport membranes for improved ASU's, more flexible fluid bed gasifiers, high temperature gas clean up for particulate and sulfur species removal, high temperature membranes for separation of hydrogen and CO₂, advanced gas turbines and cycles. This program should result in a stream of new developments improving the performance and reducing the capital cost of IGCC plants.

GASIFICATION TECHNOLOGIES: THE PATH TO CLEAN, AFFORDABLE ENERGY IN THE 21ST CENTURY

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Keywords: Integrated Gasification Combined Cycle (IGCC); Gasification; Coproduction

INTRODUCTION

The production of gas from coal dates back as far as the end of the eighteenth century, and by the middle of the nineteenth century, the underlying principals of gasification were fairly well understood. Gasification was very prominent in the latter part of the nineteenth and the twentieth centuries for the production of town gas for residential and industrial use. Gasification for the production of town gas has nearly vanished as economically advantageous resources and delivery of clean natural gas and oil fuels has satisfied that need. New applications of gasification technologies in the manufacturing and industrial sectors have been found, forcing new developments by gasification technology vendors to maintain a competitive advantage. Such developments have sustained gasification as an important industrial process for many years and have included the participation of the Department of Energy's R&D program and the Clean Coal Technology program.

The gasification process converts solid or liquid hydrocarbon feedstocks, often of lesser market value than premium gas or liquid fuels, into a synthesis gas that is suitable for use for its fuel value in producing electricity or to convert to chemicals, hydrogen, or liquid fuels. Continued enactment of stricter regulations on the manufacturing sector, coupled with opportunities and pressures to more effectively use the low-quality portion of oil resources will combine with increasing prices for delivered gas to encourage the search for appropriate technology solutions. In response, further technological advances will push gasification to even greater heights in the twenty-first century.

GASIFICATION TODAY

Today, gasification is widely deployed throughout the world in many industrial settings. Currently, there exists 128 plants worldwide with 366 operating gasifiers.¹ The vast majority of these facilities are located in Western Europe, the Pacific Rim, Africa, and North America. Combined, these plants generate over 42,000 MWth of synthesis gas. During the next 5 years, an additional 33 plants with 48 gasifiers are expected to be constructed adding another 18,000 MWth of synthesis gas capacity. Most of this expected growth will occur in the developing nations in the Pacific Rim as the need for further electrification of these nations' economies grow. The second largest growth area is expected to be in Western Europe where refineries will need to reduce fuel oil production. Growth in North America will be about half of that in Europe and will be concentrated in the refining industry. Very little or no growth is anticipated to occur in Africa or other regions of the world.

Figure 1 illustrates the worldwide historical growth in gasification capacity since 1970 as well as the future additions through 2005. Almost all of the gasification capacity through the mid-1970s can be attributed to the 19 Lurgi gasifiers operating at Sasol in South Africa. The relatively large increases in capacity in the latter part of the 1970s and the early 1980s represent the startup of 80 gasifiers associated with Sasol II and III, representing a combined increase of nearly 8,300 MWth of synthesis gas capacity. A small increase in capacity also occurred in the early 1980's with the commissioning of 14 Lurgi gasifiers at the Dakota Gasification plant in Buelah, ND, adding another 1500 MWth of capacity. Following this, capacity remained relatively flat for over a decade. However, within a few short years, capacity increased by almost 50% and is expected to grow by nearly 60% in the next 5 years. This tremendous rise in capacity is expected to continue beyond 2005.

Gasification technologies are capable of processing any carbon-based feedstock to produce synthesis gas for the production of electricity, steam, hydrogen, fuels, and chemical. Coal and petroleum residuals are by far the dominant feedstocks, together accounting for over 70% of the synthesis gas capacity. Most of the coal is consumed by Sasol and Dakota Gasification. Natural gas is also an important feedstock, accounting for about 20% of today's capacity, and is used almost exclusively in the production of chemicals. Over the next several years, most of the growth in capacity will be from the gasification of coal and petroleum residuals, with a small fraction from petroleum coke. The growth in these feedstocks, however, will be used primarily

to produce electricity, with the use of synthesis gas for the production of electricity approaching that of chemicals. No capacity additions are projected for natural gas.

TECHNOLOGY DRIVERS

Gasification has many positive attributes, compared to other technologies, that have helped to stimulate the current market. As mentioned above, gasification is the only technology that offers both upstream (feedstock flexibility) and downstream (product flexibility) advantages. All carbon-containing feedstocks including hazardous wastes, municipal solid waste and sewage sludge, biomass, etc., can be readily gasified after proper preparation to produce clean synthesis gas for further processing. Because of its ability to use low-cost feedstocks, gasification is the technology of choice for many industrial applications such as in refineries. IGCC, and gasification processes in general, is also the only advanced power generation technology capable of coproducing a wide variety of commodity and premium products, in addition to electricity, to meet future market requirements. It is this ability to produce value-added products that has made gasification economical in selected situations and will be a key driver in a deregulated power market.

Compared to combustion systems, IGCC is the most efficient and environmentally friendly technology for the production of low-cost electricity from solid feedstocks and can be made to approach that of natural gas combined cycle plants. Further increases in efficiency can be achieved through integration with fuel cells. These higher efficiencies translate to lower operating costs and carbon dioxide emissions. In addition, the gasification process can be readily adapted with advanced technologies for the concentration of CO₂ with little impact on cost and thermal efficiency. The ability of a technology to achieve higher efficiencies and concentrate CO₂ with minimal impact on the cost of final products will be major factors in technology selection for future energy plants.

Because gasification operates at high pressure with a reducing atmosphere, the products from the gasifier are more amenable to cleaning to reduce ultimate emissions of sulfur and nitrogen oxides as well as other pollutants than those from combustion processes. In general, the volume of the fuel gas processed in an IGCC plant for contaminant removal is typically one-third that from a conventional power plant. Processing lower volumes of gas translates to lower capital cost for pollution prevention. The removal of sulfur, nitrogen, and other contaminants from the reducing gas is also much easier than from combustion products. This results in sulfur and nitrogen oxide emissions being more than an order of magnitude less than those of conventional combustion processes. Gasification plants can also be configured to reach near-zero levels of emissions when required.

Unlike that from combustion processes, the by-product ash and slag from the gasification technologies have also been shown to be nonhazardous. As such, the material can be readily used for landfill without added disposal cost or can be used in construction materials or further processed to produce value-added products.

Although current cost for greenfield sites are high, gasification processes can be economically integrated into existing refineries and chemical plants. Through proper integration and the use of existing infrastructure, the overall cost of a project can be significantly reduced. Through deployment in such environments, additional knowledge and experience will be gained, thereby reducing capital and operating and maintenance costs for future facilities.

GASIFICATION IN TOMORROW'S WORLD

More intense competition resulting from deregulation, stricter environmental laws on the emissions of sulfur and nitrogen oxides, hazardous air pollutants, and particulates, tighter regulations on product end-use applications, and the potential for future worldwide greenhouse gas emission treaties will have significant consequences on industry and society alike. To be prepared to respond to these issues when required, the U.S. Department of Energy has unveiled its Vision 21 program.² This comprehensive and aggressive program seeks to achieve substantial improvements in process efficiencies, reduce emissions of sulfur and nitrogen oxides, particulates, and hazardous air pollutants to near-zero levels, capture and sequester carbon dioxide, utilize all available carbon-based feedstocks, and produce a wide variety of commodity and specialty products to meet any market application. These goals are expected to be accomplished at product costs that are equal or lower than that in today's market.

Of all advanced technologies currently under development, gasification-based technologies are the only ones that have the potential to achieve all of these ambitious goals simultaneously. As a result, gasification is considered to be the cornerstone technology of the Vision 21 program. To confront these external forces and achieve the goals, not only will continual improvement need to be made as new units are employed, but new advanced, and even step-out, technologies will have to be developed during the next decade.

ACHIEVING THE VISION

To achieve the vision set out above, the DOE's Gasification Technologies Program has developed a comprehensive and aggressive program aimed at making gasification the technology of choice for future energy plants.³ Figure 2 presents a capsule summary of the issues that need to be addressed for gasification-based processes to meet the above goals. Some of the technologies being developed in the Gasification Technologies program to address these issues, and more importantly, those technologies that are critical to achieving the above performance goals are described below. Critical technologies such as fuel cells and turbines are being addressed in other DOE programs. The proper integration of all of these technologies are necessary to achieve the vision.

Advanced Air Separation

Air separations for the production of oxygen is a very capital and operating cost intensive operation, usually accounting for 15% or more of total capital cost while consuming substantial quantities of electricity for air compression. Any technology that can offer a significant reduction in the cost of oxygen will have a substantial impact on the overall economics of gasification-based process. One novel approach that has shown tremendous potential is the use of high temperature mixed conducting ceramic membranes. The membranes simultaneously conduct oxygen ions and electrons through the membrane, thereby obviating the need for an external circuit to drive the separation. The technology produces pure oxygen. Properly integrated into the process, the technology has shown potential for significant cost reductions as well as improvements in plant efficiency.⁴ Two projects are currently in progress to develop this technology.

Ultra-Clean Synthesis Gas

Ultra-clean synthesis gas is needed not only to meet the near-zero emission goals of Vision 21, but is also required to meet the stringent gas quality requirements needed for use in fuel cell applications or for the conversion to transportation fuels and/or chemicals. The cost to achieve these goals must be no more than that of current commercial technologies and must not incur an energy penalty on the process. The current targets are: Sulfur - <60 ppb; Ammonia - <10 ppm; and Chlorine - <10 ppb. The operating range for the processes should stay above the condensation temperature of the moisture in the gas to achieve higher process efficiencies. The DOE recently awarded two projects to investigate novel process concepts while simultaneously redirecting its hot gas sorbent development program to focus on achieving greater levels of contaminant removal.

Coproduction

The production of more than one product offers the unique opportunity to adjust to swings in market demand for products while simultaneously maximizing the utilization of the capital investment. Through proper integration, coproduction can offer higher process efficiencies with little added capital.⁵ Gasification-based processes are the only advanced power generation technologies that are capable of producing multiple products while simultaneously achieving all of the other performance targets of Vision 21. The DOE has undertaken an aggressive program to accelerate the deployment of coproduct processes schemes through its Early Entrance Coproduction Plant initiative. The processes are considered to be pre-Vision 21 energy plants, meeting some but not all performance requirements. Three project teams, each consisting of strong industrial participants, are focusing on developing their own unique scheme for the production of electricity and methanol (one project) and electricity and fuels (two projects). It is believed that through the operation of these initial plants, successive plants will be built and operated, each building upon the knowledge gained previously and incorporating new advances. Through successive deployments, coproduction will become a viable option for future energy plants.

Hydrogen and Carbon Dioxide Separation

To achieve very high efficiencies and to capture carbon dioxide for sequestration or utilization, advanced technologies need to be developed that simultaneously produce hydrogen for use with fuel cells or hydrogen turbines and concentrate carbon. Two approaches are being investigated, i.e., a high temperature and a low temperature approach. The high temperature approach focuses on the use of ceramic membranes that can affect the water-gas shift reaction in the synthesis gas steam while simultaneously separating the hydrogen. The resulting pure hydrogen stream can be fed directly to a solid oxide fuel cell while the concentrated carbon dioxide steam can be sequestered. Both small pore molecular sieve membranes and proton transfer membranes are being developed. The second approach focuses on the formation of removing carbon dioxide from a shifted synthesis gas by forming CO₂ hydrates. Again, a pure stream of hydrogen is recovered along with a high pressure stream of CO₂.

PROCESS ECONOMICS

As a result of DOE's Clean Coal Demonstration program, significant progress has been made in reducing the

costs and risks of gasification-based processes. Today, the cost of a first-of-a-kind integrated gasification combined cycle plant is projected to be about \$1,250/kWe as shown by the curve on the left in Figure 3. Through successive deployment of this technology, the cost is expected to be reduced to about \$1,000/kWe. This figure also shows that further cost reductions and efficiency improvements can be realized through the development of advanced technologies such as advanced gas turbines, hot gas cleanup, and advanced air separation membranes. As shown by the curve on the right, potential exists for achieving a cost of about \$850/kWe, that which is considered by industry to be competitive to natural gas combined cycle.

Table 1 provides a capsule summary of the result of study focusing on the cost of producing hydrogen from coal, while simultaneously concentrating CO₂, using conventional as well as advanced technologies.⁶ Using conventional commercial technologies for shifting the synthesis gas and gas separation results in a cost of about \$5.60/MMBtu (\$5.28/GJ). Incorporating the use of higher pressure gasifiers, high temperature gas filtration technology, and advanced ceramic membranes can result in a substantial reduction in the cost of hydrogen. This final cost is still somewhat higher than the cost of hydrogen from natural gas at today's prices, but will be increasingly competitive as gas prices rise.

The above two studies clearly show that through the development of advanced technologies, gasification-based process can be cost competitive with other technologies and can be configured to economically produce hydrogen and, at the same time, concentrate CO₂ to more readily sequester or use the CO₂. What is needed is a mechanism to support the demonstration and commercialization of these new concepts through the first few plants to achieve the benefits of the learning curve and reduce the technical and economic risks to levels acceptable to industry and financial institutions.

CONCLUSIONS

By 2015, gasification-based technologies using all carbon-based feedstocks are expected to have gained global acceptance, penetrating not only the refining and chemical industries but also the electric utility, pulp and paper, and steel industries. The product market for gasification will not only show continued growth in the power generation and chemicals sectors but will find significant opportunities for growth in the transportation fuel productions. Ultimately, gasification will serve as a key technology in efforts to control greenhouse gas emissions and will be an important technology in the transition to a hydrogen-based economy. Gasification-based process will be the technology of choice in the future because of their low cost and superior environmental performance, and their adaptability to meet future market requirements for feedstocks and products.

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Table 1
Synthesis Gas and Hydrogen Plant
Performance and Cost Summary

	Synthesis Gas	Hydrogen (Conv.)	Hydrogen (Adv.)	Transport (Adv.)
Coal Feed, dry, t/d	2268	2268	2268	2268
Oxygen Feed, 99% (cryogenic), t/d	1927	1947	2747	2929
Hydrogen/Synthesis Gas Production, t/d	4479	288	370	354
Gypsum/Sulfuric Acid Prod., t/d	210	208	459	459
Net Power Production, MW	-9	36	42	48
Equivalent Thermal Efficiency, %	82.5	63.1	80.5	77.9
Total Plant Cost, K\$	253,445	374,273	306,605	297,044
Product Cost, \$/GJ	3.24	5.28	3.84	3.66

Figure 1
Cumulative Worldwide Gasification Capacity

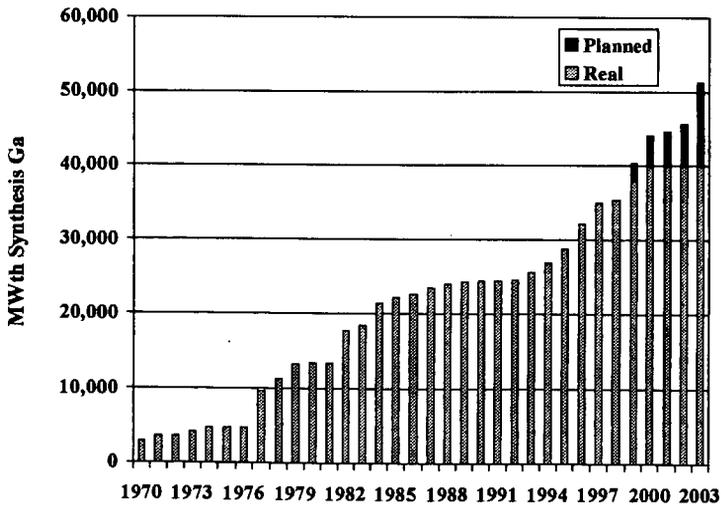


Figure 2
Gasification Technology Issues

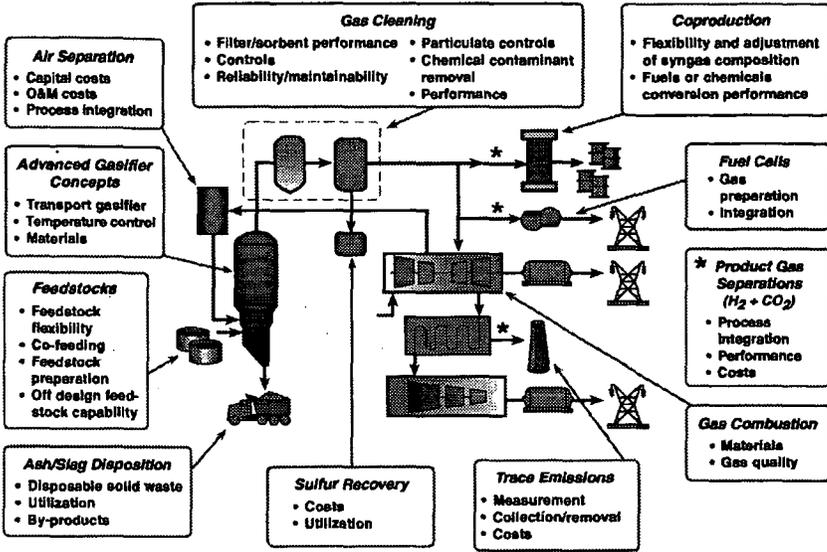
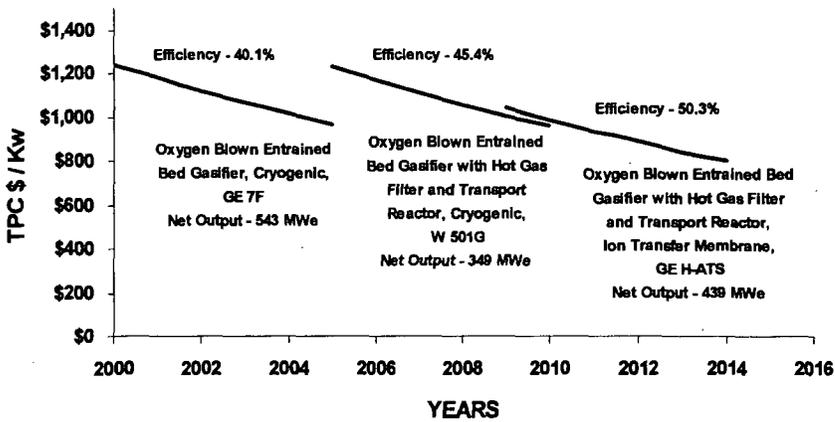


Figure 3
Effect of Technological Developments and Technology Deployment on the Cost of IGCC Plants



**DOE'S FINE PARTICULATE AND AIR TOXICS RESEARCH PROGRAM:
RESPONDING TO THE ENVIRONMENTAL CHALLENGES TO COAL-BASED
POWER PRODUCTION IN THE 21ST CENTURY**

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KEYWORDS

Fine particulate matter, air toxics, coal-based power production

ABSTRACT

In response to the many environmental challenges facing clean, efficient coal-based power production, the U.S. Department of Energy's Federal Energy Technology Center (DOE-FETC) is sponsoring research directed at the characterization and control of ambient fine particulate matter and air toxics. This focused, highly leveraged program encompasses ambient sampling and analysis, atmospheric chemistry and pollutant formation and transport studies, source emissions characterization, and control technology development. The goal of the DOE-FETC research is to provide a sound scientific and technology basis for future regulatory decision making related to ambient air quality and emissions from coal-fired power systems. This paper will present a summary of the research that DOE-FETC is currently sponsoring in the areas of fine particulates and air toxics.

BACKGROUND

The U.S. electric-utility industry has made considerable strides in reducing emissions of sulfur dioxide (SO₂), nitrogen oxide (NO_x), and particulate matter (PM) since the passage of the 1970 Clean Air Act (CAA) and its subsequent amendments¹. These declines in emissions are made even more dramatic in light of the fact that during the period from 1970 to the present there has been a greater than 150 percent increase in coal consumed to produce electricity. However, despite these successes, emissions of SO₂, NO_x, and PM from coal-fired power plants continue to be targeted for further restrictions in reaction to ambient fine particulates, visibility impairment (i.e., regional haze), and air toxics.

Several regulatory drivers are in place or have been proposed that could potentially lead to a call for further reductions in emissions of both primary and secondary fine PM and air toxics from coal-fired boilers. Arguably the most significant of these are the new ambient air quality standards and regional haze requirements. Under Title I of the 1990 CAA amendments, the U.S. Environmental Protection Agency (EPA) promulgated National Ambient Air Quality Standards (NAAQS) in July 1997 to address PM with an aerodynamic diameter of 2.5 micrometers or less (PM_{2.5}). The new PM_{2.5} standard is designed to protect human health from the chronic and acute effects associated with the respiration of fine PM.

In July 1999, a regional haze rule was announced to improve visibility in national parks and wilderness areas of the United States². The rule calls for states to establish goals for improving visibility and to develop long-term strategies for reducing emissions of air pollutants that cause visibility impairment. Since coal-fired boilers may contribute to ambient fine PM and regional haze, these regulations and requirements could result in further controls on power plants.

Particulate emissions from coal-fired boilers may also be impacted by future regulatory action under Title III of the 1990 CAA amendments. Title III requires EPA to implement regulatory standards for 189 air toxics, or hazardous air pollutants (HAPs). EPA has established a goal of reducing air toxic emissions by 75% from 1993 levels to reduce the risk of cancer and other adverse health effects associated with these toxic pollutants. To this end, EPA has recently proposed an air toxics program that would include the measurement of ambient concentrations of air toxics at monitoring sites throughout the nation to determine the need for further control measures³. Should a link between human health and emissions of air toxics from coal-fired boilers be found, a call for additional reductions would be likely.

In addition to Title III, the Toxic Release Inventory (TRI) requirements of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) may also have potential

ramifications on particulate and gaseous emissions from coal-fired power plants. TRI is a public database maintained by EPA on releases of toxic substances from various industries. Electric utilities began reporting for the first time under TRI on July 1, 1999. Although TRI is a reporting requirement, the public's reaction to the information provided could trigger further restrictions on emissions.

In response to these environmental challenges to coal-based power production, the U.S. Department of Energy's Federal Energy Technology Center (DOE-FETC) is carrying out a focused, highly leveraged research program. This program includes ambient air quality monitoring and sample analysis, atmospheric chemistry and pollutant formation and transport studies, source emissions characterization, and cost-effective control technology development. Where opportunities for synergism exist, other ambient air quality issues, such as ground-level ozone and mercury, and the impact of fine particulate matter on climate change, are being addressed.

DISCUSSION

DOE-FETC's Research Program

The goal of the DOE-FETC PM/air toxics research program is to help ensure that a sound scientific and technology knowledge base exists for future regulatory decision making related to ambient air quality and emissions from coal-fired power systems. To achieve this goal, the program has three specific objectives:

- X To characterize the chemical and physical composition of ambient fine PM, air toxics (e.g., mercury), and precursor gases;
- X To characterize the emission of primary and secondary fine particulates from coal-based power systems and to investigate the atmospheric formation and transport mechanisms associated with fine PM and the interactions between secondary fine particulate and precursor gases; and
- X To develop and evaluate technologies to cost-effectively control primary PM and associated trace metals, secondary fine particulate precursors, and acid gases.

Ambient Sampling and Analysis

The implementation of the PM_{2.5} standard requires the collection and analysis of data from a nationwide ambient monitoring network. The majority of these monitoring sites are for compliance purposes. However, a significant subset will be used to collect detailed information on the physical and chemical properties of the collected samples. In support of this effort, DOE-FETC is collaborating with EPA, local and state agencies, and industry in the operation of a number of ambient PM/air toxics monitoring stations. These sites are equipped with a variety of instrumentation necessary for the collection and analysis of the chemical, size, and time-resolved characteristics of aerosol, gas-phase, and biological PM. The data obtained from these sites will be used to apportion sources, evaluate emission inventories and air quality models, measure trends, assess diurnal, seasonal, and annual variations in ambient fine-particulate and air toxics composition, support epidemiological and human-exposure studies, and evaluate regional haze impacts. In addition, the sites serve as research platforms for field testing emerging ambient fine particulate monitoring equipment.

The following is a brief description of the projects being carried out in this area:

- Upper Ohio River Valley Project – This represents the largest component of the DOE-FETC ambient monitoring program. This effort involves the collection and analysis of data from five ambient fine particulate/air toxics monitoring sites in southeastern Ohio, northwestern West Virginia, and southwestern Pennsylvania. One of the sites is also part of the Mercury Deposition Network. The overall objective of the UORVP is to better understand the relationship between emission sources and air quality in the upper Ohio River Valley region. Collaborators include EPA, state environmental agencies, and EPRI.
- Great Smoky Mountain National Park - Under an Interagency Agreement with the Tennessee Valley Authority, ambient monitoring sites are being operated to investigate the impact of coal-fired boilers on visibility in the GSMNP. Collaborators include EPRI and the State of Tennessee

- Aerosol Research Inhalation Epidemiology Study – As part of the TVA Interagency Agreement, air quality measurements are being performed at an urban monitoring site in Atlanta, Georgia. This effort also supports a concurrent epidemiological study. The Atlanta site is part of the EPA-sponsored PM_{2.5} "supersites" program. EPRI, TVA, Southern Company, and several other electric utilities are co-sponsoring the project.
- Big Bend Regional Aerosol and Visibility Observational Study - The BRAVO study will collect atmospheric and ambient air quality data to help identify the U.S. and Mexico emission sources responsible for the haze in the Big Bend National Park in Texas. Participants in this project include EPA, U.S. and Mexican electric-power industry representatives, PROFEPA, Mexico's environmental enforcement agency, the Texas Natural Resource Conservation Commission, and the U.S. National Oceanic and Atmospheric Administration.
- Healy Clean Coal Project - Ambient monitoring is being performed as part of the Healy (Alaska) Clean Coal Technology project to ensure that the project does not impact visibility in the adjacent Denali National Park and Preserve National Park and Preserve (DNPP).

Emissions Characterization and Plume/Atmospheric Studies

The combustion of coal produces primary PM and the precursors to secondary aerosols. Key to apportioning ambient PM_{2.5} and air toxics is a well-defined source-emissions inventory. This component of the DOE-FETC fine particulate program is directed at the characterization of emissions from coal-based power systems. In addition, the program includes an investigation of the formation and atmospheric transport of fine PM and air toxics. The following is brief summary of the projects being carried out in this area:

- Cumberland Plume Study – As part of the TVA Interagency Agreement, fine PM formation in the plume of the Cumberland Fossil Plant is being investigated to assess the impact of the installation of SO₂ and NO_x control technology. Primary and secondary PM data will be gathered at various distances downwind from the plant. TVA and EPRI are co-funding this effort.
- Fine PM Characterization - McDermott Technology (Babcock & Wilcox) is characterizing primary PM and associated trace metal emissions from their 10 MW_e Clean Environment Development Facility. The focus of the project is on the impact of Low-NO_x burners on the emission of ultra-fine carbon soot. Collaborators include the Ohio Coal Development Office.

Control Technology Development

To varying degrees, the sulfate, nitrate, carbon, and trace element composition of ambient fine PM can be attributed to coal. The combustion of coal may also lead to the formation of acid gases that can create localized visibility concerns and are a major consideration relative to reporting TRI. Therefore, a critical component of the FETC particulate matter/air toxics program is the development of cost-effective control technology should further restrictions be placed on emissions from coal-based power systems.

The DOE-FETC research portfolio includes advanced technology for capturing: (1) primary fine particulates and associated trace metals (e.g., lead, mercury, arsenic, etc.); (2) secondary PM_{2.5} precursors; and (3) acid gases (e.g., H₂SO₄, HF, and HCl). These efforts will be closely allied to the ambient and source sampling and characterization activities to ensure that the control technology research focuses on the pollutants of most concern. A summary of each of these technical areas is presented below.

Primary Fine PM Control

- Advanced Hybrid Particulate Collector - The University of North Dakota Energy & Environmental Research Center will continue development of the Advanced Hybrid Particulate Collector (AHPC) technology in order to obtain necessary engineering data for scale-up to full-scale demonstration size. The AHPC optimizes the combination of electrostatic separation and collection with fabric filtration.
- ElectroCore™ Separation Technology - LSR will demonstrate at pilot scale (1.5 MW_e) its ElectroCore™ fine particle separation technology on a slipstream at the Alabama Power Company Gaston Steam Plant.

- Flue Gas Conditioning - ADA Environmental Solutions will develop and commercialize a family of non-toxic flue gas conditioning agents to improve the capture of PM at coal-fired generating units.

Secondary Fine PM Precursor Control

- Ultra Low-NOx Burner - ABB Combustion Engineering is developing an Ultra-Low NOx Integrated System that will involve an aggressively air staged, in-furnace NOx reduction system, building upon ABB C-E's TFS 2000™ system. Improvements to be investigated include milling system enhancements, low NOx oxidizing pyrolysis burners, selective non-catalytic reduction, high velocity over fire air, neural net controls, and the recovery/reuse of unburned carbon.
- Ultra Low-NOx Burner - McDermott Technology, Babcock & Wilcox, and Fuel Tech are teaming to provide an integrated solution for NOx control comprised of an ultra Low-NOx pulverized coal burner technology (B&W's DRB-4Z™) plus urea-based, selective non-catalytic reduction system (Fuel Tech's NOxOUT®).
- METHANE de-NOx® - The Institute of Gas Technology will develop a PC combustion system that is an extension of IGT's METHANE de-NOx® technology. Specifically, the technology is composed of a novel PC burner design using natural gas fired coal preheating developed and demonstrated in Russia, low-NOx burner with internal combustion staging, and additional natural gas injection with overfire air.
- Low-NOx Combustion Optimization - Reaction Engineering International will optimize the performance of, and reduce the technical risks associated with, the combined application of low-NOx firing systems and post combustion controls through modeling, bench-scale testing, and field verification. This will include the evaluation of real-time monitoring equipment to evaluate water-wall wastage, soot formation, and burner stoichiometry, demonstrating analysis techniques to improve LNFS in combination with reburning/SNCR, assessing selective catalytic reduction catalyst life, and developing UBC/flyash separation processes.
- Oxygen Enhanced NOx Reduction - Praxair will develop and demonstrate oxygen enhanced combustion and oxygen enhanced secondary control technologies for controlling NOx, as well as a novel oxygen separation process.

Acid Gas Control

- In-Furnace Control of Acid Gases - Radian is teaming with EPRI, FirstEnergy, the Tennessee Valley Authority, and Dravo Lime Company to demonstrate in-furnace control of sulfur trioxide (SO₃)/sulfuric acid, HCl, and HF emissions. Specifically, Radian will investigate the injection of four different alkaline chemicals into the upper furnace of three different full-scale boilers.

SUMMARY

The DOE-FETC is carrying out a collaborative, highly leveraged research program that will provide timely, high-quality technical and scientific data addressing key uncertainties, such as source-receptor relationships, fine-particle composition, and human-exposure and visibility impacts, associated with PM_{2.5} and air toxic emissions from coal-fired power plants. The program also includes concurrent research directed at the characterization of emissions from coal combustion, the study of plume and atmospheric processes, and the development of cost-effective control technology should further restrictions be placed on the emission of primary particulates (and associated HAPs) or secondary fine particulate precursors. The results from this program will serve to help develop, as needed, effective management strategies that target the appropriate emission sources. Moreover, it will help to further ensure that coal-based electric power generation can remain a viable, environmentally sound, component of the U.S. energy mix well into the 21st Century.

For further information on the DOE/FETC PM/Air Toxics Research Program, please visit our website at www.fetc.doe.gov/products/power/enviro/pm25/index.html.

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The principal technologies for producing syngas from natural gas feed are summarized and compared on Table 1. The predominant commercial technology for syngas generation has been, and continues to be, steam methane reforming (SMR), in which methane and steam are catalytically and endothermically converted to hydrogen and carbon monoxide. An alternative approach is partial oxidation, the exothermic, non-catalytic reaction of methane and oxygen to produce a syngas mixture. SMR and partial oxidation inherently produce syngas mixtures having appreciably different compositions. In particular, SMR produces a syngas having a much higher H₂/CO ratio. This, of course, represents a distinct advantage for SMR in hydrogen-production applications and, in large measure, accounts for its overall dominance among syngas production technologies to date.

Table 1
Comparison of Syngas Generation Technologies
(Natural Gas Feed)

Technology	Advantages	Disadvantages
SMR	<ul style="list-style-type: none"> • Most extensive industrial experience • Oxygen not required • Lowest process temperature requirement • Best H₂/CO ratio for hydrogen production applications 	<ul style="list-style-type: none"> • H₂/CO ratio often higher than required when CO also is to be produced • Highest air emissions
Heat Exchange Reforming	<ul style="list-style-type: none"> • Compact overall size and "footprint" • Application flexibility offers additional options for providing incremental capacity 	<ul style="list-style-type: none"> • Limited commercial experience • In some configurations, must be used in tandem with another syngas generation technology
Two-step reforming¹	<ul style="list-style-type: none"> • Size of SMR is reduced • Low methane slip favors high purity syngas applications • Syngas methane content can be tailored by adjusting secondary reformer outlet temperature 	<ul style="list-style-type: none"> • Increased process complexity • Higher process temperature than SMR • Usually requires oxygen
ATR	<ul style="list-style-type: none"> • Natural H₂/CO ratio often is favorable • Lower process temperature requirement than POX • Low methane slip • Syngas methane content can be tailored by adjusting reformer outlet temperature 	<ul style="list-style-type: none"> • Limited commercial experience • Usually requires oxygen
POX	<ul style="list-style-type: none"> • Feedstock desulfurization not required. • Absence of catalyst permits carbon formation and, therefore operation without steam, significantly lowering syngas CO₂ content • Low methane slip • Low natural H₂/CO ratio is an advantage for applications requiring ratio < 2.0 	<ul style="list-style-type: none"> • Low natural H₂/CO ratio is a disadvantage for applications requiring ratio > 2.0. • Very high process operating temperatures • Usually requires oxygen • High temperature heat recovery and soot formation/handling adds process complexity • Syngas methane content is inherently low and not easily modified to meet downstream processing requirements

¹ SMR followed by oxygen-blown secondary reforming

Source: Reference 2 and SFA Pacific, Inc.

As shown in Table 2, the product syngas composition from either process can, within limits, be manipulated by altering various process conditions and/or by means of additional process steps. Nonetheless, even with such manipulation; neither SMR nor partial oxidation is ideally suited to GTL applications. This is due to the fact that F-T synthesis calls for a H₂/CO ratio of about 2, a value higher than that achievable with partial oxidation and lower than that obtainable with SMR.

A solution to this dilemma is to use both technologies. For example, partial oxidation and SMR may be used in parallel to produce syngas streams that have differing compositions but, when mixed, form a total F-T feedstock of the desired composition. An alternative to this approach is autothermal reforming (ATR), which combines partial oxidation with catalytic steam reforming in one reactor. The process is "autothermal" in that the endothermic reforming reactions proceed with the assistance of the internal combustion (or oxidation) of a portion of the feed

hydrocarbons -- in contrast to the external combustion of fuel characteristic of conventional tubular reforming.

Table 2
Techniques for Adjusting Syngas H₂/CO Ratios

	Decreases Ratio	Increases Ratio
Recycle CO ₂	X	
Import CO ₂	X	
Remove H ₂ via Membrane	X	
Remove CO ₂		X
Increase Steam		X
Add Shift Converter		X

Approximate variation in H₂/CO ratio for natural gas feed:

	SMR	Two-Step Reforming ¹	ATR	POX
Import CO ₂ <i>OR</i>				
Remove H ₂ via Membrane	<3.0	<2.5	<1.6	<1.6
Total CO ₂ Recycle ²	3.0	2.5	1.6	1.6
No CO ₂ Recycle ²	5.0	4.0	2.65	1.8
Increase Steam	>5.0	>4.0	>2.65	>1.8
Add Shift Converter	∞	>5.0	>3.0	>2.0

¹ SMR followed by oxygen-blown secondary reforming

² Shaded figures show range of "natural" H₂/CO ratios.

Source: Reference 2 and SFA Pacific, Inc.

ATR properly refers to a stand-alone, single-step process for feedstock conversion to syngas. However, the same basic idea can be applied to reactors fed by partially reformed gases from a primary reformer. Such reactors form a subcategory of ATR that is commonly called secondary reforming. Due to feed composition differences -- in particular, the lower concentration of combustibles in secondary reformer feeds -- ATR reactors and secondary reformers have different thermal and soot-forming characteristics that require different burner and reactor designs. Nonetheless, the distinction between ATR and secondary reforming is not consistently drawn by technology users and vendors, with the result that secondary reformers often are referred to as ATRs. As will be discussed further, most commercial experience with autothermal reforming has, in fact, involved secondary reformers -- most notably, oxygen-blown units for methanol production and air-blown units for ammonia production.

Much of the forward-looking consideration of syngas production for GTL has focused on ATR. In part, this is due to the technology's basic compatibility with F-T feed chemistry requirements. However, this focus also reflects the perception that ATR has other attributes -- relative compactness, lower capital cost, and greater potential for economies of scale -- which will contribute significantly to the economic viability of GTL plants.

Ongoing efforts to develop lower-cost syngas generation technologies include the following:

- The development and application of "compact reformers" and of "heat exchange reformers," in which a portion of the heat of reaction is provided by heat recovery from the reformed gas, rather than by burning fuel. Potential advantages over conventional tubular reactors include improved efficiency, smaller plant footprint, lower capital cost, and reduced emissions. Companies active in this area have included Air Products, KTI, ICI, BP/Kvaerner, Kellogg, Haldor Topsoe, Krupp Uhde, and Lurgi.
- Development and application of air-blown autothermal reformer technology, thereby eliminating the need for an oxygen plant. (Air-blown secondary reforming is well-established, being commonly utilized for syngas production for ammonia plants.) The chief proponent of the air-blown approach is Syntroleum.

- New reformer reactor approaches, most notably that employed by Exxon's AGC-21 process for converting natural gas to liquids. The first step in this process is syngas generation via oxygen-blown catalytic autothermal reforming in a fluidized bed reactor. The process has been demonstrated at large pilot scale -- about 200 b/d.
- "Ceramic membrane reactors," based on the use of ionic or oxygen transport membranes, which would couple air separation and partial oxidation in one unit operation, thereby eliminating the need for a conventional oxygen plant. Although being aggressively pursued by two industrial consortia, work in this area is still at a fundamental level. One consortium, led by Air Products, is being co-funded by the U.S. Department of Energy. The participants in this effort include ARCO, Babcock & Wilcox, Chevron, Norsk Hydro and others. The second consortia, based entirely on industrial funding, involves Amoco, BP, Praxair, Statoil, Phillips Petroleum and Sasol.

Large-Scale Syngas Generation For GTL -- Relevant Commercial Experience

Commercial experience relevant to large-scale syngas generation for GTL plants may be derived principally from two areas -- (1) prior and existing F-T synthesis facilities and (2) large-scale methanol plants.

Methanol plants are relevant, in part, because they require a syngas composition similar to that required for F-T synthesis. Moreover, world-scale methanol plants have become increasingly large. Single-train methanol plants already are producing more than 2,500 mtpd of methanol, and even larger plants, approaching 3,000 mtpd, have been announced. In syngas terms, a 20,000 b/d F-T plant would be comparable to three 2,500 mtpd methanol plants. Accordingly, syngas generation in the largest methanol plants may be considered to be on a scale analogous to that required for a multiple-train F-T facility of appreciable size.

Another aspect of syngas generation in methanol plants that is relevant to GTL is the fact that methanol plants consistently have been cited as logical applications for ATR. The general rationale is that while SMR can offer good economics at small-to-moderate scale, tubular reformers do not offer significant economies of scale as single-train methanol plant capacities increase. As a result, two-step reforming and, ultimately, ATR should become the technologies of choice for larger plants. This conclusion is premised on the more favorable economies of scale offered by ATR and secondary reformer reactors and, especially, by ever-larger air separation plants. According to rules-of-thumb publicly offered by Haldor Topsoe and Lurgi, for example, two-step reforming is economically preferred over SMR for methanol plant capacities above about 1,500 mtpd, with ATR becoming the economic choice for capacities above 2,500-3,000 mtpd.

In practice, oxygen-blown ATR has yet to see application in a large-scale methanol plant, although oxygen-blown secondary reformers have seen operation in a limited number of plants, such as the 2,400 mtpd Conoco/Statoil methanol plant, of Haldor Topsoe design, that started up in Norway in 1997. This plant, which also contains a prereformer upstream of the SMR, is said to be operating well.

Interestingly, a number of large methanol plants recently built or announced -- such as those by Methanex for Chile and Qatar -- have been based on SMR, despite capacities approaching 3,000 mtpd. According to ICI, their Leading Concept Methanol (LCM) process, which employs heat exchange reforming followed by oxygen-blown secondary reforming, may be considered for the second of three 2,950 mtpd plants announced by Methanex for construction/startup in Qatar by 2006. Application of the LCM technology has thus far been limited to a small (165 mtpd) plant in Australia.

Other relevant syngas generation experience comes from Shell's F-T operation in Bintulu, Malaysia and from the operations of Moss gas and Sasol in South Africa. The 12,500 b/d Shell plant employs partial oxidation of natural gas for its primary syngas generation. A small SMR is operated in parallel with four partial oxidation reactors to provide a secondary syngas stream for adjusting the overall syngas composition. Idled by an explosion in the air separation area last year, the plant is expected to resume operation in 2000. The restarted facility will boast a 3,200

air separation facility, larger than the original plant's, to accommodate increased F-T synthesis capacity made possible by improved catalysts. [3]

The 20,000 b/d Moss gas plant consists of three trains, each equivalent (in syngas terms) to a 2,500 mtpd methanol plant. Started up in 1992, the plant utilizes Lurgi's two-step reforming process -- i.e., SMR followed by oxygen-blown secondary reforming. A unique feature of the Lurgi process is the bypassing of a portion of the natural gas feed around the SMR to the secondary reformer. Lurgi also provided two-step reforming technology for a grass roots methanol facility in Malaysia which started up in 1984. Operating experience, some of which has been documented by Lurgi and Moss gas, has included some problems with burner operation and life and with metal dusting. [4, 5]

Since the Sasol F-T operation in South Africa is coal-based, its primary syngas generation is not directly relevant to the natural gas-based plants now being considered for GTL. However, Sasol also has operated 16 oxygen-blown ATRs of Lurgi design since 1982. These units operate on recycle methane and have now been retrofitted with burner technology provided by Haldor Topsoe. [6] Although small -- each unit is about 1/10 the capacity required for a 20,000 b/d F-T plant -- these units represent the largest oxygen-blown ATRs to have been commercially operated to date.

Development of two bellwether F-T projects -- a 20,000 b/d facility by Chevron and Sasol in Nigeria and a plant of like capacity by Phillips and Sasol in Qatar -- reportedly is proceeding on the basis of using ATR technology provided by Haldor Topsoe, which (along with Chevron) now has a commercial arrangement with Sasol for providing process technology for GTL plants. Viewed in the context of the limited commercial experience previously summarized, such commercial application of ATR represents a considerable extrapolation and scale-up of prior technology.

It appears that considerable confidence is being placed in advances in the engineering tools now available for designing autothermal reforming burners and reactors. Both Lurgi and Haldor Topsoe claim to now have rigorous computer models to facilitate the scale-up and design of oxygen-blown ATRs. [7, 8] ICI claim a similar capability with respect to their oxygen-blown secondary reformers. By way of contrast, the design and scale-up of the prior Malaysian and Moss gas secondary reformers relied heavily on empiricism and engineering judgment.

Air-Blown vs. Oxygen-Blown Autothermal Reforming

The importance of syngas production to overall GTL costs is vividly illustrated in Table 3, which shows the cost distribution for a facility that is based on the use of oxygen-blown ATR. As shown, GTL costs are dominated by capital charges, which comprise about two-thirds of the total costs. Syngas production, in turn, accounts for about half of the capital investment, in part due to the significant capital cost of the oxygen plant.

Not surprisingly, the oxygen plant investment has been an attractive target of GTL cost-cutting strategies. This target has spawned both long-term strategies -- e.g., the previously mentioned ceramic membrane reactor -- and short-term strategies -- e.g., air-blown ATR. It remains to be seen how successful ceramic membrane reactor development will be. However, SFA Pacific sees no apparent advantage that would favor air-blown over oxygen-blown systems.

Indeed, air-blown reforming technology is unlikely to be economically competitive with oxygen-blown systems and appears much less flexible. Factors which more than negate the savings associated with elimination of the oxygen plant include: lower thermal efficiency, high air compression power requirements, the inability (because of its composition) to recycle F-T tail gas, and the larger downstream equipment sizes and pressure drop associated with handling the much larger volumetric flow of gas. Questions also remain about the potential for forming ammonia and other nitrogen compounds in the downstream F-T conversion units.

Table 3
Estimated Cost Of Fischer-Tropsch Liquid

Manufacturing cost (% of total)	
Natural gas @ \$0.50/Mscf	14.9
Operating labor	1.8
Other operating costs ¹	19.2
Capital charges @ 20%/yr ²	64.1
Total	100.0

- ¹ Includes catalysts, cooling water, process water, plant maintenance, overhead, property taxes and insurance.
² A capital charge of 20%/yr (simple 5-year payout) is equal to about a 12% DCF rate of return under the current U.S. tax structure.

Capital Cost Distribution¹	
Plant Section	% of Total Capital Cost²
Oxygen Plant	23
Reforming ³	28
Fischer-Tropsch Synthesis ³	24
Product Upgrade	13
Power Recovery	12
Total	100

- ¹ Basis: 20,000 bbl/day liquid product
² Exclusive of port and other general facilities
³ Including allocated portion of heat exchange cost

Source: SFA Pacific, Inc.

Also problematic with air-blown operation is the low heating value of the F-T tail gas. From an economic standpoint, utilizing this tail gas to generate power for export sale is a potentially key contributor to the overall viability of the GTL plant. However, combustion turbine technology and commercial experience with the use of such low quality gas remains quite limited.

Outlook

Although not yet confirmed by new, large-scale, commercial F-T plants, there is good reason to believe that proposed and future GTL facilities will be substantially less costly than their very expensive predecessors. In large measure, such cost reductions will be attributable to improvements in F-T catalyst and reactor design, the most significant of which have been pioneered by Sasol.

At the same time, in the absence of a breakthrough technology, economy of scale will be the only significant mechanism by which GTL can achieve greater economic viability. To be sure, additional evolutionary cost reductions due to further reactor scale-up, catalyst development and the "learning curve" benefits of repetitive plant design will materialize. However, even with such further cost reductions, the economic viability of GTL plants will remain confined to special situations until crude price levels rise substantially.

How does syngas generation fit into this picture? In the near term, prospects for reduced syngas generation cost would appear to lie with the application of ATR proposed for Qatar and Nigeria. In addition to providing a landmark demonstration of the technology's commercial readiness, these projects will help confirm its projected investment and operating cost benefits.

However, while large-scale ATR may in some sense be considered a commercial technology breakthrough, it is likely that many economic analyses of GTL already have taken credit for its assumed benefits. If so, the cost reduction potential of ATR already has been discounted, and further reductions in syngas generation cost via ATR already may be confined to less dramatic, evolutionary improvements in the technology, particularly since additional economies of scale appear to be limited. The 20,000 b/d Qatar and Nigeria projects are each proceeding on the basis of two, 10,000 b/d trains. Haldor Topsoe, Lurgi and others have variously pegged the largest ATR reactor size as that consistent with producing 5,000 to 10,000 mtpd methanol -- equivalent

in syngas terms to about 13,000 - 26,000 b/d of F-T liquids. Accordingly, further dramatic cost reductions may require the application of still newer reforming technologies. One such development to watch is Exxon's oxidation-blown, fluidized bed ATR, which could offer increased potential for economies of scale.

As discussed, considerable resources are being devoted to the development of the ceramic membrane reactor, with a goal of operating a sizable scale demonstration facility in 5-7 years and reducing GTL investment costs by 20%. If realized, these ambitious goals, which face formidable technical barriers, could legitimately make GTL economically viable at crude prices below \$20/b.

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SYNGAS PRODUCTION FOR GAS-TO-LIQUIDS APPLICATIONS: TECHNOLOGIES, ISSUES AND OUTLOOK

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Introduction

Fischer Tropsch (F-T) chemistry understandably is often regarded as the key technological component of schemes for converting synthesis gas (or "syngas") to transportation fuels and other liquid products. However, syngas production itself accounts for more than half the capital investment and a disproportionate share of the operating costs for a gas-to-liquids (GTL) complex. A study completed earlier in 1998 by SFA Pacific examines the full range of commercial and developmental synthesis gas production technologies and provides an independent assessment of syngas production options and costs for GTL applications [1].

The manner in which syngas is produced can be influenced by, and in turn can profoundly impact, many facets of the overall GTL process design, such as:

- Plant size and location
- The need for an oxygen plant or oxygen enrichment facilities
- The physical size of downstream gas-handling equipment
- Syngas composition and its associated effects on F-T chemistry and yields
- Heat integration and gas recycle options
- Gas compression requirements
- The scope and configuration of power generation alternatives

This paper examines the status of commercial and developmental syngas production technologies in the context of GTL production based on F-T synthesis. The scope of this examination includes:

- A brief review of relevant commercial experience to date
- Consideration of the direct and indirect impacts of syngas production on GTL costs
- An update on new syngas generation technologies now under development
- Comments on the relative merits of air-blown and oxygen-blown syngas generation
- The outlook for reduced GTL capital and operating costs due to improved syngas generation

Syngas Generation Technologies

In principle, synthesis gas may be generated from any hydrocarbon feedstock. This is reflected in industrial practice, which includes large-scale syngas production from a wide variety of materials that includes natural gas, naphtha, residual oil, petroleum coke and coal. However, in the context of GTL applications, natural gas -- more specifically, low-value natural gas -- is the predominant, if not the only, feedstock of interest.

In large part, this is a reflection of the high investment costs of GTL processes which, in the absence of special circumstances, require a low or, even better, negative value feedstock to achieve attractive overall economics. Low quality residual oil or coke can, of course, have a low or even negative value. However, conversion of such feedstocks -- via gasification -- entails greater capital investment, in part due to the costs associated with materials handling, soot removal and syngas cooling and purification. The focus for GTL has thus been on associated gas, so-called stranded or remotely-located gas reserves, and larger gas reserves that are not currently being economically exploited. In the near-term, associated gas may offer the greatest potential, particularly where such gas is subject to flaring constraints and associated reinjection costs.

Chemicals from Coal: The Acetyl Value Stream

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Abstract

Well-established technologies for the conversion of syn-gas can be utilized to manufacture each of the primary materials that constitute the acetyl value chain, i.e., methanol, acetic acid (acetic anhydride) and vinyl acetate. Interest in driving the utilization of syn-gas resources further down the acetyl value chain arises not only from the necessity to efficiently utilize domestic carbon sources but also from issues of global competitiveness. The first-discovered commercializable low-water containing homogeneous catalyst system for the production of acetic acid utilizes a non-noble metal catalyst (nickel). A number of studies, including our own, have indicated that phosphines are important not only to stabilize the catalyst but they also have a substantial effect on the rate of carbonylation. We will discuss a study of this catalyst system that is based upon both kinetic and in-situ monitoring results.

Introduction

Eastman Chemical Company has demonstrated a long-term commitment to the utilization of syngas in the commercial manufacture of acetyl chemicals. Our "Chemicals from Coal" complex practices the carbonylation of methyl acetate to acetic anhydride, a

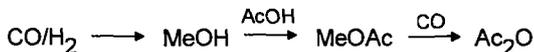


Figure 1: Eastman's Chemicals from Coal Stream

process utilizing only syngas derived feedstocks. In this facility the synthesis of acetic acid is accomplished by the methanolysis of acetic anhydride. Typically, however, the large-scale production of acetic acid is carried out by the homogeneously catalyzed low-pressure carbonylation of methanol. Commercial facilities currently utilize either a rhodium or iridium based homogeneous catalyst and a methyl iodide promoter. Early attempts to utilize less-expensive nickel catalysts indicated that severe process conditions (pressures as high as 26.7 kPa and temperatures in the range of 250-300°C) were required to achieve reasonable reaction rates. More recently, it was found that the severity of the required process conditions could be considerably reduced by the use of appropriate promoters and the nickel-catalyzed reaction became a viable competitor to other commercial catalyst systems.

The catalyst system for the nickel-catalyzed acetic acid process consists of nickel and molybdenum compounds, an iodide promoter and a phosphine. Under reaction conditions the phosphine exists largely as the phosphonium iodide (adduct with methyl iodide). However, high-pressure infrared studies suggest that substantial quantities of the free phosphine are present and available to act as ligands in the catalytically active metal complex. This is consistent with the notion that the phosphorous component of the catalyst mixture is important in suppressing the formation of the inactive $\text{Ni}(\text{CO})_4$ which is present only in trace amounts when the steady-state catalysis is rapid. It also provides an ability to modify the behavior of the catalytic process as changes in the electronic and steric properties of the phosphine are reflected in both the amount of free phosphine present under catalytic conditions and in the nature of the catalytically active species. Indeed, we have been able to observe changes in the rate of catalysis as the nature of the phosphorus promoter changes.

Experimental

The reaction systems described here have been studied by an in situ CIR-FTIR reactor. This equipment and the experimental conditions have been described.¹ Measurement of the rate of various reactions was obtained by monitoring the number of moles of carbon monoxide consumed by the reaction mixture. This was accomplished by either the use of mass-flow control meters or by monitoring the pressure-drop in a surge tank used to supply carbon monoxide to the reaction vessel. In a typical experiment NiI_2 (1.72g), PPh_3 (5.76g), $\text{Mo}(\text{CO})_6$ (0.89g), methyl iodide (25.8g), acetic acid (53.5 mL), methanol (53 mL), water (7.3mL) and methyl acetate (11 mL) were loaded into a 300 mL stirred

autoclave constructed from all Hastelloy C components. The autoclave was sealed, purged with CO and then pressurized to 11.3 kPa with CO and the pressure monitored for evidence of leaks. If no leaks were evident the autoclave was vented, stirring begun and 0.9 kPa of H₂ and 4.1 kPa of CO added. After heating to 210°C the total autoclave pressure was increased to 11.3 kPa with carbon monoxide and the pressure maintained by adding additional carbon monoxide as needed. The quantity of carbon monoxide added was recorded at three-minute intervals for a total reaction time of 5 hours. Regression analysis of the slope of the region of steady-state carbon monoxide consumption and a knowledge of the reaction volume charged to the autoclave allowed the calculation of the space-time yield (moles/L-Hr). After the reaction was complete, the autoclave was cooled to room temperature, vented and unloaded. Exact autoclave compositions for the experiments were determined by routine gas chromatographic analysis of the product mixture.

Results and Discussion

A mechanistic scheme that explains the major features of the reaction and is consistent with both the kinetic and in situ CIR-FTIR observations² is shown in Figure 2. It suggests that a catalytically active nickel(0) species is available as a result of both a hydrogen enabled reduction from Ni(II) and the delivery of free phosphine ligand from the equilibrium dissociation of the phosphonium salt. The catalytic cycle itself is fairly unremarkable when compared with similar postulated mechanisms for the rhodium catalysts. Methyl iodide is delivered to the catalytic carrier and an oxidative addition results in the formation of a Ni(II) alkyl iodide complex. The addition of carbon monoxide is followed by an alkyl migration and a subsequent reductive elimination allows the recovery of acetic acid product and regeneration of the carrier.

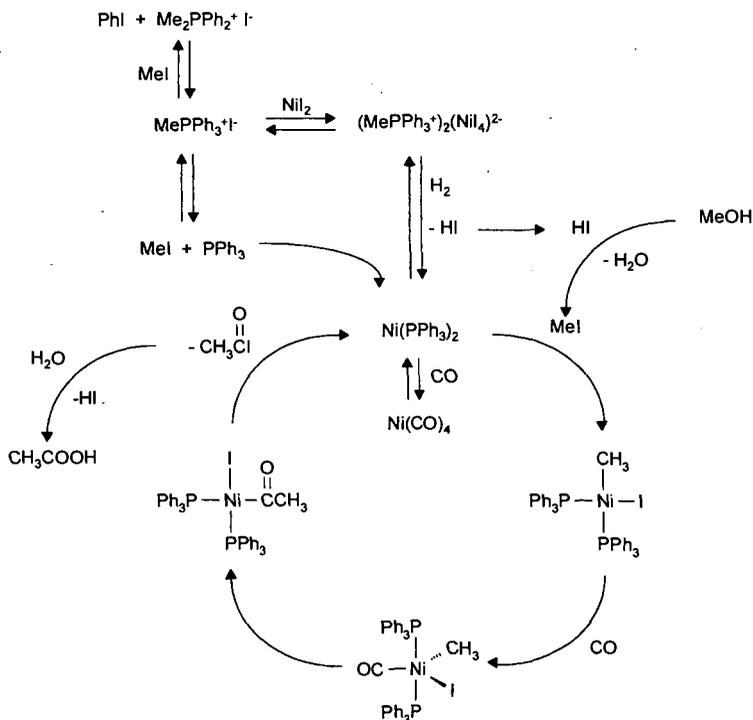


Figure 2: Mechanism of the Nickel Catalyzed Carbonylation of Methanol

CIR-FTIR observations indicate that there is no build-up of nickel carbonyl species during the course of the reaction so that the slow step(s) of the process must occur before the addition of carbon monoxide.

The course of a typical batch reaction, as measured by the uptake of carbon monoxide (Figure 3), can be used to examine catalyst activation. In this particular case one can note a persistent induction period that spans about 40 minutes followed by a period of well-behaved steady-state catalysis and finally the loss of rate associated with depletion of the reactants.

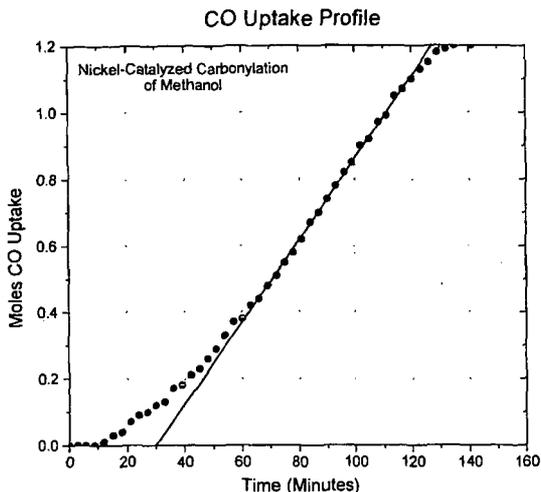


Figure 3: Course of Typical Batch Reaction

The length of the induction period has been shown to depend upon both the nature of the nickel compound charged to the reactor as well as the partial pressure of hydrogen present in it. With NiI_2 , triphenylphosphine and the reaction conditions as indicated in the experimental section the induction period is minimized. However, the details of the reduction process have not yet been elucidated and we cannot distinguish between the direct formation of " NiI_2 " or the intermediate formation of $\text{Ni}(\text{CO})_4$ which subsequently reacts with free ligand.

The rate of the reaction shows first-order dependence upon the concentration of nickel and methyl iodide. The reaction is also first-order with respect to carbon monoxide at lower pressures. These results are consistent with the CIR-FTIR observations noted above. However, at higher carbon monoxide pressures the rate of reaction is inhibited indicating that it is possible for carbon monoxide to compete effectively with the free ligand present in solution. In fact, as one might predict from this mechanism, higher concentrations of phosphine promoter are required in order to obtain the maximum rate of reaction at higher carbon monoxide partial pressures.

Also consistent with the above mechanism is the observation that the rate of catalysis depends upon the identity of the phosphine promoter used. The identity of the phosphine determines the position of the dissociative equilibrium from the phosphonium iodide and thus the amount of free ligand available as well as the rate of the reaction of the various ligand substituted nickel intermediates. It was shown that both the steric and electronic properties of the phosphine promoters play a role in determining reaction rates.

Conclusions

The mechanism of the phosphine promoted nickel-catalyzed carbonylation of methanol has been shown to involve the equilibrium dissociation of free phosphine from the phosphonium iodide present under reaction conditions. This free phosphine is able to compete effectively as ligand with carbon monoxide in the formation of the catalytically active zero-valent nickel intermediates. The rate of reaction can be favorably influenced by the nature of the phosphine promoter used and under conditions which provide rapid rates for carbonylation $\text{Ni}(\text{CO})_4$ is present in only trace quantities.

Acknowledgements

The CIR-FTIR results and rate measurements in the CIR-REACTOR were obtained at Worcester Polytechnic Institute by Professor William R. Moser and Barbara J. Marshik-Guerts.

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FISCHER TROPSCH: A FUTURISTIC VIEW

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KEYWORDS: Fischer-Tropsch, Natural gas conversion, Liquid fuels

INTRODUCTION

During the last couple of years there has been a renewed interest in the use of Fischer-Tropsch technology for the conversion of natural gas to liquids. Some of the factors that contributed to this are:

- (i) An increase in the known reserves of natural gas.
- (ii) The need to monetize remote or stranded natural gas.
- (iii) Environmental pressure to minimize the flaring of associated gas.
- (iv) Improvements in the cost-effectiveness of Fischer-Tropsch technology resulting from the development of more active catalysts and improved reactor designs.

The process to convert natural gas to liquids can be divided into three process steps:

- (i) Syngas generation
- (ii) Syngas conversion
- (iii) Hydroprocessing

Although all three of these technologies are well established, individually optimized and commercially proven, the combined use is not widely applied. This poses an interesting challenge to the designer, namely to obtain the most cost-effective combination of these three technologies. In order to make the Gas-to-Liquids (GTL) technology more competitive, the challenge goes beyond the optimization that deals only with the known aspects of these technologies. It also includes those aspects that are not commercialized yet and that may still be in the very early stages of development.

OPTIMIZATION OF EXISTING TECHNOLOGIES

SYNGAS GENERATION

To convert natural gas (mostly methane) to syngas (a mixture of H_2 and CO), the designer can choose from the following four well established reforming technologies:

- (i) Steam reforming
- (ii) Partial oxidation (POX)
- (iii) Autothermal reforming
- (iv) Combined or two-step reforming

The choice of reformer technology will have an influence on the thermal efficiency of the plant as a whole and on the capital costs of the reformer, oxygen plant (where applicable) and the Fischer-Tropsch section. One of the biggest challenges is to optimize the energy integration between the syngas generation and syngas conversion sections.

STEAM REFORMING

An obvious advantage of steam reforming is that it does not need an oxygen plant. However, since steam reformers are more costly than either POX or autothermal reformers, there is a minimum plant size above which the economy of scale of a

cryogenic oxygen plant in combination with a POX or autothermal reformer is cheaper than a steam reformer on its own.

Other disadvantages of steam reforming are:

- (i) Syngas with a H_2/CO ratio (>4) which is much higher than what is optimally needed by the Fischer-Tropsch section.
- (ii) Lower methane conversion due to a maximum operating temperature of below $900\text{ }^\circ\text{C}$.
- (iii) The high usage rate of water makes it unsuitable for arid regions.

Recycling of CO_2 and removal of the excess H_2 by means of membranes can lower the H_2/CO ratio to a level acceptable to the Fischer-Tropsch reaction. Since the methane conversion is also a function of the operating pressure, decreasing the operating pressure of the reformer can increase the methane conversion. Due to the costs involved with these steps, it is most likely that steam reforming will only be considered when one or more of the following conditions hold:

- (i) A relative small GTL plant with a capacity of well below 10 000 bpd.
- (ii) The additional H_2 can be used for other applications like methanol or ammonia production.
- (iii) The natural gas has a high CO_2 content.
- (iv) Suitable water can be obtained at a low cost.

PARTIAL OXIDATION REFORMING

The non-catalytic partial combustion of methane produces syngas with a H_2/CO ratio (<2) close to the optimum needed by the Fischer-Tropsch section. This low H_2/CO ratio gas results from the very little, if any, steam that is used in the process. Due to the absence of catalyst, the reformer operates at an exit temperature of about $1400\text{ }^\circ\text{C}$. This high temperature and the absence of catalyst have the following disadvantages as compared to an autothermal reformer:

- (i) Formation of soot and much higher levels of ammonia and HCN, which necessitates the use of a scrubber to clean the gas.
- (ii) Higher oxygen consumption.
- (iii) Due to the absence of the water-gas shift reaction, the unconverted methane as well as the methane produced by the Fischer-Tropsch reaction can not be recycled to the reformer without removing the CO_2 from the Fischer-Tropsch tail gas.

Depending on the energy needs of the plant, the syngas from the reformer can either be cooled by means of a water quench or by the production of steam in a heat exchanger. A quench system is the less costly of the two, but is also less thermally efficient. In designing a POX based GTL plant, the choice between a quench or a waste heat reboiler will depend on the relative cost of capital and energy.

AUTOTHERMAL REFORMING

Unlike partial oxidation reforming, autothermal reforming uses a catalyst to reform the natural gas to syngas in the presence of steam and oxygen. Due to the milder operating conditions (exit temperature of $\pm 1\ 000\text{ }^\circ\text{C}$) and the use of steam (S/C ratio normally more than 1,3), the syngas is soot free and less ammonia and HCN are produced as compared to a POX. However, at a S/C ratio of 1,3 the syngas will have a H_2/CO ratio of about 2,5, which is higher than the ratio needed by the Fischer-Tropsch section. The H_2/CO ratio can be controlled by a combination of lowering the S/C ratio and recycling the CO_2 to the reformer. Although S/C ratios below 1,3 are not commercially used, Haldor Topsøe and Sasol have successfully completed low S/C ratio tests on a commercial scale at Sasol's synfuels plant in South Africa.

Some of the other design parameters of the syngas section that influence the cost and thermal efficiency of the GTL plant are:

- (i) The preheat temperatures of oxygen and natural gas. The higher these temperatures are, the less oxygen will be used. The maximum preheat temperatures are determined by safety factors and by the need to prevent soot formation.

- (ii) The pressure of the steam generated in the waste heat reboiler. The higher the steam-pressure, the more efficient energy can be recovered from the steam, but the more costly the steam and boiler feed water treatment systems become. The optimum steam pressure will be determined by the relative cost of capital and energy.

COMBINED REFORMING

By combining a steam reformer with an autothermal reformer, better energy utilization can be obtained than with either steam or autothermal reforming alone. Depending on the degree of energy integration and the specific operating conditions, the thermal efficiency of the GTL plant can be improved by about 1 to 2 percentage points. Although less expensive than steam reforming on its own, this type of reforming is more expensive than autothermal reforming and the choice between combined and autothermal reforming will depend on the cost of the natural gas.

SYNGAS CONVERSION

Due to its high activity and long life, cobalt-based Fischer-Tropsch catalyst is currently the catalyst of choice for the conversion of syngas to liquid fuels. The exothermic nature of the Fischer-Tropsch reaction combined with the high activity of the Co catalyst makes the removal of heat from the reactor of critical importance. In the case of a tubular fixed bed reactor, this becomes even more problematic due to the inherent temperature profiles inside the tube. This problem can be controlled by finding the balance between the tube diameter and the usage of a "quench" medium such as the recycle of inerts.

Due to the good mixing and heat transfer characteristics of a slurry phase reactor, the temperature control in such a reactor is much less of a problem than in a tubular fixed bed reactor. Care must however be taken in the design of such a reactor that, during normal operating conditions and also during the shutdown of the reactor, no stagnant zones with poor mixing occur which may result in localized hot spots. If the catalyst is exposed to too high a temperature, carbon will be formed, which may damage the structural integrity of the catalyst.

Another critical design aspect of a slurry phase reactor is the separation of the catalyst from the wax. Sasol was successful in the development of a very efficient catalyst/wax separation system. By matching the characteristics of the catalyst with those of the separation system, the loss of catalyst can be restricted to a few ppm of catalyst in the wax produced by the Fischer-Tropsch process.

Since the H_2/CO ratio of the syngas is an important design variable to maximize the production of high quality diesel, the designs of the reformer and the Fischer-Tropsch sections can not be done in isolation. The most cost effective design for both units can only be obtained by taking the mutual interaction between these units into account.

HYDROPROCESSING

The wax and hydrocarbon condensate produced by the Fischer-Tropsch process is predominantly linear parafins with a small fraction of olefins and oxygenates. The hydrogenation of the olefins and oxygenates and the hydrocracking of the wax to naphtha and diesel can be done at relatively mild conditions.

In the design of the hydrocracker, a balance must be found between the per-pass conversion, diesel selectivity and diesel properties. The higher the per-pass conversion, the smaller the cracker will be due to the lesser recycle of material back to the cracker. This will however be at the expense of the diesel selectivity, since over cracking of the liquid to gasses will occur. Another complicating factor is that the per-pass conversion also influences the diesel quality. The higher the per-pass conversion, the better the cold flow properties but the lower the cetane value will be, due to the increased degree of isomerisation.

CAPITAL AND OPERATING COSTS

CAPITAL COST

Studies done by Sasol indicated that the total installed cost of a two train 30 000 barrel per day GTL plant is in the order of about \$24 000 per daily barrel. It is also believed that the capital cost can be further decreased to about \$20 000 per daily barrel by:

- (i) The economy of scale of larger single train capacity plants.
- (ii) The economy of scale of adding trains.
- (iii) Improved process integration and optimization.
- (iv) Progressing up the learning curve.

The capital cost associated with the syngas generation section is more than 50% of the total IBL cost of the plant.

OPERATING COST

Based on a gas cost of \$0,5 per MM BTU, the estimated operating cost is in the order of about \$10 per barrel of which the gas cost is \$5 per barrel. The main areas of energy loss from the process are the syngas generation and syngas conversion sections. The oxygen plant and reformer combination is responsible for about 45% and the Fischer-Tropsch section for about 50% of the energy losses from the plant.

About 50% of energy loss from the Fischer-Tropsch plant is due to condensing of the reaction water produced by the Fischer-Tropsch reaction and the balance results from the inefficiency with which energy is recovered from the relatively low pressure steam.

FUTURE IMPROVEMENTS

In order to have the greatest impact on the economics of the process, future breakthroughs should be in areas that decrease the capitals cost of syngas generation and/or improve the thermal efficiency of the plant as a whole.

An obvious way of improving the thermal efficiency of the process is to combine it with a power generation plant. Such a combination will create a more efficient utilization of the low pressure steam produced by the Fischer-Tropsch process. If the energy associated with this steam is sold at the same price as that of the natural gas (\$0,5 per MM BTU), an additional income of about \$0,5 per barrel can be obtained.

Some of the changes to the reforming section that can increase the thermal efficiency of the process are:

- (i) The use of a heat exchange reformer in combination with an autothermal reformer.
- (ii) The use of a feed/product heat exchanger to recover energy from the reformer outlet.

HEAT EXCHANGE REFORMING

The combination of a heat exchange reformer with an autothermal reformer is very similar to combined reforming, the major difference being that the energy to the steam reformer is not supplied by a fired heater but by the exit gas from the autothermal reformer.

The potential benefits of such a reforming configuration are:

- (i) Savings of about 30% in oxygen consumption.
- (ii) An increase of about 4 percentage points in the thermal efficiency of the plant.

One of the technical issues that must be solved is the potential problem of metal dusting in the heat exchange reformer.

FEED/PRODUCT HEAT EXCHANGE

The oxygen consumption can be decreased by about 3,5% and the production of liquid fuels can be increased by about 2,5% if a feed/product heat exchanger is used to

preheat the natural gas to the reformer. As in the case of heat exchange reforming, metal dusting is also one of the major technical problems that would have to be solved.

OXYGEN TRANSFER MEMBRANES

Another way of eliminating the oxygen plant is to use ceramic membranes to separate the oxygen from the air. In addition to the capital cost savings associated with the elimination of an oxygen plant, the thermal efficiency of the plant can also be improved by combining the oxygen removal and reforming sections into one unit. Early indications are that this technology should significantly reduce the capital cost of the syngas generation section of the GTL plant.

Some of the technical issues that are being researched include the maximization of the oxygen flux and the mechanical strength of the ceramic tubes.

OTHER POTENTIAL IMPROVEMENTS

The Co catalyst can be improved by:

- (i) Increasing the catalyst life by making it more resistant to irreversible sulphur poisoning.
- (ii) Changing the selectivity dependency on the H_2/CO ratio to such an extent that high diesel yields can be obtained at H_2/CO ratios similar to the usage ratio. The advantage of such a catalyst would be that, due to the increase in reaction rate at higher H_2/CO ratios, much less catalyst would be needed for the same conversion. To obtain the same conversions at H_2/CO ratios of 2 and 1,6, 50% more catalyst is needed at the lower H_2/CO ratio.

CONCLUSIONS

Although the three main processing steps of a GTL plant have been individually optimized for other applications, opportunities do exist to decrease the capital and operating costs by re-optimizing these processing steps for GTL applications. In addition to these optimization opportunities, there are other potential breakthroughs that can also significantly reduce the operating and capital costs of a GTL plant.

Fischer-Tropsch Synthesis: Current Mechanism and Futuristic Needs

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KEYWORDS: Fischer-Tropsch Synthesis; reaction mechanism; isotopic tracer studies

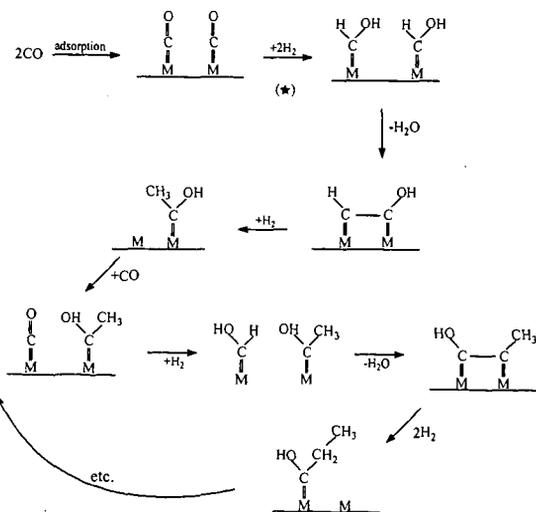
INTRODUCTION

The original **carbide mechanism** for the formation of hydrocarbon and oxygenate products with the Fischer-Tropsch synthesis (FTS) included the formation of the metal carbide followed by hydrogenation of the metal carbide to produce the products [1]. It was eventually recognized that this mechanism was inconsistent with thermodynamic data for the formation of hydrocarbons by hydrogenation of the carbide at the temperatures used for the synthesis reaction [2,3]. The direct hydrogenation of the metal carbide was investigated by Kummer et al. [4]. These workers performed iron carbide by the reaction of a reduced iron catalyst and ^{14}C O. The fraction of methane that is $^{14}\text{CH}_4$ when synthesis is effected with unlabeled CO is a measure of the contribution of direct hydrogenation of the preformed iron carbide to the synthesis. The data showed that carbide hydrogenation could be responsible for no more than 8 to 30% of the methane that is formed. These authors made a special effort to obtain data at low conversion levels that would represent the hydrogenation of only a percent of the total surface carbon; even under these conditions direct hydrogenation was responsible for only a small fraction of the methane produced. In addition, the same conclusion applied for the higher carbon number compounds. This study led most investigators to abandon the formation of a bulk metal carbide as an intermediate in the FTS mechanism.

About 1950, the **oxygenate (enol) mechanism** gained widespread acceptance [5,6]. This mechanism involves the chemisorption of CO which reacts with adsorbed hydrogen to form a species such as:



This structure grows by a combination of condensation and water elimination steps using adjacent groups. This enol group can condense as depicted in Scheme I below [7].

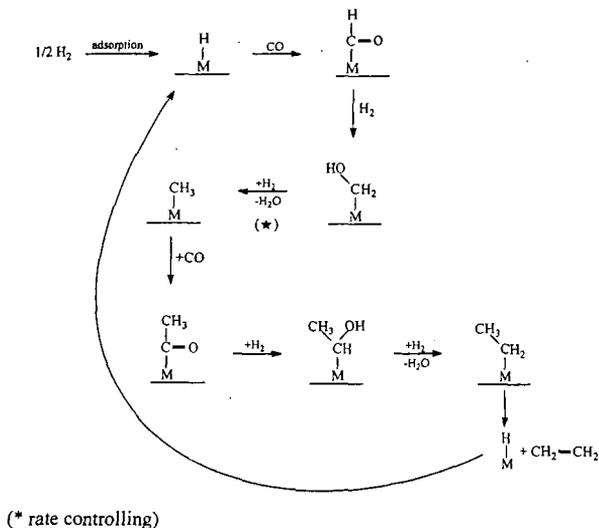


(* rate controlling)

Scheme I

The results obtained by Emmett and coworkers [2,8-12] for their ^{14}C -tracer studies provided strong support for this mechanism. In these studies, ^{14}C -labeled alcohol or alkene was added together with the synthesis gas and the distribution of the isotopically labeled products was determined. It was found that the added alkene or the alcohol was able to serve to initiate chain growth. Much of the work by Emmett and coworkers was conducted at atmospheric pressure. However, our later work [13] using medium pressure synthesis and slurry phase reaction conditions produced results that were in agreement with the conclusions of Emmett and coworkers. In addition, our work showed that ethanol was incorporated 50 to 100 times as rapidly as ethene when the two reactants were converted under the same reaction conditions [14].

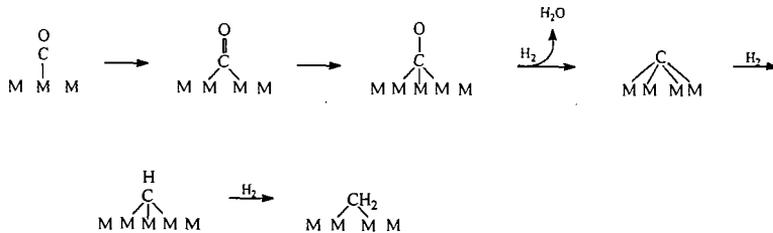
An **insertion mechanism** involves the insertion of CO into a metal-methyl or metal-methylene carbon bond which is then hydrogenated to produce an alcohol or alkene; the alcohol or alcohol precursor can also eliminate oxygen to produce an alkene product. One form of this mechanism is shown in Scheme II below [7,15]:



Scheme II

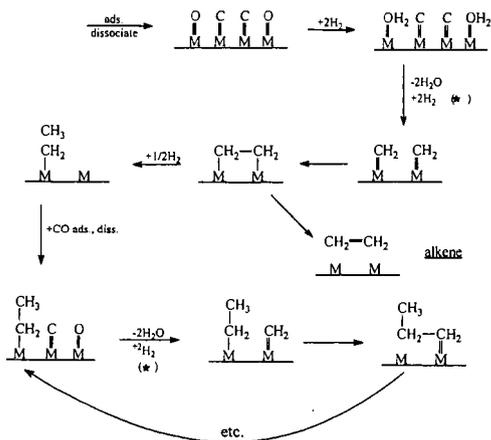
Hydrogenation and water elimination of the COH_2^* surface species are assumed to be the rate controlling step.

With the general availability of surface science instruments, it was found that CO adsorbs on single crystal metal surfaces to produce a surface covered with carbon, and little oxygen. This led to the conclusion that the CO chemisorbs and dissociates to adsorbed C and O. This step is followed by the rapid hydrogenation of adsorbed O to produce water. The hydrogenation of adsorbed carbon to form CH_2 is much slower. This mechanism may be viewed as a revival of the carbide theory but with the requirement that carbide formation is limited to the surface, or near surface, layer. Maitlis [16] has advanced this mechanism as the Fischer-Tropsch-Brady-Pettit-Biloen-Sachtler Mechanism and is illustrated in Scheme III below:



Scheme III

A more elaborate version of this mechanism has been provided by Dry and is shown in Scheme IV:

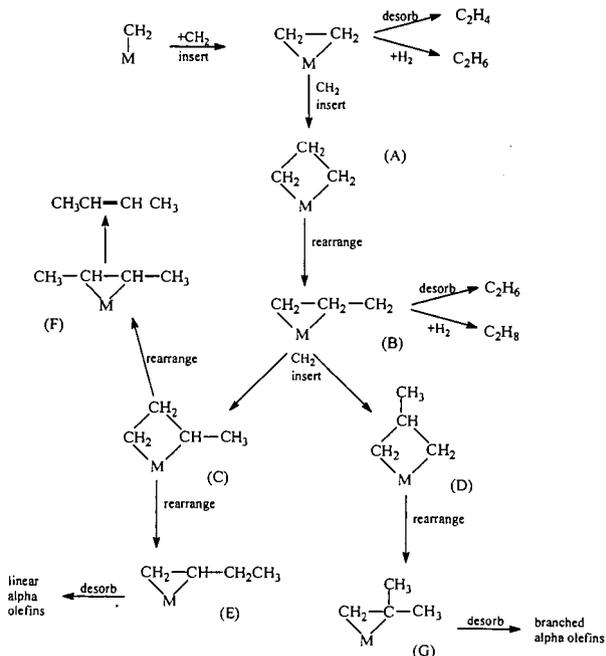


(* rate controlling)

Scheme IV

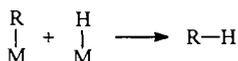
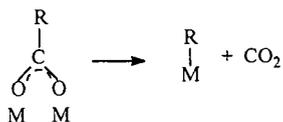
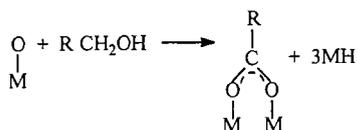
Dry considers the step(s) involving the hydrogenation of surface C to be rate-limiting; the other reactions are assumed to be at equilibrium.

A current view of the **carbide (carbene) theory** is illustrated in Scheme V [7]:

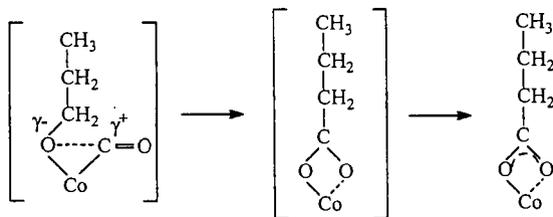
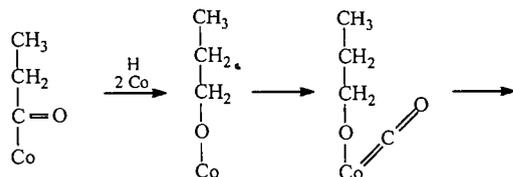
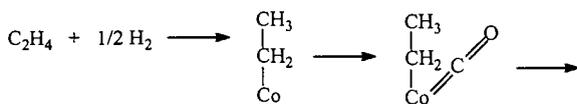


Scheme V

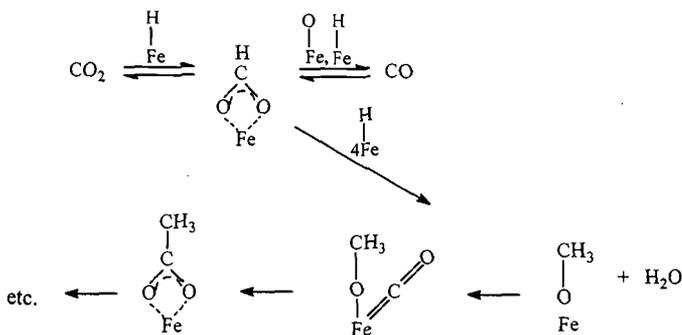
In the following we consider characterization data and try to combine this with results from isotopic tracer studies in an attempt to provide a mechanism that more nearly applies under conditions amenable to industrial practice. The consideration will be limited to the lower severity conditions likely to be encountered in slurry phase synthesis with an iron catalyst.



The conversion of ^{14}C labeled alcohols is consistent with the following reaction pathway: This reaction pathway allows for the direct formation of CO_2 and an alkane with one less carbon than the added alcohol, and is in agreement with the experimental results. Furthermore, there is valid infrared data to support the type of structure as being formed on metal (Fe and Co) surfaces. Thus, Blyholder et al. [17] offers the following mechanism for the reaction of CO , H_2 and C_2H_4 :



A similar adsorption model has been proposed by Kölbl and Tillmetz [18]. A pathway similar to the above would account for the chain initiation by CO_2 ;



The oxygenate mechanism is able to account for the initiation by CO_2 as well as requiring chain propagation to occur only by CO since it appears unreasonable to expect CO_2 to be adsorbed with the structure shown in the Blyholder model.

In summary, there is clearly evidence for the participation of an oxygenate intermediate in the Fischer-Tropsch synthesis using an iron catalyst. It is also clear that a carbide is the more active form of the iron catalyst. The intermediate leading to the 1-alkenes remains to be identified.

On the other hand, the tracer studies with a cobalt catalyst are in agreement with a mechanism involving the carbene intermediate. Both CO_2 and alcohols behave as inert gases for the cobalt catalyst.

The next step is to provide more conclusive data to show that the mechanism for the iron and cobalt catalysts are indeed different. If, as the data suggest, they are different then the objective is to define the catalyst properties responsible for the difference.

ACKNOWLEDGMENT

This work was supported by U.S. DOE contract number DE-FC26-98FT40308 and the Commonwealth of Kentucky.

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recovery technology continues to improve, one should expect that this price range will continue into the foreseeable future. However, this same history shows that the margin gap between gasoline prices and crude oil costs has been collapsing for the oil refining industry. Therefore, if crude oil prices continue to stay near \$20 per barrel, and the refining margins and gasoline prices continue to decline, it will be economically difficult to justify developing alternative fuel substitutes for gasoline and diesel.

Chart 5 shows the whole sale prices of a number of possible alternative fuels (on a energy equivalent basis) compared to conventional gasoline [4]. Only CNG (compressed natural gas) and LPG (liquid petroleum gas) appear to have some economic advantage relative to gasoline while ethanol, methanol and electricity are at a severe economic disadvantage. However, even these simple economics do not capture the added cost necessary to build the supporting fuel distribution infrastructure as well as the added cost of the vehicle to use that alternative fuel. These added costs will usually eliminate most if not all of CNG's and LPG's economic advantage over gasoline and further disadvantages the other alternative fuels. These unfavorable economics help explain the very small market share of AFVs that has developed since the crude oil price spike of the early 1980's. As shown in Chart 6, all the AFV fleets combined represent less than a quarter percent of the total U.S. vehicle fleet, and even these AFVs are usually found in niche markets that are supported by central fueling locations and favorable tax supports[5].

The economics do not appear to support the switch to alternative fuels and may not in the foreseeable future if crude prices stay near \$20 dollars a barrel. Therefore, AFV supporters have been using non-economic arguments such as using AFVs to reduce mobile source emissions from the vehicle fleet. Air quality agencies have been reducing tailpipe emission standards which provides an incentive to switch to AFVs with their lower emissions. In response, the oil and auto industries combined have found ways to further clean up gasoline and diesel fuels which not only reduces the emissions from the current vehicle fleet, but also allows the automakers to develop even cleaner burning vehicles that approach the lower emissions of the AFVs. Chart 7 shows the estimated emission reductions using the typical California Reformulated Gasoline in the current fleet relative to using 1990 industry average gasoline. As a result of the cleaner burning gasoline, the auto industry is now introducing cars that not only meet California's ULEV (ultra low emission vehicle) standard but also the SULEV (super ultra low emission vehicle) standard without using AFVs [7-11]. As new model gasoline vehicles becomes cleaner, the shrinking emission advantage of the AFVs diminishes to a point where the cost of reducing this small remaining emission becomes very costly compared to other options for reducing emissions elsewhere.

The most recent social quest has been to reduce the production of greenhouse emissions (mainly CO₂). To decrease mobile sources of these gases, the drive has been to reduce vehicle fuel consumption by moving to a higher efficiency vehicle with a fuel economy of 80 miles per gallon or 3 liters per 100 kilometers. To achieve this goal, many have thought it would require using a higher efficiency power train such as a fuel cell running on an alternative fuel such as hydrogen or methanol. However, the old workhorse combustion engine again appears to be rising to the challenge with the development of the high efficiency diesel engines coupled with hybrid drive trains [8,9,12-17]. Although the responsiveness and performance of the diesel engine has been improved to be comparable to that of the gasoline engine, a major hurdle still exists for reducing the diesel's NO_x (nitrogen oxides) and PM (particular) emissions to be comparable to gasoline engines. To help reduce these emissions, the reformulation of diesel continues to be studied. An example of recent work is shown in Chart 8 which shows that increasing the hydrogen content of the fuel will help reduce PM emissions by as much as 30 %. In addition, adding as much as 5 % oxygen can reduce emissions by another 25%[6]. With some success, the exhaust after-treatment technology for reducing emissions further may be able to decrease diesel tailpipe emissions enough to be comparable to that of gasoline [9,12-14,16].

CONCLUSIONS

When one looks at the recent history and current events, it suggests that the fuels of the foreseeable future will still be gasoline and diesel, but be improved, cleaner burning versions. These cleaner fuels will allow automakers to further develop even cleaner vehicles that will produce minimal emissions and consume much less fuel. Major improvements in the diesel engine performance and cleanliness will likely create a shift in the light duty vehicle market toward the higher efficiency and more economical diesel engine vehicle that seems to be occurring already in Europe. Future crude oil supplies always seem to be more plentiful than estimated in the past, and the technology and economic hurdles to convert other alternative energy sources into diesel and gasoline-like fuels also continues to improve. As a result of all these improvements combined, the economic incentives to switch to AFVs will not likely exist in the foreseeable future except for niche markets.

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Chart 1

Non-OPEC Oil Production Forecasts for 1987-89

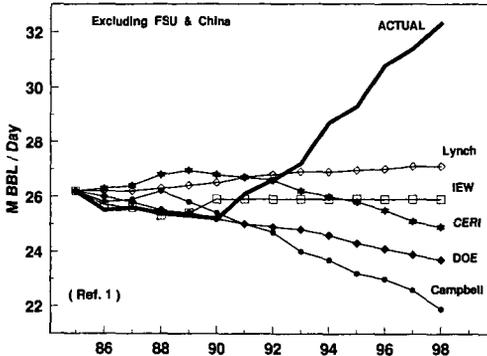


Chart 2

1987-89 Crude Oil Price Forecast

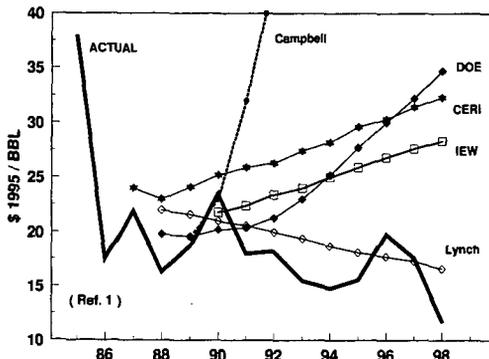


Chart 3

World Oil Consumption vs Oil & Gas Resources

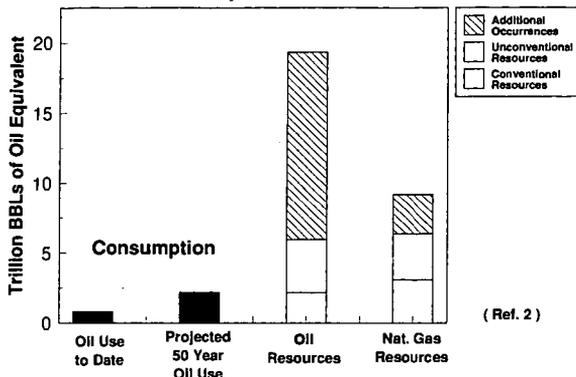


Chart 4

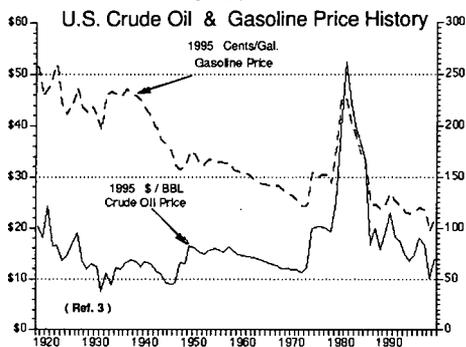
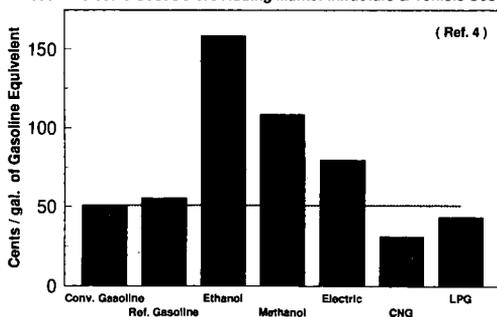


Chart 5

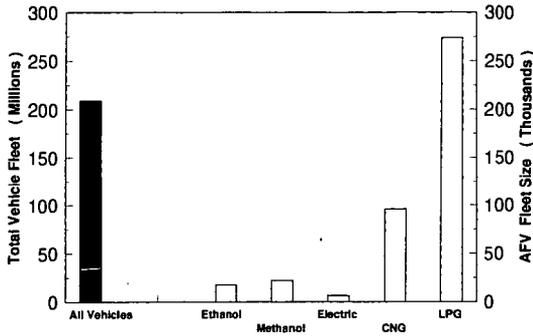
Economics Of Gasoline Alternative Fuels 1995 Wholesale Cost Before Adding Market Infrastructure & Vehicle Costs



Source: Alternative Transportation Fuels: A Comparative Analysis, AICHE Government Relations Committee, Sept 1997

Chart 6

1999 U.S. Vehicle Fleet: Alt. Fuel Vehicles vs Total Fleet



(Ref. 5)

Chart 7

Emission Reductions with Calif. Reformulated Gasoline

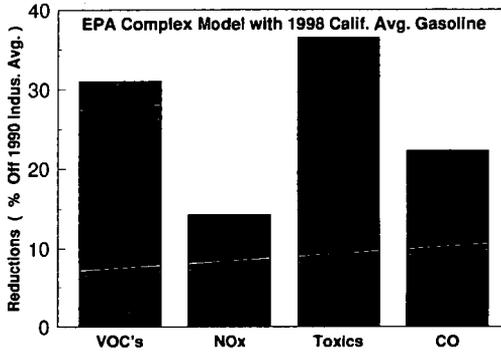
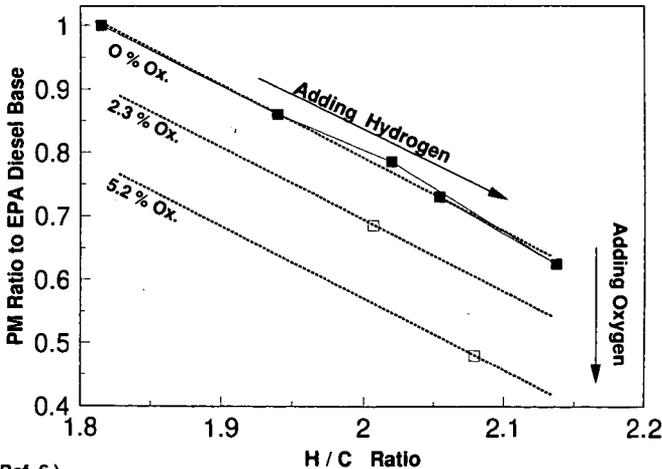


Chart 8

Adding Hydrogen & Oxygen Reduces Diesel PM



(Ref. 6)

Fuels of the Future?

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Keywords: Crude Oil, Alternative Fuels, Diesel

INTRODUCTION

Since the first Oil Embargo, many in governments, industry and academia have been operating on the belief that alternative transportation fuels (and vehicles) will need to be developed to meet society's future mobile transportation requirements. The reasons for their beliefs varied over time from projected future high crude oil prices (economics), energy security, reducing mobile source pollutants and more recently, green house gases. As energy prices stabilized or declined, the economic and security arguments have diminished. An example of using AFVs (alternative fuel vehicles) for reducing mobile source pollutants was the U.S. Administration's original proposal in the 1990 Clean Air Act Amendments that would require the use of methanol fueled vehicles in the ten highest polluted cities. That policy proposal was eventually replaced by the Reformulated Gasoline (RFG) program. California made a similar attempt with their M85 (methanol) fuel program that has since seemed to stagnate.

In more recent years, California ratcheted down the tailpipe emission standards which pressured automakers to consider AFVs. However, the automakers found that they could take advantage of the cleaner burning properties of the reformulated gasoline to develop vehicles that could meet the tighter standards without investing in the more expensive AFVs. The most recent argument for AFVs has been to reduce green house gases. In response, the auto industry appears to be developing combustion engine technologies that may achieve the high fuel economy goals without switching to AFVs. Therefore, it appears that in the future the marketplace will more likely be converting the alternative energy sources into synthetic liquid fuels that look like gasoline or diesel instead of converting the vehicles to run on alternative fuels. Pursuing this pathway avoids much of the infrastructure economic hurdles that has burdened the development of the AFV market.

Does society or the marketplace need to switch to alternative fuels for future mobile transportation? Past and recent experience suggests that as gasoline and diesel quality becomes cleaner, the automakers are finding that they can burn these conventional fuels in vehicles more efficiently and cleanly by improving both the combustion engines and exhaust after-treatment technologies. This dampens, if not eliminates, the need for society to change over to an entirely new power train technology such as fuel cells. Therefore, it is highly likely that the fuel of the future will be a very clean gasoline or diesel. What is probably a more appropriate question is what will be the future hydrocarbon energy source for making gasoline and diesel in the future (natural gas or biomass?) as crude oil resources are eventually depleted. The following discussion reviews some of the issues that has driven the need (or belief) to switch to Alternative Fuel Vehicles (AFV).

DISCUSSION

The Oil Embargoes of the 1970's created a fear that oil supplies were declining and therefore helped spur the creation of the U.S. Department of Energy and the original push to develop fuel alternatives for gasoline derived from crude oil. Even though crude oil and energy is a commodity product, energy forecasters in the 1980's projected that crude supply alternatives to OPEC controlled crude would not develop (Chart 1)[1]. As a result, they ignored doing the fundamental cost analysis of the marketplace's ability to develop alternative crude supplies, and therefore projected that crude oil prices would climb much higher than \$20 per barrel (Chart 2)[1].

A common flaw in projecting a tightening crude supply market is to compare future oil consumption to the present estimate for conventional crude oil reserves, and thereby ignore the much larger supply of other oil resources and additional occurrences. The flaw in this economic supply demand analysis is the implicit assumption that oil recovery technology will not substantially improve to tap into these other potential oil supplies. When projected consumption is actually stacked against all oil sources, Chart 3 suggests that there may be a century worth or more of oil supply available for future oil markets [2]. Chart 4 shows that historical crude prices (corrected to a 1995 dollar basis) lie mostly between \$10 and \$20 per barrel [3]. Assuming oil

**CLIMATE CHANGE AND ENERGY OPTIONS:
DECISION MAKING IN THE MIDST OF UNCERTAINTY**

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KEYWORDS: Climate change, Energy options, Economic opportunities

Understanding the world's natural systems, and how our own activities may be affecting those systems, are crucial for the long-term well-being of our society and of all the inhabitants of this world. One of the most complex of these is the global climate system. The nature and extent of significant alterations to the global climate system due to increasing emissions of greenhouse gases, resulting from human activity such as energy, production and manufacturing processes, is still the subject of considerable uncertainty and, indeed, controversy. However, the possible consequent effects on ecological systems and human society may be of such profound gravity, that continuing research into the causes and effects of climate change, and development of viable technology solutions for mitigation of these effects, are essential. Understanding the global climate system, determining how our activities may be influencing it, and taking responsible actions to protect it for future generations, may be among the greatest challenges that humanity has ever faced.

Background

For over a hundred years, scientists have been carefully gathering and verifying data on the Earth's temperature and precipitation patterns. The most recent data reveal some striking trends:

- 12 of the warmest years in this record occurred during the 17 years prior to 1998. New temperature records continued to be set in 1997, and the average global temperature in 1998 was higher than it had been during the previous 1,000 years [1].
- In large areas of the United States, temperature increases in a range of 2 - 4 °F (1 - 2 °C) have been measured during this century.
- The global average surface temperature has risen approximately 0.7 °C (1.2 °F) in the past 100 years.

Until recently, climate scientists were uncertain whether these developments reflected natural variations in the Earth's climate, or whether in fact human activities contributed to this warming. But in 1995, in the largest peer-reviewed international scientific assessment of any scientific issue ever undertaken, the Intergovernmental Panel on Climate Change – an international body charged with studying this issue – reached the conclusion that the observed increase in global average temperature during the 20th century "is unlikely to be entirely natural in origin" and that "the balance of evidence suggests that there is a discernible human influence on global climate" [2]. Subsequent analyses of these data affirmed that the warming trend in the second half of the 20th century could "exclude purely natural forcing, and [be] attributed largely to the anthropogenic components" [3].

The Earth's climate is the result of extremely complex interactions among the atmosphere, the oceans, the land masses, and living organisms – including human industrial activity – all of which receive energy from the sun. This energy ultimately radiates back into space, but a sufficient fraction is retained in the Earth's atmosphere to maintain an average temperature of approximately 15°C (59°F). This temperature is maintained by energy absorption in heat-trapping gases (the "Greenhouse Gases", or GHG's), which include water vapor, carbon dioxide, ozone, nitrous oxide, methane, and several trace gases of industrial origin (CFC's, hydrofluorocarbons, perfluorocarbons, and sulphur hexafluoride). Over the course of the Earth's history, living creatures have

evolved and adapted to function optimally in this temperature regime, and in turn human society has organized itself to function as well as possible in this climate.

During the past 150 years, atmospheric levels of many GHG's (except water vapor, which is controlled by evapotranspiration and precipitation) have undergone significant increases, recently at an accelerating pace. The connection between GHG emissions and temperature change is not merely that the two seem to be correlated in time, but also that detailed physical models of the atmosphere predict the global warming effect. The magnitude of the effect, however, is subject to considerable uncertainty, as a result of still imperfect knowledge about the interplay between GHG's, atmospheric water vapor, ozone, clouds, aerosols, and particulates. If carbon dioxide concentrations were to double over current levels during the next 100 years – a possible scenario given the trend of economic development – current models predict overall global average temperature increases somewhere between a low estimate of 1 °C (~2 °F) and a high estimate of 3.5 °C (6.5 °F). Furthermore, because of the long residence time of carbon dioxide in the atmosphere, increased CO₂ levels due to fossil fuel combustion will persist long after emissions are reduced [4].

While the low estimate given above may indeed present few challenges, the high estimate – which is just as likely to be true as the low estimate – would have extremely serious consequences. During the last great Ice Age which ended 10,000 to 12,000 years ago, during which the northern U.S. and Europe were covered with a sheet of ice a mile thick, global average surface temperatures were only about 5° C lower than they are today. A global average surface temperature 2 °C higher than current levels would be unprecedented in recent human experience, and an increase of 5° to 6° would correspond to the climate which prevailed during the age of the dinosaurs! It should be noted that these predicted temperature rises are not uniform, but would be significantly higher than the average in specific parts of the Earth, particularly in the Polar regions. Most significantly, these changes are predicted take place, not over geological times of thousands or millions of years, but within a few decades or centuries, far more rapidly than natural ecosystems are able to evolve or adapt.

The possible consequences of this predicted change in global average temperature range from modest, in some cases even benign effects, to severe effects which are difficult to predict with any accuracy but which could be truly catastrophic if they occur. There is a wide variation in the level of confidence with which any specific effect can be forecast [5]; however, all of the following have been predicted on the basis of plausible models and assumptions.

- Increased number and severity of heat waves, droughts, and other extreme weather events which place stress on plant and animal species, including humans.
- Since an increased temperature enables the air to hold larger amounts of water vapor, major changes in precipitation patterns could occur, wreaking havoc with current agricultural practices.
- Ranges and habitats of a wide variety of plant and animal organisms could be affected. This could lead to loss of many species, including many beneficial to humanity, as well as exposure of vulnerable populations to disease-bearing organisms such as mosquitoes, ticks, and rodents.
- Sea levels could rise by 1 foot to as much as 5 feet by year 2100, due to loss of polar and landlocked ice and thermal expansion of the oceans. This would submerge significant areas of low-lying, populated territories, affect the salinity of estuaries and coastal aquifers, and damage or destroy wetlands and coral reefs responsible for much of the ocean's biological productivity. Several scientists have suggested the possibility of even larger sea level rises resulting from breakup of polar ice sheets.
- Projected precipitation increases at higher latitudes could also act to reduce the ocean's salinity and therefore its density. This, in turn, might interfere with oceanic circulation patterns – possibly altering or even suppressing the Gulf Stream which maintains Europe's current temperate climate [6].

Conclusions

In arriving at an appropriate course of action in the face of profound uncertainty about both the magnitude and effects of human-induced climate change, and its impacts on life

on Earth and on human economic activity, we must consider both the costs of taking action and the considerable risks of taking no action [7]. International agreements are now under consideration which will begin to limit allowable levels of GHG emissions. Numerous questions still exist among governments, the scientific community, and the general public about the need for such agreements and the most effective technological, economic, and political strategies to achieve such emission limits. A vigorous and well-coordinated research effort is needed to narrow these uncertainties and to develop science and technology options in the case that rapid responses to changing climate conditions become necessary. We recognize, however, that we may never succeed in eliminating all the uncertainties surrounding the climate change issue, and that it may be necessary to take action, sooner rather than later, even in the face of such uncertainties. The longer action is delayed, the more difficult and costly it will be to institute limits on GHG emissions should such limits prove to be necessary.

Many uncertainties remain in the area of Global Change Science, and research still needs to be carried out to reduce these uncertainties. Among these are:

- the effects of clouds, aerosols, particulates, and especially atmospheric water vapor on climate change;
- the coupling between overall global climate change and regional climate variations;
- ocean-atmosphere interactions;
- effects of climate changes on both ecological and social-economic systems.

In addition to continuing to study the basic phenomena of climate change, modern industrial societies must begin to take action to address this issue. Climate change has "massive market transforming potential" [8], with potential impacts on many industry sectors including petroleum and other energy resources, energy production, transportation, agriculture, residential and commercial construction, and not least the chemical industry. Making the transition to a more energy-efficient, less carbon-intensive economy presents a tremendous long-term economic opportunity for those industries willing to undertake the necessary research and development, and invest in the new technologies that will achieve these goals. Some of these opportunities include:

- Chemical manufacturing processes may be redesigned to improve energy efficiency and reduce GHG emissions while reducing or eliminating production of toxic waste. These goals have been summarized in *Technology Vision 2020: The U.S. Chemical Industry* [9] and are the basis of "Green Chemistry" strategies [10].
- Carbon dioxide sequestration may offer a route to partial reduction of net emissions. CO₂ could be captured in industrial processes and removed from the atmosphere by reforestation and planting, which also benefits habitat and biodiversity preservation.
- Alternative energy sources should be developed which minimize GHG emissions, such as advanced fossil-fuel technology, fuel cells, renewable energy technologies such as biomass, wind, and solar energy sources, and nuclear power [11].
- In addition, proposed GHG and carbon emission limits may have a significant *indirect* impact on chemical process industries, since changes in refinery product streams, driven by alternative fuel demand, may affect chemical feedstock availability. A systematic study of such interactions needs to be undertaken, and alternative sources of starting materials identified.

Attaining an understanding of how the global climate system operates and how our own activities may be influencing it, and of undertaking responsible actions to protect that system for the well-being of future generations, may be among the greatest challenges that humanity has ever faced. Arriving at the necessary decisions and taking appropriate actions in the face of substantial uncertainty is neither new nor unfamiliar in our society – corporations always have to make business plans for an uncertain future, and individuals do this whenever they purchase an insurance policy or set up an estate plan. The climate system, on which the global ecology and economy depend, deserves at least the same degree of care and attention. Research on Climate Change and its possible effects must be continued and strengthened, the public must be informed and educated about this issue, industry must adopt proactive strategies for energy conservation and greenhouse gas reductions, and prudent and responsible actions must be undertaken as needed to address this challenge which confronts us all.

Acknowledgments

The author gratefully acknowledges the assistance of colleagues at M.I.T.'s Center for Global Change Science and Joint Program for the Science and Policy of Global Change, who provided essential information and insights concerning the complex phenomena involved in global climate change. Any factual errors or misinterpretations are the responsibility of the author, not of these sources. Financial support was provided by the Alliance for Global Sustainability through a project on "Spectroscopic Approach to Local and Global Management of the Earth's Atmosphere" and by MIT's Center for Environmental Initiatives.

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CONCERNS ABOUT CLIMATE CHANGE AND THE ROLE OF FOSSIL FUEL USE

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KEYWORDS: Climate, Greenhouse Effect, Greenhouse gases

INTRODUCTION

Climate is defined as the typical behavior of the atmosphere, the aggregation of the weather, and is generally expressed in terms of averages and variances of temperature, precipitation and other physical properties. The greenhouse effect, the ability of certain gases like carbon dioxide and water vapor to effectively trap some of the reemission of solar energy by the planet, is a necessary component to life on Earth; without the greenhouse effect the planet would be too cold to support life. However, human activities are increasing the concentration of carbon dioxide and several other greenhouse gases, resulting in concerns about warming of the Earth by 1-5 K over the next century. Recent increases in global averaged temperature over the last decade already appear to be outside the normal variability of temperature changes for the last thousand years. A number of different analyses strongly suggest that this temperature increase is resulting from the increasing atmospheric concentrations of greenhouse gases, thus lending credence to the concerns about much larger changes in climate being predicted for the coming decades. It is this evidence that led the international scientific community through the Intergovernmental Panel on Climate Change (IPCC, 1996) to conclude (after a discussion of remaining uncertainties) that "Nonetheless, the balance of the evidence suggests a human influence on global climate". More recent findings have further strengthened this conclusion. Computer-based models of the complex processes affecting the carbon cycle have implicated the burning of fossil fuels by an ever-increasing world population as a major factor in the past increase in concentrations of carbon dioxide. These models also suggest that, without major policy or technology changes, future concentrations of CO₂ will continue to increase largely as a result of fossil fuel burning. This paper briefly reviews the state of the science of the concerns about climate change that could result from fossil fuels and other human related emissions.

GASES AND AEROSOLS

Without human intervention, concentrations of many atmospheric gases would be expected to change slowly. Ice core measurements of the gases trapped in ancient ice bubbles indicate this was the case before the last century. However, since the beginning of the industrial age, emissions associated with human activities have risen rapidly. Agriculture, industry, waste disposal, deforestation, and especially fossil fuel use have been producing increasing amounts of carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), chlorofluorocarbons (CFCs) and other important gases. Due to increasing emissions, atmospheric levels of these greenhouse gases have been building at an unprecedented rate, raising concerns regarding the impact of these gases on climate. Some of the gases, such as CFCs, are also responsible for large observed depletions in the natural levels of another gas important to climate, ozone. Of these gases, two, carbon dioxide and methane, are of special concern to climate change and are discussed further.

Carbon Dioxide

Carbon dioxide has the largest changing concentration of the greenhouse gases. It is also the gas of most concern to analyses of potential human effects on climate. Accurate measurements of atmospheric CO₂ concentration began in 1958. The annually averaged concentration of CO₂ in the atmosphere has risen from 316 ppm (parts per million, molar) in 1959 to 364 ppm in 1997. The CO₂ measurements exhibit a seasonal cycle, which is mainly caused by the seasonal uptake and release of atmospheric CO₂ by terrestrial ecosystems. The average annual rate of increase over the whole time period is about 1.2 ppm or 0.4% per year, with the rate of increase over the last decade being about 1.6 ppm/yr. Measurements of CO₂ concentration in air trapped in ice cores indicate that the pre-industrial concentration of CO₂ was approximately 280 ppm. This data indicates that carbon dioxide concentrations fluctuated by ± 10 ppm around 280 ppm for over a thousand years until the recent increase to the current 360+ ppm, an increase of over 30%.

Why has the atmospheric concentration of CO₂ increased so dramatically? Analyses with models of the atmosphere-ocean-biosphere system of the carbon cycle, in coordination with observational analyses of the isotopes of carbon in CO₂, indicate that human activities are primarily responsible for the increase in CO₂. Two types of human activities are primarily responsible for emissions of CO₂: fossil fuel use, which released about 6.0 GtC into the

atmosphere in 1990, and land use, including deforestation and biomass burning, which may have contributed about 1.6 ± 1.0 GtC in addition to that from fossil fuels. Evaluations of carbon releases from vegetation and soils based on changes in land use indicate that land use decreased carbon storage in vegetation and soil by about 170 Gt since 1800. The added atmospheric carbon resulting from human activities, as described above, is redistributed within the atmospheric, oceanic, and biospheric parts of the global carbon cycle, with the dynamics of this redistribution determining the corresponding rise in atmospheric CO₂ concentration. In the future, as the amount of CO₂ increases in the atmosphere and in the ocean, it is expected that the oceans will take up a smaller percentage of the new emissions. Analyses of the carbon budget have implied that there is a mismatch between observed levels of CO₂ and known loss processes. This discrepancy suggests that a missing carbon sink has existed during recent decades. This sink now appears to be largely explained through increased net carbon storage by the terrestrial biomass stimulated by the CO₂ fertilization effect (increased growth in a higher CO₂ concentration atmosphere).

Carbon dioxide is emitted when carbon-containing fossil fuels are oxidized by combustion. Carbon dioxide emissions depend on energy and carbon content, which ranges from 13.6 to 14.0 MtC/EJ for natural gas, 19.0 to 20.3 for oil, and 23.9 to 24.5 for coal. Other energy sources such as hydro, nuclear, wind, and solar have no direct carbon emissions. Biomass energy, however, is a special case. When biomass is used as a fuel, it releases carbon with a carbon-to-energy ratio similar to that of coal. However, the biomass has already absorbed an equal amount of carbon from the atmosphere prior to its emission, so that net emissions of carbon from biomass fuels are zero over its life cycle.

Human-related emissions from fossil fuel use have been estimated as far back as 1751. Before 1863, emissions did not exceed 0.1 GtC/yr. However, by 1995 they had reached 6.5 GtC/yr, giving an average emission growth rate slightly greater than 3 percent per year over the last two and a half centuries. Recent growth rates have been significantly lower, at 1.8 percent per year between 1970 and 1995. Emissions were initially dominated by coal. Since 1985, liquids have been the main source of emissions despite their lower carbon intensity. The regional pattern of emissions has also changed. Once dominated by Europe and North America, developing nations are providing an increasing share of emissions. In 1995, non-Annex I (developing countries; includes China and India) nations accounted for 48 percent of global emissions.

Future CO₂ levels in the atmosphere depend not only on the assumed emission scenarios, but also on the transfer processes between the major carbon reservoirs, such as the oceans (with marine biota and sediments) and the terrestrial ecosystems (with land use changes, soil and forest destruction. Recent work for the new IPCC assessment show, based on projections of fossil-fuel use and land use changes, that the concentration of CO₂ are expected to increase well above current levels by 2100 (75 to 220 % over pre-industrial concentrations). None of these scenarios leads to stabilization of the CO₂ concentration before 2100.

Methane

Although its atmospheric abundance is less than 0.5 percent that of CO₂, on a molecule by molecule basis, a molecule of CH₄ is approximately 50 times more effective as a greenhouse gas in the current atmosphere than CO₂. When this is combined with the large increase in its atmospheric concentration, methane becomes the second most important greenhouse gas of concern to climate change. Based on analyses of ice cores, the concentration of methane has more than doubled since preindustrial times. The current globally averaged atmospheric concentration of methane is about 1.75 ppm.

Continuous monitoring of methane trends in ambient air from 1979 to 1989 indicates that concentrations had been increasing at an average of about 16 ppb (~1percent per year). During much of the 1990s, the rate of increase in methane appeared to be declining. Although the cause of the longer-term global decline in methane growth is still not well understood, it may be that much of the earlier rapid increase in methane emissions from agricultural sources are now slowing down. However, since 1997 the CH₄ growth rate has increased to about 10 ppb per year. There are some indications that this increase in the growth rate may be due to a response of emissions from wetlands in the Northern Hemisphere responding to global warming over the last decade.

Methane emissions come from a number of different sources, both natural and anthropogenic. One type of human related emissions arise from biogenic sources from agriculture and waste disposal, including enteric fermentation, animal and human wastes, rice paddies, biomass burning, and landfills. Emissions also result from fossil fuel-related methane sources such as natural gas loss, coal mining, and the petroleum industry. Methane is emitted naturally by wetlands, termites, other wild ruminants, oceans, and hydrates. Based on recent estimates,

current human-related biogenic and fossil fuel-related sources for methane are approximately 275 and 100 TgCH₄/yr while total natural sources are around 160 TgCH₄/yr.

Sulfuric and other aerosols

Emissions of sulfur dioxide and other gases can result in the formation of aerosols that can affect climate. Aerosols affect climate directly by absorption and scattering of solar radiation and indirectly by acting as cloud condensation nuclei (CCN). A variety of analyses indicate that human-related emissions of sulfur, and the resulting increased sulfuric acid concentrations in the troposphere, may be cooling the Northern Hemisphere sufficiently to compensate for much of the warming expected from greenhouse gases. Volcanic emissions can influence climate for short periods (1 to 3 years) through emissions of sulfur dioxide into the lower stratosphere.

Over half of the sulfur dioxide, SO₂, emitted into the atmosphere comes from human-related sources, mainly from the combustion of coal and other fossil fuels. Most of these emissions occur in the Northern Hemisphere. Analyses indicate that anthropogenic emissions have grown dramatically during this century. Other SO₂ sources come from biomass burning, from volcanic eruptions, and from the oxidation of di-methyl sulfide (DMS) and hydrogen sulfide (H₂S) in the atmosphere. DMS and H₂S are primarily produced in the oceans. Atmospheric SO₂ has a lifetime of less than a week, leading to formation of sulfuric acid and eventually to sulfate aerosol particles. Gas-to-particle conversion can also occur in cloud droplets; when precipitation doesn't soon occur, the evaporation of such droplets can then leave sulfate aerosols in the atmosphere.

RADIATIVE FORCING

A perturbation to the atmospheric concentration of an important greenhouse gas, or the distribution of aerosols, induces a radiative forcing that can affect climate. Radiative forcing of the surface-troposphere system is defined as the change in net radiative flux at the tropopause due to a change in either solar or infrared radiation. A positive radiative forcing tends on average to warm the Earth's surface; a negative radiative forcing tends to cool the surface. Analyses of the direct radiative forcing due to the changes in greenhouse gas concentrations since the late 1700s give an increase of about 2.3 Wm⁻². To put this into perspective, a doubling of CO₂ from pre-industrial levels would correspond to about 4 Wm⁻²; climate models studies indicate this would give 1.5 to 4.5 C increase in global temperature. Approximately 0.5 Wm⁻² of the increase has occurred within the last decade. By far the largest effect on radiative forcing has been the increasing concentration of carbon dioxide, accounting for about 64 percent of the total change in forcing.

Changes in amounts of sulfate, nitrate, and carbonaceous aerosols induced by natural and human activities have all contributed to changes in radiative forcing over the last century. The direct effect on climate from sulfate aerosols occurs primarily through the scattering of solar radiation. This scattering produces a negative radiative forcing, and has resulted in a cooling tendency on the Earth's surface that counteracts some of the warming effect from the greenhouse gases.

Changes in tropospheric and stratospheric ozone also affect climate, but the radiative effects from the increase in tropospheric ozone over the last century and the decrease in stratospheric ozone over recent decades have had a relatively small combined effect compared to CO₂. Changes in the solar energy output reaching the Earth is also an important external forcing on the climate system. The Sun's output of energy is known to vary by small amounts over the 11-year cycle associated with sunspots and there are indications that the solar output may vary by larger amounts over longer time periods. Slow variations in the Earth's orbit, over time scales of multiple decades to thousands of years, have varied the solar radiation reaching the Earth, and have affected the past climate. Solar variations over the last century are thought to have had a small but important effect on the climate, but are not important in explaining the large increase in temperatures over the last few decades.

Evaluation of the radiative forcing from all of the different sources since pre-industrial times indicates that globally-averaged radiative forcing on climate has increased. Because of the hemispheric and other inhomogeneous variations in concentrations of aerosols, the overall change in radiative forcing is much greater or much smaller at specific locations over the globe.

THE TEMPERATURE RECORD AND OTHER CLIMATE INDICATORS

There is an extensive amount of evidence indicating that the Earth's climate has warmed during the past century. Foremost among this evidence are compilations of the variation in global mean sea surface temperature and in surface air temperature over land and sea. Supplementing these indicators of surface temperature change is a global network of balloon-based of atmospheric temperature since 1958. As well, there are several indirect or *proxy* indications of temperature

change, including satellite observations (since 1979) of microwave emissions from the atmosphere, and records of the width and density of tree rings. The combination of surface-, balloon-, and satellite-based indicators provides a more complete picture than could be obtained from any given indicator alone, while proxy records from tree rings and other indicators allow the temperature record at selected locations to be extended back for a thousand years. Apart from temperature, changes in the extent of alpine glaciers, sea ice, seasonal snow cover, and the length of the growing season have been documented that are consistent with the evidence that the climate is warming. Less certain, but also consistent, changes appear to have occurred in precipitation, cloudiness, and interannual temperature and rainfall variability.

Thermometer-based measurements of air temperature have been systematically recorded at a number of sites in Europe and North America as far back as 1760. However, the set of observing sites did not attain sufficient geographic coverage to permit a rough computation of the global average land temperature until the mid-nineteenth century. Land-based, marine air, and sea surface temperature datasets all require rather involved corrections to account for changing conditions and measurement techniques. Analyses of these records indicates a global mean warming from 1851 to 1995 of about $0.65 \pm 0.05^\circ\text{C}$.

In addition to limited sampling of temperature with altitude, satellite-based sensors, known as microwave sounding units (MSUs), are being used to examine global temperature changes in the middle troposphere (mainly the 850-300 HPa layer), and in the lower stratosphere (~ 50-100 Hpa). None of the channels sample at the ground. The MSU measurements have been controversial because some earlier versions of the satellite dataset have indicated a cooling in the lower troposphere in contrast to the warming from the ground-based instruments. However, several errors and problems (e.g., due to decay in the orbit of the satellite) with the MSU data have been found, and the latest analyses of MSU corrected for these problems show a warming, albeit somewhat smaller than that found at the ground.

Proxy temperature indicators, such as tree ring width and density, the chemical composition and annual growth rate in corals, and characteristics of annual layers in ice cores, are being used at a number of locations to extend temperature records back as much as a thousand years. The reconstruction indicates the decade of the 1990s has been warmer than at any time during this millennium and that 1998 was the warmest year in the 1000-year record.

Recent studies with state-of-the-art numerical models of the climate system have been able to match the observed temperature record well but only if they include the effects of greenhouse gases and aerosols. These studies indicate that natural variability of the climate system is not sufficient to explain the increasing temperatures in the 1990s.

CONCLUSIONS

Human activities already appear to be having an impact on climate. The latest evaluation for future global warming by 2100, relative to 1990, for a business-as-usual set of scenarios based on varying assumptions about population and economic growth is 1.3 to almost 5 K. Potential economic, social and environmental impacts on ecosystems, food production, water resources, and human health could be quite important, but require much more study. A certain degree of future climatic change is inevitable due to human activities no matter what policy actions are taken. Some adaptation to a changing climate will be necessary. However, the extent of impacts and the amount of adaptation will depend on our willingness to take appropriate policy actions. The consensus grows that we must follow a two-pronged strategy to conduct research to narrow down uncertainties in our knowledge, and, at the same time, take precautionary measures to reduce emissions of greenhouse gases.

ACKNOWLEDGEMENTS

This study was supported in part by grants from the U.S. Department of Energy, from the U.S. Environmental Protection Agency and from the National Science Foundation.

THE BRIDGE FROM COLD FACTS AND HOT RHETORIC
TO RATIONAL CLIMATE POLICY

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KEYWORDS: CLIMATE CHANGE, GLOBAL WARMING, KYOTO PROTOCOL

ABSTRACT: The academic community must expand its role in the political debate over Climate Change policy. The field is characterized by a cacophony of competing scientific claims, scare tactics, and propaganda. Scientists, particularly those in the academy, are badly needed in the role of upholders of the principles of scientific inquiry and standards of evidence upon which rational public policy depends. They should weigh into the conflict more heavily, not on one side or the other, but to point out when the participants on either side are exceeding the bounds of rational analysis. This will not only contribute to more informed policy but also preserve the integrity of science which is essential for continued human progress.

PAPER:

The theme of my presentation concerns the importance of academic and intellectual institutions, a category which clearly includes the American Chemical Society, to the scientific and policy debate over Climate Change and the Kyoto Protocol.

These institutions are much more than simply private associations of their members. They are also major *public* institutions, dedicated to public service as well as to research and education. This role requires the institutions, or, more precisely, their members to go beyond the ivory tower of intellectual inquiry by bringing scientific rigor to bear on important national policy debates so that we choose policies that are scientifically defensible and economically realistic.

This is an important function. It is also an exceedingly difficult one. I have a deep respect for science, and for those who devote their lives to it. I learned through a 12-year affiliation with the University of Rochester the power and value of the scientific method -- the clear statement of testable hypotheses, careful testing and evaluation of evidence, gloves-off peer review, and replication. The scientific approach and the pursuit of knowledge have been and will continue to be two of the great engines of human progress. A commitment to seek the truth no matter where the quest leads reflects a calling of the highest order. In the words of Norbert Wiener, the founder of cybernetics, a good scientist "has a consecration which comes entirely from within himself."¹

These values make the objective of combining science with relevance to the current Climate Change debate not only lofty but also daunting. The scientific values of careful statement, reliance on evidence, relentless pursuit of truth, and willingness to confess error sadly are not the currency of the political marketplace. Indeed, too often the values that hold sway in politics are the exact reverse of those that govern the scientific enterprise. Science in public policy is used increasingly as a campaigning enterprise instead of a means of measuring evidence and seeking truth. As a nobel laureate recently observed, in science facts matter and perceptions are negotiable while in politics perceptions matter and facts are negotiable.

In 1961, the distinguished historian Daniel J. Boorstin published a prescient book called *The Image: A Guide to Pseudo-Events in America*.² Its thesis is that many aspects of American life, including politics, are losing their connection to reality. Instead, they are dominated by "pseudo-events," events staged to attract the attention of the megaphone of the media, and which manipulate opinion by exploiting the gap between what we need to know and what we can know.

If Boorstin was worried in 1961, when his book appeared, he must be horrified by today's world. The triumph of Gresham's Law seems complete as the false coin of image drives out the gold of truth. The spinners often seem actively hostile to thinking about reality, as if any need to consider truth would only inhibit their creativity in crafting an image to promote what they judge to be worthy goals. We are living in a time in which the belief that the end justifies the means is all too frequently dominant.

One of the most disturbing aspects of the debate over Climate Change is the extent to which it has been driven by pseudo-events and pseudo-arguments. These are displacing good science and reliance on evidence with synthetic truths and treating as settled matters that are extremely uncertain.

This may sound like rhetoric, so let me provide some examples.

First, I will begin with a few things that are known about Climate Change. The Greenhouse Effect is indeed a fact. Certain gases, such as CO₂ and -- far more important -- water vapor do trap some of the sun's warmth. This is a good thing, since without it the temperature of the earth would be about zero degrees Fahrenheit.

Second: The temperature of the earth has gone up over the past 150 years by about one degree Fahrenheit. At least, it appears to be about a degree. Measurements from the 19th Century are inexact, so it is hard to be sure, but we are certain it has increased.

Fact three: During the past 150 years the atmospheric concentration of CO₂ has risen from about 278 parts per million to 365 ppm. It is commonly stated as a certainty, but the methodology underlying the estimates of CO₂ concentrations in the 19th Century has been criticized as possibly underestimating these pre-industrial levels, and thus overstating the increase.³ It is clear that we are only beginning to understand the complexities of the global carbon cycle.

Now, those three facts exhaust most of what is known with reasonable certainty about the risk of human-induced Climate Change. Everything else is immersed in a sea of uncertainty and subject to debate. For example, it is often stated that human activity has caused the increase in CO₂ concentration because burning fuel releases CO₂. This is a reasonable hypothesis — and I stress *hypothesis*. But other hypotheses are also reasonable. There is strong evidence that at times in the history of the earth, CO₂ concentrations were as much as 20 times as high as they are today, and this was long before the age of fossil fuels.⁴

Take another “known fact” that is simply another hypothesis: It is asserted that since CO₂ concentrations have gone up over the past century, and so has the temperature, then the CO₂ caused the temperature rise. This sounds logical, but it does not fit the data or climate history. Most of the rise in temperatures occurred before 1940, and thus preceded most of the increase in CO₂ concentration. Despite the increase in CO₂, over the past 20 years, highly accurate satellite data show no increase in lower atmosphere temperature. And, satellite data closely correlate with weather balloon measurements.

So, to what do we attribute the rise in temperature over the past century? One hypothesis that fits the data is that increases in temperature are correlated with solar activity — sun spots.⁵ And it is entirely possible that the chain of causation is the reverse of conventional wisdom — rises in temperature might cause increases in CO₂ concentrations as the oceans re-balance. Finally, the end of the last century marked the end of a “little ice age,” so natural variability is a major factor in explaining this century’s temperature increase.

If you start with the assumption that CO₂ is primarily responsible for the rise in temperature over the past century, then it is also logical to assume that further increases in the release of greenhouse gases will cause further rises in temperature. This is a legitimate concern but it still is only a hypothesis. The models that predict warming as a result of increases in greenhouse gases (GHGs) rely heavily on assumptions about a water vapor feedback cycle, assumptions that have little empirical basis. If this feedback cycle does not exist or was modest then increases in GHG concentrations would have very little impact on temperature.

The list of other “facts” that turn out to be less than solid grow with the intensity of the rhetoric. Mark Twain once observed that he wasn’t troubled by all the things that people don’t know. He was troubled by all the things they do know that just aren’t so. This applies to Climate Change. Predictions of the rise in temperature to be expected as a result of human activity has been steadily reduced. In 1990, the Intergovernmental Panel on Climate Change (IPCC) best estimate was an increase of 3.2° C. by the year 2100. Five years later, the estimate was down to a 2.0° C. But this does not reflect the latest research. Some observers believe that advances in knowledge and models should reduce the best estimate to 1° C.

In spite of reduced estimates of temperature increase, dubious predictions abound. One reads that global warming will cause catastrophic rises in sea levels, or about an increase in infectious diseases, or rising deaths due to heat waves, or a steady stream of record high temperatures, or more hurricanes and other extreme weather events. None of these bugaboos are probable. Few are even remotely plausible. None are supported by science. All represent the politics of doom to advance through fear an agenda that cannot stand on its own merits.

Since in our Alice in Wonderland paradigm, policy is based on “sentence first, trial afterwards,” it is important that scientists become more involved in this debate. And it is crucial that they maintain focus on applying the rigors of science, because they have a powerful role to play in helping to re-focus the debate back on rationality, evidence, and fact. Scientists can take a lead in applying relentless skepticism to the claims of all parties, because of a primary allegiance to truth, to reality. Most of the parties to the debate have interests that expose them to temptation to subordinate objective reality to their particular interests. Knowing that their claims will receive close scrutiny from disinterested scientists is the best way to build resistance to this temptation.

I am not exempting industry from this prescription, either. I represent the petroleum industry, a special interest which has a large economic stake in the outcome of this debate. No one should accept automatically anything said by me or any other industry representative. Whatever the topic, the audience should bring scientific skepticism to bear and ask: “Tell me why you think that — show me the evidence, and show me your logic.”

However, since I am from industry I am used to such skeptical challenging. While I may not always enjoy it, it is good for me, and for others who engage in advocacy. I do not ask that scientists go easy on me. But, in fairness, their vigilance should be extended to others, since it would be equally foolish to accept without question the views of other participants. Advocates of the Kyoto Protocol wrap themselves in robes of concern for the environment. Some of this is real, but some of it is gamesmanship. They are also special interests of various sorts, including

economic ones. Some businesses see the possibility of subsidies, market share, and competitive advantage. Other parties see chances for government grants, foreign travel, and lucrative future consulting. Some government officials see opportunities for power, office, and bureaucratic aggrandizement. Environmental organizations see a lever to promote a broader agenda, one that often crosses the border from concern about the environment into opposition to industrial activity and to the personal freedom and mobility that are among our core values as Americans.

So I urge all scientists to treat everyone's claims with even-handed skepticism.

This role of imposing scientific order and honesty on the public debate is only part of the scientists' job, though. It is surprising how little we know for certain about the Climate Change issue. A serious criticism of the Clinton Administration is for its rush to judgment and hyping of a supposed solution before we even know if a serious problem exists. This has diverted energy from thoughtful efforts to explore the existence and scope of the threat and to develop actions that are consistent with our state of knowledge.

For example, we need to know more about past CO₂ levels. The history of the pre-satellite temperature record needs close scrutiny, and serious concerns about possible distortions need to be resolved. While I have dismissed concerns about extreme weather events, infectious diseases and similar issues, there is no doubt that these are matters of concern to the public. They need continuing scientific attention. Research is needed on solar activity and the mechanism by which solar activity impacts global temperature.

This only begins the list of scientific tasks on Climate Change. We need better climate models to reduce the variability between models and the enormous uncertainty surrounding projected impacts. This means we need more scientific knowledge about the impact of clouds, water vapor feedback cycles, snow and ice accumulation and reflectivity, the phenomenon of desertification, and other scientific dimensions of climate issues.

Often, when I raise these issues I am accused of using scientific uncertainty as an excuse for inactivity and delay. This mis-states the issue and my position. Our choices are not between action or inaction but between responsible and irresponsible actions. Thus my final point concerns the Climate Change issue as a problem in public policy, as a problem in choosing actions that are consistent with our state of knowledge and economic objectives.

My own background is not in science but in economics, business, and policy analysis. To those of my ilk, the details of the Climate Change issue are complicated, but the basic structure of the problem is simple -- Climate Change is a problem in decision-making under conditions of uncertainty. Those of us in business confront similar problems every day, and we know the rules for dealing with them.

The first rule is to be slow to commit. Until you must, do not bet your company (or your country) on something that might turn out to be an error. If at all possible, postpone major decisions while you reduce uncertainties.

Given this rule, the first question to ask is, "Do we have time?" With respect to Climate Change, the answer is clearly, "Yes." We do not need to drastically reduce emissions in the short term because nothing we do in the next 15 or 20 years will have any appreciable impact on the world's average temperature in 2050 or 2100. In fact, nothing the U.S. does in the next 10 or 20 years will have much impact on the atmospheric concentration level of greenhouse gases in the year 2020. According to the former Chairman of the Intergovernmental Panel on Climate Change, the effect of the Kyoto Protocol on CO₂ concentration levels in 2010 is four-tenths of one percent (0.4%). And it would not be much greater in the following decade.

Since concern should be with the total accumulation of CO₂ and not with emissions *per se*, decisions on accelerated reductions in emissions can be safely postponed. This fact is crucial, because the costs of these reductions are exceedingly sensitive to timing. Many capital investments, including those in energy, are long term. If change can be deferred until current equipment reaches the end of its useful life, and can be replaced by more efficient technology, costs will decline drastically.

Recently, some confusion over the potential costs of Kyoto was triggered by the Administration's release of an optimistic study by the Council of Economic Advisors (CEA). The Council reached its rosy conclusion only by three assumptions, all of them unrealistic. It assumed the U.S. could meet 80 per cent of its emission reduction obligations by buying credits from abroad. Put another way, only 20 percent of our obligations would be met by domestic action. The Kyoto Protocol does not provide for this and no mechanism for accomplishing such a result is in place. CEA made two other critical assumptions: First, that there is a truly global emissions trading system in place, even though 138 developing countries are exempted from the Protocol. Second, that electric utilities would largely switch from coal to natural gas in 10 years. This is economically impractical. Dr. Boorstin might call the Council's work a pseudo-analysis.

A more realistic recent appraisal came from the Energy Information Administration, which estimated that Kyoto could, by 2010, raise gasoline prices 53 percent, raise electricity rates 86 percent, and reduce GNP by 4.2 percent.⁶

Make no mistake. A commitment to link decisions on Climate Change to the true state of knowledge and advances in it will produce long term environmental and economic benefits.

This leads logically to the second rule for making decisions under uncertainty: Invest in information. Spend money to narrow the range of possibilities. Use sensitivity analysis — what information forms the hinge of the decision, and how can we get it? We need to invest in gaps in climate science that have been identified by the National Research Council. We need better climate models. We also need to invest in analyzing basic issues. And we need to invest in creating contingency plans.

The third rule is called “no regrets.” Look for actions that will produce benefits under any set of circumstances. Business has developed a list of emission-control and policy actions that will be worthwhile even if the threat of Climate Change turns out to be a hobgoblin, and we have shared it broadly. In contrast, the Administration policy of committing to near-term emissions rollbacks, regardless of the state of knowledge or the timing of investment decisions, is guaranteed to cause a lot of regret.

The final rule is to consider alternatives. It is a truism that the further ahead you try to predict, the greater the number of uncertain factors, and the larger the probability that any single guess will be wrong. This wisdom that a broad net should be cast to be sure that all alternatives are considered certainly applies to Climate Change. Even if the problem turns out to be real, it is likely that a crash program of prevention is the wrong option. In much of the world the impact of warming could be neutral or even benign. In other cases, it might make more sense to commit resources to adaptation. These options need serious consideration and analysis, and serious scientific work. They are not getting it to the extent that they should.

These four rules — use time as a friend rather than an enemy; invest in information; look for “no regrets” actions; consider all the alternatives — provide the basis for a sound national and international policy on Climate Change. Their wisdom is thoroughly supported by the facts and by the logic of a learn, act, learn strategy.

So, to return to my initial theme — the role of scientists — I urge all scientists to hold firm to their scientific habits of mind in their work on the Kyoto Protocol, whether that work takes the form of research, education, or participation in the policy debate. I think the Administration is acting in the unfortunate tradition of political leaders who try, by command or demagoguery, to repeal the laws of reality when these conflict with their ideology.

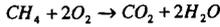
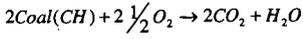
Science and the scientific method should not be campaigning tools, used to gain advantage by promoting fear and stifling debate. As Ted Koppel eloquently observed, in a discussion he had with Al Gore on *Nightline* several years ago: “The measure of good science is neither the politics of the scientists nor the people with whom the scientist associates. It is the immersion of hypothesis into the acid of truth. That’s the hard way to do it, but it’s the only way that works.”

It is heartening that a TV newscaster can be quoted on the importance of science and truth. These values need to be restored as part of the shared consciousness of the society. Actions do have consequences and a frightened society can talk itself into stagnation. Looking at the future, the greatest threats to continued progress are the illusion of knowledge and the corrosive effects of anxiety run amok. It is the job of scientists to replace the illusion with real knowledge, and the anxiety with reason. Beyond producing a more informed climate policy, a renewed commitment to science and engineering provides society with the foundation for human creativity and progress.

NOTES

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1. Norbert Wiener, quoted in *Bartlett's*, p. 691.
 2. Harper Colophon Books, 1964 (paperback edition).
 3. Tom V. Segalstad, “Carbon cycle modeling and the residence time of natural and anthropogenic atmospheric CO₂: on the construction of the ‘Greenhouse Effect Global Warming’ dogma,” in Roger Bate (ed.), *Global Warming: The Continuing Debate*, European Science and Environment Forum, Cambridge, England, Jan. 1998, pp. 184, 187-89.
 4. Arthur B. Robinson, Sallie L. Baliunas, Willie Soon & Zachary W. Robinson, “Environmental Effects of Increased Atmospheric Carbon Dioxide,” Jan. 1998 (Published by the Oregon Petition Project).
 5. Virginia Postrel & Steven Postrel, “Stars in Her Eyes: An Interview with Sallie Baliunas,” *Reason*, Oct. 1998, p. 42.
 6. EIA, *Impacts of the Kyoto Protocol on U.S. Energy Markets and Economic Activity* (Oct. 9, 1998).

unit of combustion products. Two thirds of coal combustion products are CO_2 versus one third of methane.



Therefore, the utilization of the methane contained in natural gas hydrate would not only ensure the adequacy of world energy resources, but would also mitigate global climate change.

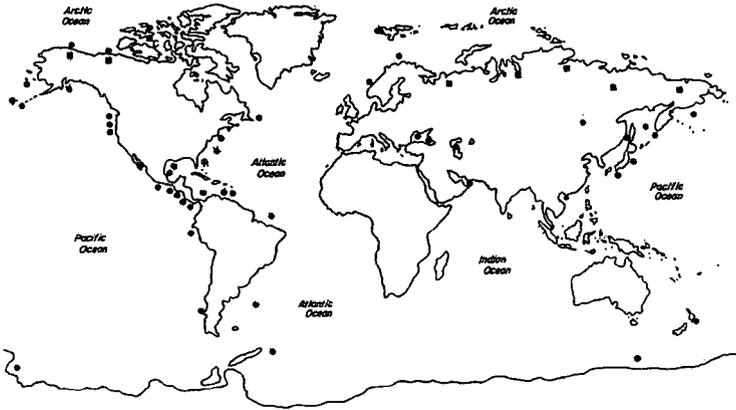


Figure 2. Map of In-Situ Hydrate Locations
Reference: Kvenvolden, K. A., *Chem. Geol.*, 71, 431 (1988).

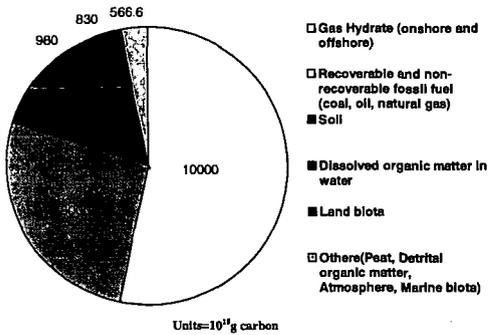


Figure 3. Distribution of organic carbon in earth (excluding dispersed organic carbon such as kerogen and bitumen)
Reference: Keith A. Kvenvolden, *International Conference on Natural Gas Hydrates*, Ann. N. Y. Acad. Sci. vol. 715, 232-246 (1994)

PHASE EQUILIBRIA

For studying about methane gas recovery from hydrates, phase equilibria between the hydrate phase and the gas phase is very important. The fundamental model is based on statistical thermodynamics and developed by van der Waals and Platteeuw (1959). Later, Parish and Prausnitz (1972) modified it and recently, a distortion model was developed by Lee and Holder (1999). Figure 4 shows the three phases curves for several hydrates. Q_1 is the triple point and Q_2 is the quadruple point. As can be seen, low temperature and high-pressure favor hydrate formation.

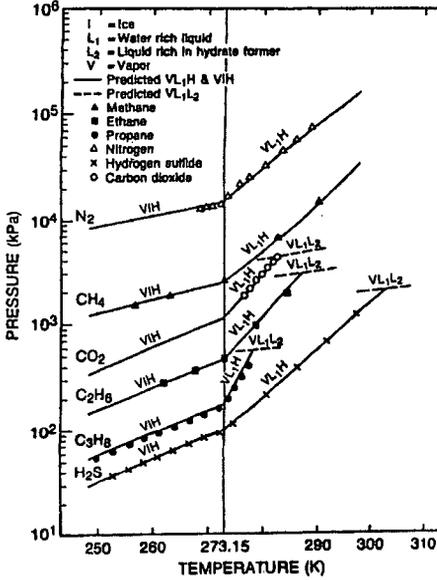


Figure 4. Hydrate Forming Conditions for Several Gases.
Reference: Holder et al., *Review in Chemical Engineering*, Vol. 5, 1-70 (1988).

THE RECOVERY OF GAS FROM HYDRATED RESERVOIRS

First, solid hydrates probably need to be dissociated for gas recovery from hydrates. The dissociated gas can then be transported in the same manner as conventional natural gas. Dissociation of gas hydrates can be accomplished in three ways. The first method is thermal injection, the second is pressure reduction and the last is slurry mining.

When heat is added at constant pressure, the system temperature can rise up to the dissociation temperature. At the dissociation temperature, all heat that is added is spent on hydrate dissociation. The energy required to dissociate hydrate ranges from 50 kJ/mole (for methane) to 130 kJ/mole (for propane) (Holder, 1988). The problem with this method is the heat lost to reservoir rock and water. Without heat loss the injected energy is about 10% of the recovered energy. With heat loss the injected energy may exceed the heating value of the gas. This method is also expensive and has to simultaneously move hot fluid downward and gas upward (Max et al, 1997).

The second technique is the depressurization technique. It operates by lowering the pressure in an adjacent gas reservoir. When the pressure reaches the dissociation pressure, gas hydrates at the interface convert to gas and water. This technique has been used in the Messoyhaka gas field in the western Siberia hydrocarbon province (Max et al., 1997). The last method, slurry mining, has not studied yet but is suggestive of grinding up the ocean bottom to

recover a slurry of solid hydrates which are likely to dissociate in the riser. Holder et al. (1984) notes that depressurization and hot water injection seem to be the most promising techniques for further evaluation because of lower heat losses compare to steam injection.

A complication of producing gas from hydrate is the possible formation of gas hydrates in the transportation lines. There are four thermodynamic ways to prevent hydrate formation (Sloan, 1997). They are 1) remove the water (it can lower the dew point), 2) keep the system temperature higher than hydrate formation temperature, 3) keep the system pressure lower than hydrate formation pressure, and 4) use inhibitors. These methods are used individually or jointly in production operations today.

Recently, research about replacement of naturally occurring methane hydrates with carbon dioxide hydrate has been also studied. Methane gas hydrates need higher pressure to be stabilized compare to carbon dioxide gas hydrates. Over a certain pressure, methane gas hydrate is unstable, while carbon dioxide gas hydrate is stable. However, very complex phase behaviors are likely to make this process difficult.

CONCLUSION

Natural gas, primarily methane is an excellent fuel for combustion for a number of reasons. Methane produces less carbon dioxide per mole than any other fossil fuel when it is used as fuel. Thus, it can reduce the amount of anthropogenic emissions of dioxide gas, which may cause a green house effect. In addition, natural gas contains very little sulfur or phosphates that can cause air pollution. Additionally, the amount of fossil fuel in hydrate form is twice as large as in all other forms. Thus, methane gas hydrate has a potential to be used as a new energy source.

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Methane Hydrates: Fuel of the Future?

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ABSTRACT

Gas hydrates are crystalline solids that form from mixtures of water and light natural gas such as methane, carbon dioxide, ethane, propane and butane. They are of considerable interest for their potential as an energy resource and for their role in global warming. From an energy resource point of view, the enormous amounts of methane hydrate under the ocean and beneath arctic permafrost represent an estimate 53% of all fossil fuel (coal, oil, natural gas) reserves on earth, about 10,000 gigatons. The difficulty with recovering this source of energy is that the fuel is in solid form and is not amenable to conventional gas and oil recovery techniques.

INTRODUCTION

Gas hydrates are crystalline molecular complexes formed by the physical combination of water and low molecular weight gases. They have the general formula $M_n(H_2O)_p$, where one or more hydrate forming molecules M called "guest" associated with p "host" water molecules. The guest gas molecules are physically engaged in interstices or cavities in the lattice structure formed by the water molecules that are held by hydrogen bonds (Holder et al, 1988). There are three different kinds of gas hydrates according to its structure; Structure I, structure II and structure H. A typical illustration of structure I gas hydrate is shown in figure 1 (Sloan, 1997).

Estimations of world hydrate reserves are very high but somewhat uncertain. Kvenvolden estimated it as 10^{16} m^3 (1994). Figure 2 gives sites with evidence of either on-shore or off shore hydrate deposits and figure 3 gives the relative magnitude of gas hydrates as a reservoir of organic carbon on earth. Methane hydrates, which form structure I gas hydrate, store immense amount of methane and occur in abundance in marine and Arctic sediments (Kvenvolden, 1994). One unit volume of methane hydrates can contain over 160 volumes of gas and less than one unit of water at standard conditions. According to estimations by Collett, as much as 200,000 trillion cubic feet of methane may exist in hydrates in the U.S. permafrost regions and surrounding waters (DOE, 1998). Because of its huge quantities, methane hydrates represent a potentially enormous natural gas resource.

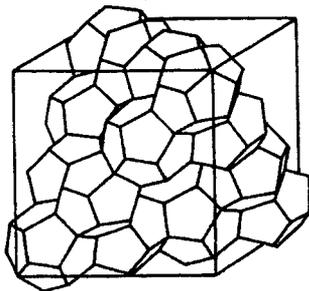


Figure 1. Unit cell of a gas hydrate of structure II

Reference: Mak, T.C.W., McMullan, R. K., *J. chem. Phys.*, 42, 2732 (1965).

Another important factor is that methane is less carbon-intensive fuel than coal or oil. Methane from hydrates (or other sources) produces only half as much carbon dioxide as coal per

THE FUTURE OF NUCLEAR ENERGY

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KEYWORDS: Nuclear, Electricity, Waste

A PERSPECTIVE ON NUCLEAR POWER DEVELOPMENT

Nuclear power started with the discoveries before and during World War II, a remarkable time in our history. The defining event took place at the University of Chicago on December 2, 1942 when it was demonstrated that nuclear fission could be sustained and controlled. This ushered in the nuclear age.

Following World War II, the United States government and the University of Chicago organized Argonne National Laboratory (ANL) to continue research into peaceful uses of this awesome power. Soon there was need for a site that could host the construction of experimental nuclear power plants. Idaho was chosen by then Argonne director Walter Zinn. It led to the construction of the Experimental Breeder Reactor I (EBR-I), the first reactor to produce electricity, and the boiling water reactor (BORAX), which tied into the grid and made Arco, Idaho the first town in the world to be lit with nuclear energy. From this simple beginning – a string of eight dim light bulbs and four hours of power to a small desert town – nuclear power has grown to account for about 17% of energy production world wide with more than 400 plants in operation. In the United States, there are more than 100 plants in operation, accounting for slightly less than 20% of our electric power production. It is important that even though there have been no new nuclear plants built in the last 15 years, we as a nation have been able to meet our growth in electric energy consumption primarily because of improvements in the efficiency and reliability of operation of nuclear power plants. They are now on-line, producing power, close to 90% of the time. The point is that despite all of the negative press, commercial reactors are operating very well and are an important part of our energy mix.

These reactor designs currently in use evolved from work primarily associated with what was done by the Navy. Westinghouse was a major contractor for the Navy, developing the pressurized water reactor that represents most of the plants in operation in the United States today. There are a few boiling water reactor designs, developed by General Electric, but they are in the minority. Sodium cooled reactors, such as EBR-I which besides producing the first electricity could create more fuel than it burned, never caught on. Water-cooled reactors were preferred by the Navy, so they got a leg up in the early days. There is a mature technology with these plants, there is not a shortage of fuel, and the technology has been deployed world wide. Water-cooled reactors do, however, create a great deal of spent fuel that we are just now beginning to grapple with. As the needs grow, different designs will take their place.

There are other designs scattered around the world, such as the Chernobyl type reactors that are a derivative from the Russian weapons program. Gas-cooled reactors operate in a few places. And there are a few operating sodium cooled reactors of a type that when eventually deployed, can greatly extend the available fuel supply.

It is worth commenting that many nuclear plants are becoming hugely profitable in the United States, primarily because they are becoming available at fire-sale prices. At least two operating companies have organized to buy them and operate them. The operating reactor at Three Mile Island (TMI) is a case in point. It cost several billion to construct, but was sold for about \$30 million to a company called PepCo, a very competent operator of nuclear plants. We will see much more of this as individual utilities go out of the business and operating companies begin to take over, largely a result of deregulation of the electrical power industry. Many of the problems we know today developed because in the early history of nuclear power it was very fashionable for individual utilities to own a nuclear power plant, and many got into the business without the technical and management expertise to build and operate them. Witness the WPSS plants on the Columbia river in Washington state. This problem is now sorting itself out.

All of this experience, positive and negative, is laying the basis for what nuclear power will become. The future will be different than what we see today.

The world's population has reached 6 billion people and is projected to reach 10 billion in the next

century. More than 30% live in poverty without access to electricity. Their life span averages less than 40 years. With access to even a little electricity and the benefits it brings, life span increases dramatically, to about 65 years. Significantly, the quality of life also increases dramatically.

Deregulation is spurring much innovation in the power generation business favoring small distributed generating sources that may well be suitable for many of these developing nations in the beginning of their expansion. Natural gas will grow in importance, particularly in the United States. But many countries either don't have access to gas, or the infrastructure to support it, or both. Electricity can be produced by many means, but only nuclear, coal and natural gas together have the potential to meet the needs of the next century, driven by the rapid growth of developing countries. To keep up, electricity production is expected to triple by the middle of the next century.

Some would say that we can't afford such growth. However, we cannot deny to the growing population of the world the benefits of a high standard of living. Just as important, it has been demonstrated over and over again, that countries with high standards of living have low population growth and less environmental degradation. So, besides improving the lives of individual people, such economic growth can also benefit the globe environmentally. That is really the key question, can we manage energy growth in a way that we can meet the needs of a hungry world, stabilize economics and protect the environment. This is a challenge worthy of us all.

Coal, in its present, cannot be a major part of that solution for a simple reason, global warming. The science to predict effects of CO₂ emission is still immature, and there is much uncertainty, but if the predictions are correct, it will have profound effects on climate, even at current levels of emissions. There is now no real question that global temperatures are increasing and that we will see the effects of human activity on global climate. What those effects will be and what to do about them are the present questions. There is talk of CO₂ sequestering but it is a technology far off. Natural gas can help, but only to a certain extent. We can talk about energy conservation, but that is for the developed nations, not the developing nations. We can talk about new technologies, solar, biomass, etc., and they have their place, but they will play only a part.

In spite of all its benefits, it is very unlikely that nuclear can fill the gap by itself, even if it is fully embraced. The required growth is phenomenal. For nuclear to provide even one-third of the carbon-free energy supply necessary to stabilize CO₂ levels would require building the equivalent of 100 large plants per year, starting now. If nuclear power is to play an essential part in addressing the greenhouse problem, slow steady growth will not be enough.

THE CHALLENGES FOR NUCLEAR POWER

Proliferation of Weapons Material

The first challenge for substantial growth of nuclear power is to prevent the proliferation of material that could be diverted to use in nuclear weapons. This is probably the greatest and most reasonable fear of those who strongly oppose nuclear power, especially its use in developing countries. It is such an emotional issue that there is talk about putting the genie back in the bottle. The nuclear genie cannot be put back into the bottle, so we will have to learn to control it. Nuclear has immense capability for good or for destruction. Frankly, our present problem is that nuclear power grew out of the weapons programs of Russia and the United States and we have ended up with technologies that are closely linked. We can do better. The first step is to burn down, to destroy, and to eliminate the excess weapons material that we currently have available. Burying it is not good enough. Let me say that again: burying it is not good enough. What we are talking about is not just the material produced for the weapons program, but the greater quantity of separated material produced in the civilian nuclear power programs. Burning the inventories down will greatly assist in management of the material that remains. Simply speaking, if the remaining material is locked up in reactor systems, it can't be used for weapons. Even more importantly, it can easily be monitored. What we need are reactor systems and associated fuel cycles that make it extremely difficult or impossible to divert material to weapons use. And we need the monitoring systems to make any attempt at diversion obvious to all.

Waste Management

Waste management is also an issue dominated by emotional considerations. The fundamental difficulty, as I have said, is that we are presently hung up on putting the genie back into the bottle. To this end, the permanent repository at Yucca Mountain in Nevada is intended to permanently lock material away, for a million years or more. This approach, of course, is hugely wasteful of a tremendously valuable resource, and probably can't be done to the standards being imposed anyway. Others outside our disciplines are beginning to understand this. There is currently an intense debate

in Congress over employing interim storage instead of permanent disposal and transmutation of the waste, using reactors or accelerators is also being considered. There are international studies looking at the same questions. There are also international studies looking at improved methods of fuel management that include recycle. One thing is clear, burning less than 1% of the available fuel and discarding the rest as we are doing today is bound to create a huge waste problem. It is simply better to recycle, as we do with so many of our other products. This will come. It is a question of time and the right technology. I would emphasize that it is recycle for the purpose of burning down the inventory of material, not creating more. To this end, the Russians and the Japanese are entering into an agreement for fueling a Russian sodium-cooled reactor with weapons plutonium, recycling the fuel in a proliferation resistant system using electrorefining. We can expect other international initiatives to develop, such as deep burn reactors and other concepts. We also should be exploring long life reactor cores that produce and burn their own fuel without need for external separation of material.

Economics

Any power source must make sense in a competitive market. Nuclear power suffers from the fact that each plant built in this country was one of a kind, with only a few exceptions. Further, each one had to be a Cadillac to satisfy safety requirements, requirements which were continually being changed.

The automobile industry could not succeed on a broad scale until it moved away from hand building individual luxury cars and moved toward mass production of vehicles that comply with known and excepted standards. The same applies to nuclear plants. The cars of today are vastly superior in every respect, especially safety, to those that preceded them, hand built or not. They are a great value.

The same must happen with nuclear power. Smaller, modular plants produced in factories are part of the answer. Standardization of a few designs is another part of the answer. Surprisingly, cheaper and simpler can also mean safer.

Safety

The enemy of safety is complexity. Our nuclear plants have become increasingly complex, in part, ironically, because of the addition of many safety systems. It is always more straightforward to engineer a safety fix with the addition of a new system. Rather, I think we need to return to the fundamental design and take advantage of the inherent physics to ensure that it will respond safely. It is possible to design an aircraft that can glide after the engines are lost, and to stall at such a slow speed that it can be landed safely on rough terrain. Likewise, it is possible to design a reactor that will coast down in power on its own after losing all electrical power, without requiring active safety systems. This concept was proved at Argonne in 1986 when all safety systems and cooling systems were disabled at full power on EBR-II. Because this reactor employed inherent safety in its design, it coasted down safely and never over heated. Such features are being incorporated into the newest designs. Unfortunately, they are not being built in this country so we cannot directly see their benefits. One huge benefit is that their safety systems can then be simplified, and costs reduced. This is a field of research and development with great promise for the future.

Perhaps, though, the biggest challenge in the meantime is avoiding accidents. Another accident on the scale of Chernobyl, or continuing accidents like the criticality in Japan, would have a devastating impact on the nuclear industry. Yet today, there are 26 of the oldest Soviet designed power plants in operation; 14 of the RBMKs and a dozen of the VVER-440-230s. They have no containment vessels and inadequate to non-existent emergency core cooling systems. Genuine safety risks exist elsewhere where rapid growth is foreseen without the infrastructure to support it. The United States must provide the leadership to ensure that these problems are addressed.

THE FUTURE FOR NUCLEAR POWER

Advanced Reactor Development

We are then confronted with the challenges of proliferation, waste, economics and safety. These are not new challenges. We addressed them at Argonne in the early 80s with the development of the Integral Fast Reactor (IFR) program, and created a great deal of excitement in the process. We demonstrated that a proliferation resistant fuel cycle, that is transparent for those who would monitor it, could be developed. We demonstrated that fuel could be recycled to the reactor, so that fuel and fission products could be burned, not added to the waste and buried. We demonstrated that we could simplify the design, greatly improving the economics. And we demonstrated that safety could be

assured while greatly simplifying reactor design. In short, the IFR program was a great technical success. It made significant progress in both defining the questions to be asked, and in answering them. Even though the IFR was terminated for political reasons in 1994, it has laid the groundwork for important work in the future. Much of this work is happening in the international arena.

There is much being done in the international arena. Unfortunately, much of it has to do with correcting the mistakes of the past, cleaning up contamination from many sites associated with the weapons programs and properly managing material and reactors that remain.

It is important that the United States maintain its expertise if it is to maintain international leadership. Problems will arise and it is important that we are able to deal with them. Developing nations will turn to nuclear power to improve the lives of their people, and it is important that we are at the table to assure that this is done in a safe and secure manner. The only way for other nations to respect the United States as a leader in policy is to be a leader in the technology.

Fortunately, there are important initiatives emerging. Congress has funded the Nuclear Engineering Research Institute (NERI) at \$19 million, a relatively low level, but an important beginning. The money funds a number of nascent, innovative research initiatives from universities and national laboratories to develop new approaches to nuclear reactor design, among other things. Let me describe one such initiative. There is being developed a water-cooled reactor with a core that is envisioned to operate for 14 years without refueling. At 14 years, the whole core will be replaced. Because there is no need for refueling, there is no need for a refueling system and the cost it entails. Because there is no movement of fuel, there is no risk of diversion of material.

In addition, the design will maximize the inherently safe response to upsets. For example, the core can be cooled by natural convection only, without need for pumps or electric power. Such simplification can enhance safety and reduce cost.

Probably the best demonstration of what can be achieved was with the sodium cooled reactor, EBR-II. In 1986, two landmark demonstration tests were conducted before an international audience. The reactor was subjected to the two worst events that can befall a power reactor.

In the first, the reactor was brought to full power, the automatic shutdown system was disabled and all electric power to the reactor cooling systems was removed. The coolant flow to the core immediately began to decrease, the reactor temperature started to rise, but instead of melting the core, it shut itself down without damage. It glided to a safe landing where it remained.

In the second test, the reactor was again brought to full power, the automatic shutdown system was disengaged and all power was cut to the pumps that reject heat from the reactor. The response was even more benign in this test than in the first. Again, the reactor shut itself down with no damage.

Such designs are possible and have captured the imagination of an international audience. In the example mentioned for a light water reactor design, the French and the Japanese are participating. Another reactor design, a pebble-bed gas cooled reactor, has attracted an even broader international audience.

CONCLUSION

We can all be thankful for nuclear power, for it may well be essential to the long term survival of civilization. Within the seeds of its potential for great good, are also the seeds for great harm. We must ensure that it is applied for great good. What is not in question is whether we can live without it, we cannot.

United States leadership is crucial in determining how this technology is developed and applied. The size and capability of the United States technical community is decreasing, a trend that cannot be allowed to continue. It is my belief that in the future, the need, the vision and the confidence in nuclear power will be restored, but only if we address the immediate challenges before us. It is a national challenge worthy of the best people this nation has to offer.

BIOMASS AND RENEWABLE FUELS

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Keywords: biomass; fuels from biomass; biological hydrogen production; sustainable energy systems; carbon constrained world

ABSTRACT

Biomass is an important contributor to the world economy. Agriculture and forest products industries provide food, feed, fiber, and a wide range of necessary products like shelter, packaging, clothing, and communications. However, biomass is also a source of a large variety of chemicals and materials, and of electricity and fuels. About 60% of the needed process energy in pulp, paper, and forest products is provided by biomass combustion. These processes could be improved to the point of energy self-sufficiency of these industries. Today's corn refinery industry produces a wide range of products including starch-based ethanol fuels for transportation. The biomass industry can produce additional ethanol by fermenting some by-product sugar streams. Lignocellulosic biomass is a potential source for ethanol that is not directly linked to food production. Also, through gasification biomass can lead to methanol, mixed alcohols, and Fischer-Tropsch liquids. The life science revolution we are witnessing has the potential to radically change the green plants and products we obtain from them. Green plants developed to produce desired products and energy could be possible in the future. Biological systems can already be tailored to produce fuels such as hydrogen. Policy drivers for increased use of biomass for energy and biobased products are reviewed for their potential contributions for a carbon constrained world.

INTRODUCTION

In the future, our energy systems will need to be renewable and sustainable, efficient and cost-effective, convenient and safe. Can the integrated development and use of our nation's biologically-derived renewable resources contribute significantly to our energy independence, increased energy diversity, and reduced carbon emissions while at the same time fostering rural development, technological innovation and commercialization?

We address biomass, derived fuels and energy, and biological hydrogen production.

TODAY'S BIOMASS ECONOMY FROM AN ENERGY VIEWPOINT

The United States consumes about 94.2 quads (1 quad = 1 quadrillion Btu = 1.055 EJ) of all forms of energy self generated or imported. Of those, 7.1 quads are renewable energy. More than 3 quads provide residential and commercial heat, heat and power in industry, direct electricity production, as part of the energy and environmental services in residue disposal and landfill gas use, and transportation fuels from biomass. These various sources of bioenergy and their relationship with the conventional biomass industries are shown in Figure 1 [1].

As a primary energy source, biomass (43%) is just behind hydropower (51%) among the renewable resources. The Public Utilities Regulatory Policy Act (PURPA) of 1978 provided the incentive for industry to invest \$15 billion, establish 66,000 jobs and create a biomass power industry worth \$1.8 billion/year (see Figure 2). A total of 0.75 quads or 1% of U.S. electricity is from biomass power, and more than twice that amount of energy is generated and used within the forest products industry. Waste to energy represents another 0.5 quads. More than a thousand biomass facilities generate electricity or cogenerate for their own use [2].

Utility restructuring is challenging many of these operations because of competition with facilities in which capital costs have already been amortized and can produce electricity at lower costs. Some and added bioenergy capacity cannot compete on cost alone because natural gas-fired combined cycle plants have lower capital cost and moderate fuel costs

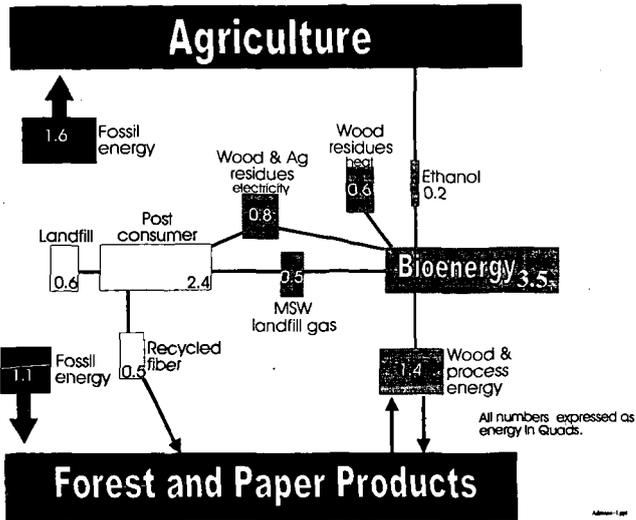


Figure 1. United States Bioenergy (1997)

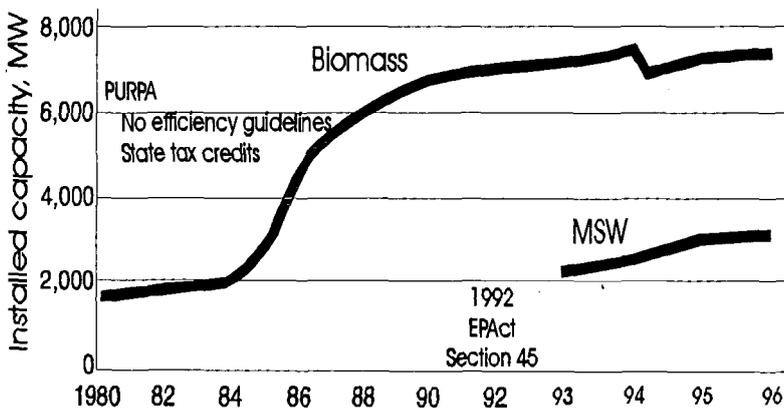


Figure 2. Electricity from Biomass in the United States.

and are predicted to be stable. One way in which bioenergy can be helped is by finding ways to pay for the environmental service it can provide such as landfill avoidance. Another way is the renewable portfolio standard, which ensures a minimum level of renewables in the electricity portfolios of power suppliers in implementing jurisdictions.

Today's bioenergy industry also produces liquid fuels, primarily ethanol, using approximately 6% of the corn grain produced each year. Production started in the late 1970s and capacity has increased steadily due to the Federal tax incentive and various state and local tax credits. Bioethanol production from lignocellulosic biomass is beginning to emerge due to recent advances in conversion technology. The same biotechnology revolution that is driving near-term commercialization will drive down the cost of bioethanol manufacture over the next 10 years. A point of cost competitiveness with the wholesale gasoline price of today will be reached based on the use of inexpensive residues [3].

POLICY DRIVERS TO INCREASE BIOENERGY AND BIOBASED PRODUCTS

The President issued Executive Order 13134 on August 12, 1999 to coordinate Federal efforts to accelerate the development of 21st century bio-based industries that use trees, crops, and agricultural and forestry wastes to make fuels, chemicals, and electricity. The

Order is titled "Developing and Promoting Biobased Products and Bioenergy". The Order and related Executive Memoranda [4] were based on extensive literature and findings [3, 5] from which the following can be concluded:

1. There is a sufficient supply of biomass materials to provide food, feed, fiber and some level of energy, fuels and materials. The precise level and impact of energy production varies but a tripling of biobased products and bioenergy by 2010 is a Presidential goal. By 2020, the goal is a tenfold increase.
2. Several drivers provide impetus to a bioenergy and biobased products effort. These include emerging market opportunities, increased rural development needs, reducing environmental impacts, increasing energy security and diversity, reduce fossil carbon emissions, and meeting the growing need for energy and materials with sustainable technologies.
3. Many companies developing bioenergy and biobased products are emerging and others are large and generally more mature (corn refining and pulp and paper). Because of the nascent nature of the "business" a large emphasis on research, development and deployment is needed.
4. There is no single agency, industry, or sector that can meet the challenges and needs to accomplish these aggressive goals on their own. All of these studies call for integrated efforts across federal agencies, current industrial sectors, academia, national laboratories, non-profit organizations, professional societies, public interest groups, etc.

Several Congressional bills have emerged with strong bipartisan support. These have aligned objectives with the Executive Order and Federal Agency actions. They are summarized below:

Bill	Date Introduced	Principal Sponsor	Summary	Status
S.935	4/30/99	Lugar (IN)	Would authorize \$49 million a year for FY 2000-2005 for research into biobased products and chemicals.	Hearings held (Senate Agriculture, Nutrition and Forestry Committee)
H.R.2819	9/8/99	Udall (CO)	Biomass Research and Development Act of 1999. To create an initiative for research and development into the utilization of biomass for fuel and industrial products.	Referred to the Committee on Science, and to the Committee on Agriculture.
H.R.2827	9/9/99	Ewing (IL)	National Sustainable Fuels and Chemicals Act of 1999. Companion bill to Sen. Lugar's S.935.	Referred to the Committee on Agriculture, and to the Committee on Science.
S.1177	5/27/99	Harkin (IA)	Would amend the Food Security Act of 1985 to permit harvesting of crops on land subject to conservation reserve contracts for recovery of biomass used in energy production.	Referred to Senate Agriculture, Nutrition and Forestry Committee
S.882	4/27/99	Murkowski	Energy and Climate Policy Act of 1999. Strengthens provisions of the Energy Policy Act of 1992 and the Federal Nonnuclear Energy Research and Development Act of 1974 to promote voluntary efforts to reduce or avoid greenhouse gas emissions.	Referred to Committee on Energy and Natural Resources

NEAR-TERM INCREASED BIOMASS USE

Current industrial biomass use is primarily of residues of agriculture, forest products operations or urban and industrial residues. Additional crop residues could be collected for product or energy purposes. Additional increases in supply would have to come from

crops specially planted for these purposes. Figure 3 shows an example of a supply curve considering the residues and at what point some dedicated feedstock supply is needed. Life cycle analysis of a dedicated poplar plantation and electricity production through an integrated gasification combined cycle shows that there are almost no net carbon emissions [6]. The current conventional energy values are also included.

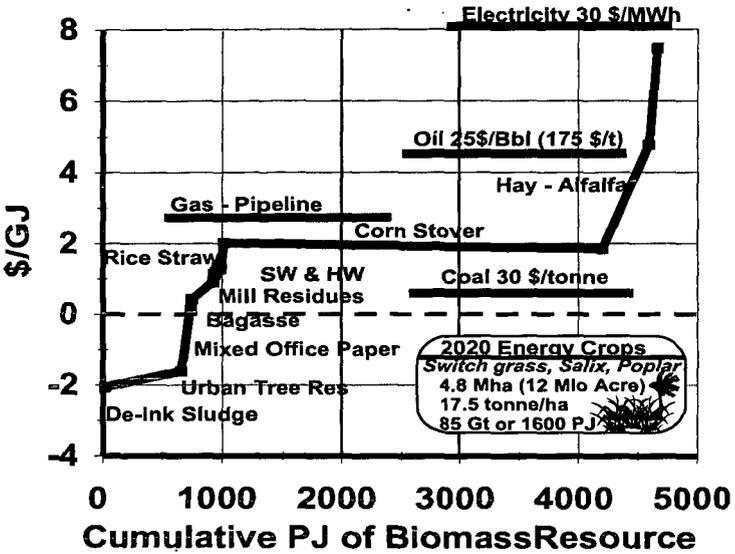


Figure 3. Supply curve of various biomass residues and dedicated feedstock plantations, for instance, of switchgrass, Salix, and poplars.

MULTIPLE ENERGY OPTIONS FROM BIOMASS

Biomass is a complex resource that can be processed in many ways leading to a variety of products. Biological routes can convert the carbohydrate portion of the lignocellulosic feedstock into ethanol, an oxygenate that can also be used as a fuel additive. The lignin component cannot be used this way and is combusted to generate heat and electricity. Gasification provides a way to generate syn-gas and from it the clean conventional fuels: Fischer Tropsch liquids, methanol, and others (see Figure 4).

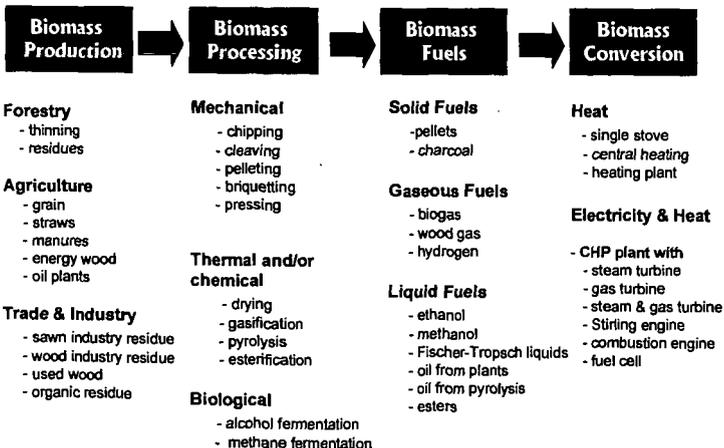


Figure 4. From multiple biomass resources to a variety of fuels and energy products

A proxy for how well some of these various processes perform is the overall process efficiency starting with lignocellulosic biomass [7].

Fuels from Biomass	Efficiency (HHV)	Comment
Methanol	54	From gasification
Hydrogen	60	From gasification
Fischer-Tropsch liquids (FTL)	49	From gasification
FTL (single pass) + electricity	26.5 (FTL); 17.2 electricity	From gasification, lower capital costs
Ethanol	50% (1999); 63% (2015)	From hydrolysis and fermentation

LONG-TERM RENEWABLE HYDROGEN PRODUCTION TECHNOLOGIES

The use of solar energy to split water into oxygen and hydrogen is an attractive means to directly convert solar energy to chemical energy. Biological systems are reviewed below. There are also chemical and electrochemical systems that have long-term (>10 years), high-risk, high-payoff technologies for the sustainable production of hydrogen. These systems have been summarized by Padro [8]. The biological processes include:

1. Algal hydrogenases that evolve hydrogen at a rate that is 4 times that of the wild type, and are 3-4 times more oxygen tolerant [9].
2. Photosynthetic organisms with light harvesting, chlorophyll-protein complexes that effectively concentrate light and funnel energy for photosynthesis. These cells showed photosynthetic productivity (on a per chlorophyll basis) that was 6-7 times greater than the normally pigmented cells [10], a phenomenon that could lead to significant improvements in the efficiency of hydrogen production on a surface-area basis. Various reactor designs are under development for photobiological hydrogen production processes (single-stage vs two-stage, single organism vs dual organism) [11].
3. Systems to convert CO (found in synthesis gas) to hydrogen via the so-called water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) at ambient temperatures. Microorganisms isolated from nature are used to reduce the level of CO to below detectable levels (0.1 ppm) at temperatures of around 25-50°C in a single reactor [12,13]. This process has significant potential to improve the economics of hydrogen production when combined with the thermal processing of biomass or other carbon-containing feeds.

THE ROLE OF RENEWABLE FUELS IN A CARBON-CONSTRAINED WORLD

Decarbonization of fossil fuels is a way to increase energy consumption without increasing carbon consumption in a carbon-constrained world. Removal of carbon from fossil fuels prior to use in energy production is likely to be far less costly than attempting to remove CO_2 from dispersed sources. If fossil fuels are converted to hydrogen in a central facility, the collection of CO_2 (or elemental carbon, depending on the process) is relatively simple compared to collecting CO_2 from every fossil-fuel-consuming vehicle on the road. Carbon neutral biomass-derived transportation fuels offer solutions to this.

CONCLUSIONS

For renewable processing of biomass or direct biological hydrogen production the cost of the technologies still needs to be decreased through research, development, demonstrations, and diffusion of commercialized new technologies. Valuing the environmental and social contributions that biomass inherently makes can also help increase its use. Broad societal consensus on land and water use issues is needed. Each route still requires significant integrated efforts across federal agencies, multiple industrial sectors, academia, national laboratories, non-profit organizations, professional societies, public interest groups, etc. The challenge to make renewable resources a major commercial reality is equated to putting the man in the moon. The versatility of biomass and conversion technologies makes it suitable to either adapt to today's fuel and vehicle

infrastructure or to be a part of a new infrastructure for hydrogen fuels and super efficient vehicles of the future.

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CATALYSIS AND OPPORTUNITIES FOR THE PRODUCTION OF H₂

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KEYWORDS: Hydrogen; catalysis; steam methane reforming

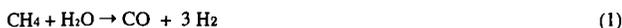
ABSTRACT

This presentation will describe the increasing importance of H₂ in our world. Since the bulk of the world's H₂ is produced by catalytic processes, often involving multiple types of catalysts, it is clear that catalysis plays a critical role in the production of H₂. The focus will be on the use of catalysis in the current and future production of H₂. Steam methane reforming will be a focal point of the discussion, and it is interesting to view the large number of catalysis steps that are used in this major technology. Some background will be provided to give a perspective of the dramatic change in the supply and demand for H₂ in the past decade, followed by a review of how it is produced commercially, with a view to how multiple types of catalysis contributes to the total process for H₂ production. Issues of carbon management and CO₂ emissions will also be discussed. In addition, some alternative catalytic approaches [fuel cells, photocatalysis, membrane reactors, etc] for H₂ production will be discussed and specific barriers to progress and opportunities for further research in this area.

INTRODUCTION

Hydrogen is forecast to become a major source of energy in the future. Prior to the early 1990s, H₂ was plentiful with refineries being major producers. Now that picture has changed due to environmental demands to reduce sulfur emissions and the production of less aromatics for gasoline; thus, refineries have had to build additional H₂ production units nearby [1]. H₂ offers the potential of a clean burning fuel if it is combined with only O₂ and would result in no extra CO₂ emissions, as long as H₂ were obtained from non-fossil fuels. With H₂ production being localized and without a large scale distribution system to move this hydrogen to more customers, H₂ is currently not a cheap fuel alternative; it simply has too much value as a chemical reductant. Limitations of space for this manuscript do not permit a complete discussion below of issues associated with the production of H₂; thus, the reader is encouraged to examine the references for greater detail.

Steam methane reforming, SMR, is the largest and generally the most economical means to produce H₂. SMR is not just one reaction, but a series of well balanced operations often including most of the following: desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and NO_x removal. The key reaction is represented by equation 1. Several good reviews describe this and other commercial approaches to the



production of H₂ [2,3]. Since the desired product is H₂ and not CO, the CO is usually taken through the water gas shift reaction to produce more H₂ (equation 2). This produces CO₂; in



Table 1
Steps in SMR which employ catalysts [from reference 1]

Process operation	Temperature, °C
Sulfur conversion [HDS]	290-370
H ₂ S removal [ZnO]	340-390
Chloride removal [Al ₂ O ₃]	25-400
Pre-reforming	300-525
Steam methane reforming	850
High temperature water gas shift	340-360
Low temperature water gas shift	200
Methanation	320
NO _x removal [NH ₃ SCR]	350

addition, one must consider that the heat derived to drive the very endothermic reaction¹, often comes from natural gas burners, which also produce more CO₂. There is an aggressive worldwide R&D effort to develop other cost effective and energy efficient means to produce H₂, especially for small volume use in remote areas of the world.

H₂ production is linked to CO₂ production when fossil fuels are reformed. In order to reduce CO₂ emissions, use of natural gas instead of coal [a higher C/H feedstock] is preferred if one must use a fossil fuel. Fuel cells as a source of power usually consume H₂. While fuel cells are widely promoted for their fuel efficiency, they must be assessed based upon the levels of CO₂ produced from the fuels used to power the fuel cell. In the near term, there is interest in using increased carbon sequestration to provide some intelligent carbon management approaches for fossil fuel routes to H₂. In the long term, we need to focus on the production of H₂ from non-fossil fuel sources or on truly renewable fuels.

There has been much excitement in the literature to use CO₂ as a feedstock to make chemicals. However, even if we had existing technology to convert CO₂ to more valued chemicals, the volume of chemicals would still be very small relative to the level of CO₂ emissions being discussed. Further, using H₂ on a massive scale to chemically reduce CO₂ to CO or CH₄ has questionable value because of the cost of the H₂. In addition, most of the world's H₂ is made from SMR which co-produces CO₂; thus it makes little sense to use SMR derived H₂ to reduce global CO₂ levels.

BARRIERS TO PROGRESS

In considering new approaches to H₂ production and/or SMR improvements, several technical barriers exist:

- Heat transfer seriously restricts operating temperatures
- More literature data needs to be gathered by studying reactions closer to the high pressure operations of existing processes and the demands for high pressure H₂
- Advances in reactor design are needed
- Overcoming limitations of material components with regard to metal dusting or high temperature seals
- Need for more ex-situ surface science techniques which allows one to characterize working catalysts under extreme temperatures [850°C] and pressures [400 psig]
- Developing process conditions which assure safe operation

OPPORTUNITIES FOR ADDITIONAL RESEARCH

Overcoming the barriers noted above will also open up new avenues for research, including:

- More laboratory units capable of studying SMR under actual process conditions
- Need for a simple, accelerated aging test to assess catalyst life
- More efficient ways to provide or utilize the energy needs for SMR
- Catalysts which minimize the formation of elemental carbon
- Non-fossil fuel sources for commercial H₂ production
- Use of CH₄ as a substitute for H₂ in the production of chemicals

ALTERNATIVE MEANS FOR PRODUCING H₂

Identifying the barriers, enables one to define new opportunities for research, not only for existing approaches but also for alternative means to produce H₂. While there is a need and demand for new routes to cost effective production of large volumes of high pressure H₂, there are niche opportunities where small volumes of low pressure, very pure H₂ are also attractive. Technologies which could address these needs [with some specific hurdles in brackets] include:

- methane decomposition [need to resolve how to handle and use all the huge amount of by-product carbon]
- use of membrane reactors [still limited by materials deficiencies, high temperature seals, and membrane configuration issues] [5]
- solar energy for electrolysis of water [must use visible light with high quantum yields]
- selective oxidation of methane [must provide convincing evidence for safe operation]
- oxidative dehydrogenation [issues of by-product coke formation which leads to fouling and an olefin co-product which must be in huge demand]

- biomass conversion [need pilot demonstration which addresses all the scale up, cost, and environmental issues]

SUMMARY

Steam methane reforming is the dominant technology for H₂ plants, and it comprises many different catalytic operations, including desulfurization, pre-reforming, reforming, high and low temperature water gas shift, methanation, and deNO_x. As long as natural gas and petroleum based hydrocarbons are still relatively low cost fuels, SMR will continue to be a cost effective approach for making H₂. Steam reforming is a mature technology, but there is fertile ground and room for technological improvement. Beyond 2010 future economic or environmental issues may eventually force adoption of substitute, alternative technologies since steam reforming is an energy intensive, endoergic process, CO₂ is a co-product, and H₂ purification is necessary. At the fundamental research level, there is a need for more catalyst studies at >20 atm where the chemistry is actually practiced and the bulk of customer demand exists. The life of the catalyst is an important criteria in benchmarking new catalysts versus commercial SMR catalysts and suitable accelerated aging tests need to be devised which provide meaningful assessments of alternative catalysts or technologies.

There are a number of emerging and attractive approaches to H₂ production, but the greatest opportunities in the future would seem to lie with non-fossil fuel based H₂ technologies, where major breakthroughs are needed. In considering new technologies for H₂ production, one has to consider the entire process. That is, one must have separation and purification steps, consider net energy demands and balance, the quality of the feed, etc. Ultimately, the route one chooses to produce H₂ will be a function of not only the technology advances, but also economics, the environment, specific customer needs, and market demands.

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Molecular and Molecular Assembling Approaches to Develop Efficient Catalytic Processes of Hydrocarbon Fuels

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Introduction

Hydrocarbon fuels are expected to play major roles to meet energy demands on the earth in the initial half of 21 century. Nevertheless, their efficient use and up-grading are strongly required to save the sources, and reduce environmental load. The up-graded products of the highest efficiency and least contaminants are designed through an adequate structural understanding of hydrocarbon fuels and their up-grading catalytic processes based on their structural information about the feeds, intermediates and products. Catalysts are the keys for up-grading processes. Designs of their adequate uses and materials for higher activity, selectivity and life are equally concerned.

Results and Discussion

Structural Understanding of Hydrocarbon Fuels and Molecular Understanding of Gasoline and Gas oils

Environmental regulation such S, N and aromatic contents as well as the combustion performance such as octane and cetane numbers require severer up-grading. The molecular basis reaction design which requires the reactivity of every constituents molecules is now studied by describing structure and contents of every molecules. GC-AED developed by Hewlett-Packard and Chevron is a powerful tool to analyze every molecules by classifying them according to their elemental composition detected by AED(atomic emission detector) after the separation by GC.

Figure 1 illustrates chromatograms of a gas oil by detecting C, S and N, respectively. Thus, the elemental composition of every species detected is obtained by this tool. By combining GC-MS to identify the molecular weight of the every peak, molecular composition of the peak is identified. There is, of course, limitation due to the chromatographic separation as shown in the N chromatogram where a broad hump is observed in a particular gas oil. The acid-extraction separates species in the hump from the other nitrogen species as basic nitrogen species, giving individual peaks to be identified as shown in Figure 2.

Approaching to Molecular Understanding of Vacuum Gas Oil

Vacuum gas oil is an important feed stock to be further up-grading rather easily by catalytic cracking through hydrosulfurization/hydrodenitrogenation and hydrocracking. Their molecular identification has not been achieved yet by GC-AED. However, narrow cut distillation and selective separation(nitrogen by acid extraction

and sulfur by PdCl chromatogram) are expected to separate it suitable for GC-AED analyses.

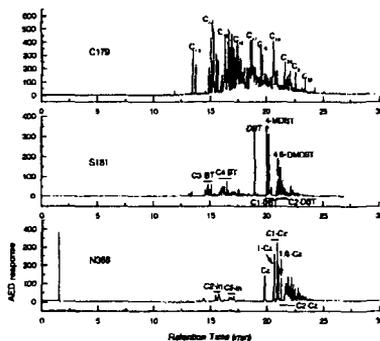


Figure 1. C, S and N chromatograms of MCO measured by GC-AED. C_n:normal paraffin with number of C and C1-C4:1~4 substituted methyl groups.

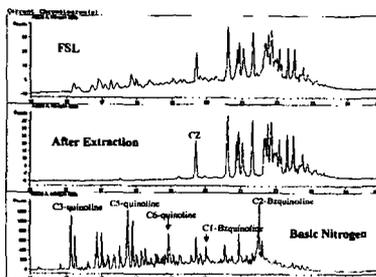


Figure 2. Basic fraction of FSL extracted by sulfuric acid. Background was successfully removed and it was analyzed as quinoline and benzoquinoline derivatives using GC-MS.

Molecular and Molecular Assembling Understanding of Resid and Coal

Resid and coal consist basically of polyaromatic-polynuclear macromolecules. The aromatic rings carry alkyl chains, being linked through methylene, aryl-aryl, ether, and thioether bonds. The aromatic ring carries also the heteroatoms within the ring. The sizes of molecules, aromatic ring and alkyl chains as well as the number of nuclei vary according to coals and crudes, although there are several trends which describe empirically such structural parameters.

Complex mixtures of molecular species in resid and coal carries parafins and naphthalenes of large molecular size. Such mixtures of macromolecules gather to form micelle or solid glass, through the intermolecular linkages. Hydrogen bonding, charge-transfer, alkyl entanglement and π - π ring stacking are proposed to exist. Figure 3 illustrates XRD profile of resid and coal. Definite diffractions are observed at around 20 and 26, which are ascribed to alkyl entanglement and π - π ring stacking.

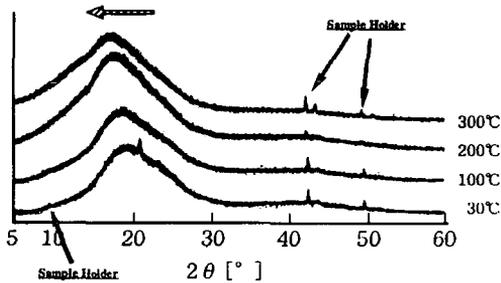


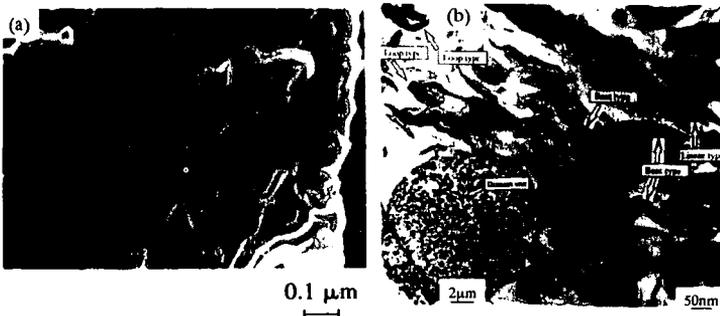
Figure 3. XRD of coal and resid (Measuring Temp. : 30~300°C, Step Scan : 4sec/0.01 °C, He atmosphere).

Resid and coal also carry same inorganic constituents. V=O and Ni porphyrins, minerals and ion-exchangeable cation are representative inorganic components in the former and latter fuels, respectively. Such inorganic constituents often provide bridges between macromolecules, or macromolecular chains.

Structure of Char

High molecular weight hydrocarbons tend to give char/coke when heated, liberating smaller molecules and cracked products. Such char/coke is a trouble maker as plugging and poisoning substances in the process, as well as combustible and gasifiable solid fuel. Their structure is also important to prevent their formation and to enhance the reactivity. Although the char/coke tends to carry some heteroatomic material when formed at lower temperature, it consists basically of hexagonal network. The size of hexagons and their stacking varied according to its experienced temperature, forming conditions and starting feed, approaching to the graphitic structure. Such microscopic stacking units gather to form micro domain, domain, and texture by orienting the microcrystallines and their assembles, respectively.

Recent development of high resolution SEM, TEM and STM/AFM in addition to XRD clarifies such micro, meso and macroscopic structure of char/coke. Figure 4 illustrates typical high resolution SEM, TEM and STM photographs of mesophase pitch based carbon fiber to show a series of structure.



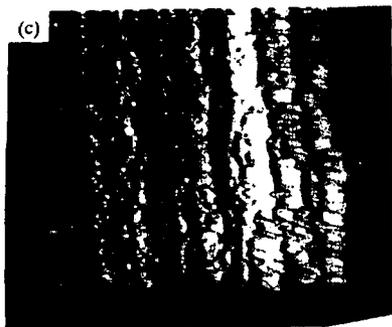


Figure 4. SEM, TEM and STM photographs of mesophase pitch based carbon fiber (a)HR-SEM photographs (outer section) (b)TEM BF images of the transverse section (total transverse image in the rectangular) (c)STM images of the longitudinal section.

Structural Understanding of Up-grading Schemes

Desulfurization and Denitrogenation of Gas Oil

The problem in the deep desulfurization of gas oil has been identified as the low reactivity of 4 and 6 alkyldibenzothiophenes. Their desulfurization has been proposed to proceed through hydrogenation of outer phenyl ring prior to the desulfurization at the relatively lower temperatures and direct desulfurization as another major desulfurization route at relatively higher temperatures.

GC-AED can follow the schemes of the substituents among other thousands of coexisting partners in the real feed which are strongly influenced by the coexisting partners as well as the catalyst performances. The former influences are defined as inhibitions which often restrict the deep desulfurization of the targeted level. Nitrogen and aromatic species, H_2S and NH_3 and their products are major inhibitors, their inhibiting factors being quantified to design the reactor, the process, and the catalyst. It is to be noted that the inhibitors are reactive to change their forms, strengthening or weakening the inhibition. GC-AED can also follow such change of structure and inhibitors at the same time.

Denitrogenation is also a target of refining. Reactivity, inhibition and susceptibility to inhibition of other nitrogen species are studied similarly. Figure 5 illustrates the reactivity of nitrogen species and the changes of their forms during the reaction, conforming the reaction scheme.

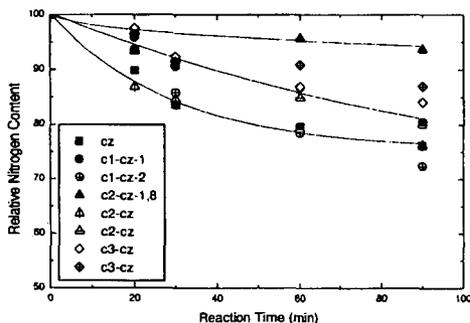


Figure 5. Reactivity of nitrogen species in FSL hydrotreated over $NiMo/Al_2O_3$ catalyst at $340^\circ C$ under 5Mpa of H_2 . Background is removed in calculation. Number before and after symbol means number of methyl group and its location.

Desulfurization and Hydrocracking of Vacuum Residue and Coal Liquefaction

Longer term operation and higher middle distrate yield have been continually pursued in the desulfurization of vacuum residue. The reactivity of asphaltene for coking or strong adsorption as well as cracking, hydrogenation, desulfurization and removal of metals in asphaltene are major concerns. The higher conversion of asphaltene is a key to improve the efficiency in the coal liquefaction.

Changes of polymeric structure in the reaction suggest the route of distillate production. GC-AED is a powerful tool to identify the cracked products as the elemental parts of asphaltene.

Changes of asphaltene tell us schemes for dry-sludge and coke/carbon formation. The authors are interested in clarifying by XRD the change in the entanglement and stretching of the asphaltene in the heated solvent through the hydrogenation, cracking, and dealkylation.

Reactivity of Char for Gasification

The reactivity of char, coke/coal or the graphite has been major research interest. However severer conditions in terms of temperature rather than the reaction, non-catalytic process and gasifying reagent appear to suggest that the reactivity is basically governed by rather physical factors to influence the reactivity for gasifying conditions. The gasification of the next generation may revive the catalytic one under mild conditions to produce products of higher calorific value. The reactivity to achieve complete conversion of carbon may reflect the chemical structure of the hexagons and their assembles. The contact or holding and transfer of the catalyst are the other concerns.

Catalyst and Process Designs of Hydrocarbon Fuel Up-Grading

Deep desulfurization

Gasoline and diesel fuel have been regulated to carry S contents less than 30 and 50 ppm, respectively by the year around 2005. Desulfurization has been a major target of petroleum refinery, and further revolutionary reduction of S is now within the scope.

Process and catalyst designs are equally pursued. According to the references, how to enhance the reactivity of refractory sulfur species and to reduce the inhibition are keys for the design.

Multi-stage processes have been proposed for this purpose. Reduction of product inhibition, in addition to selective activation of refractory sulfur species and suppression of partner's inhibition, is a key issue for the process. The author proposed a reactor of a novel concept as shown in Figure 6. There are problems to be solved in the catalyst form. Nevertheless, I believe it is possible and useful.

The removal of trace refractory species is another way to achieve deep desulfurization. The regeneration of remover and use of removed species are the tasks to be solved. Carbon with catalytic function can be a promising candidate for this purpose.

The catalyst for deep desulfurization has been continuously looked for. Higher activity of alumina supported sulfide has been achieved to satisfy the present regulation. Novel supports in addition to combinary sulfides can be targets to be studied. Acidity of the support is now concerned in the desulfurization in terms of hydrogenation, isomerization and resistivity against H₂S. Basic nitrogen species including NH₃ must be taken care of to reduce their inhibition and catalyst deactivation.

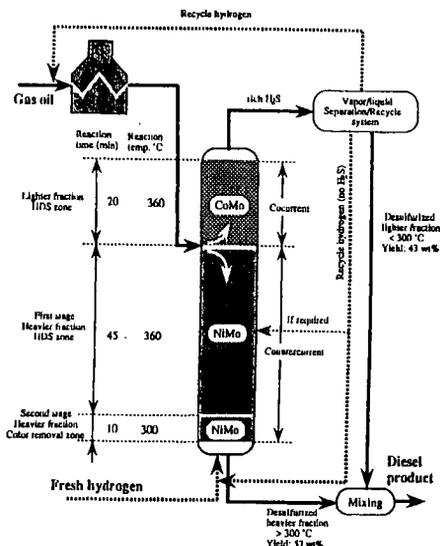


Figure 6. Deep HDS reactor design with cocurrent and countercurrent liquid-gas contact in separate catalyst beds.

Hydroprocessing of Vacuum Residues

Hydroprocessing of vacuum residue has been designed to consist of several steps, removal of solid contaminants such as NaCl and FeS, catalytic demetallation, catalytic modification of

heavy asphaltene and catalytic desulfurization of whole VR including asphaltene. Removal of solid contaminants is very important for the life of the catalytic reaction, because they are triggers of coke plugging in the guard and catalyst bed front although the step is often ignored. Soluble precursors of the iron often pass through the filter to deposit on the guard where FeS accelerates physically and chemically the coke formation.

Deep demetallation and capacity of the demetallation agent are most wanted to prolong the continuous operation time. Better demetallation agents are strongly wanted. Chevron patented a moving bed demetallation, enlarging the capacity by continuous feed of the agent. Pore size is considered very important to accept heavy asphaltene which carries most of porphyrins. Large surface area to fix the metal sulfides is also important for large capacity. Hence pore size and surface area are compromised.

HDS of asphaltene requires also enough size of pores to asphaltene. Thus, the digestion of asphaltene is key factor of the hydroprocessing and hence liberation of micelle is particularly important. Otherwise only maltene and light asphaltene are hydrotreated, leaving heavy asphaltene unreacted or thermally dealkylated, resulting in the formation of dry sludge.

The author has proposed prehydrogenation of asphaltene at lower temperatures to break mineral, reducing the coking to enhance the demetallation and HDS. Nano-particle carbon composite can be a candidate for these purposes. Such carbons carrying NiMoS have been proved an excellent catalyst for coal liquefaction. Low gravity allows the recovery from ash minerals after the liquefaction.

Catalytic Gasification

The author believes that the catalytic gasification of new generation is in time of development after the slugging and fluidized bed gasification. The catalytic activity of highly dispersed catalytic materials on the char surface has been reported remarkably high through the spillover mechanism. The difficulty of the catalytic gasification is how to keep the intimate contact between the catalyst molecules and chars both of which are usually solid of certain particle size. Fluidized bed of char in the catalyst bed materials may realize such a catalytic gasification. However the contact of the catalyst particle and the char is limited only at their outer surface, catalytic efficiency becoming so low. The formation of sulfate, chloride or even carbonate deactivates the catalyst. The present authors have proposed a catalytic missile of alkali metal which can go back and forth between char surface and support. Perovskite type oxide has been proved to play such a role of support. Another important feature is to activate the inactive form of the metal salts by virtue of catalytic reduction with char on the support surface. Such a reduction allows the repeated travel between the char and support. The demonstration by the moving bed is now under planning.

Conclusions

Fuel science in 21 century must emphasize three aspects.

1. Very basic understanding and problem shooting of on-going fuel processing technology
 2. Support to the developing processes in terms of smooth operation with lower cost and better efficiency
 3. New concepts for fuel processes of the next generation
- Fuel science can help or create the novel processes and essential trouble shorts based on the better understanding of fuels and their natures at their fundamental levels.

Acknowledgement

The author is grateful to Dr. D.D. Whitehurst, John Shinn, David Grudoski, Peter, Barry Cooper, and Henrik Topsoe for their discussion and support as well as his coworkers at Kyushu University.

Key words : hydrocarbon fuel, catalytic process, molecular approach.

SUPPRESSION OF NITROGEN OXIDES EMISSION BY CARBONACEOUS REDUCTANT

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Keywords: Coal Combustion, NO_x , Surface Complexes

Abstract

For several decades many attempts have been made to suppress the NO_x emission from coal-fired power plant. In order to meet a more stringent environmental regulation in future, it is necessary to develop new technologies. In this paper, the effective measures achieved so far will be summarized and then the unsolved problems will be discussed. Among them, the understanding of the heterogeneous reactions, where char surface is involved, is not enough. Thus we have investigated the heterogeneous reactions of the NO_x formation and destruction over char surface. The formation of NO during coal char combustion was examined by paying attention to the role of surface nitrogen species on char. The reactions of model carbon with NO as well as N_2O were also examined both experimentally and theoretically.

The Present State of the Art

In the 21st century, we may have to use more coal to meet the increasing energy demand, but unfortunately the use of coal results in many pollution problems. NO_x is the cause of acid rain, photochemical smog and greenhouse effect. N_2O is another important greenhouse gas and contributes to ozone depletion. The suppression of these gases is one of the most urgent subjects for us. Without any measures coal-fired power plant may emit NO_x of more than 700 ppm. Thanks to many efforts in the last 25 years, emission was reduced to a considerable extent. As primary measures, low NO_x burners, air staging (overfire air), fuel staging (reburning), flue gas recirculation and others were developed (Fig. 1), and selective catalytic reduction (SCR) or selective non-catalytic reduction are widely used as secondary measures [1]. Simply speaking, the purpose of these technologies is either to decrease NO_x formation by moderating combustion temperature or to enhance the reduction of NO_x once formed. Main reducing agents in furnace are hydrocarbon radicals and coal char, while NH_3 and urea are used to reduce NO_x in flue gas.

The present state of the art can be summarized as follows. Primary measures achieve 30-70% reduction in NO_x when applied separately. Higher reductions, up to 90%, can be achieved with their combination. Therefore, the reduction to 150-200 ppm level is easily achieved in advanced coal-fired power stations without SCR unit. If these primary measures are combined with SCR, the emission level can be suppressed to as low as 50-70 ppm. The most recent study even claims the success of designing a burner to reduce the NO_x level below 100 ppm, by keeping the amount of unburnt carbon at 3%. In Japan, legislation to limit NO_x emissions was enforced in 1970's, with more stringent standards in 1987. Occasionally even severer regulation is enforced by regional authority. Most frequently used primary measures are the combination of low NO_x burner and air staging. Sometimes flue gas recirculation or reburning is used in addition. SCR unit is also installed in many plants. The situations in other countries are quite different. For example, common power plants in the US use only low NO_x burners and the NO_x emission level is around 240 ppm.

These technologies became possible only through a fundamental understanding of the formation and destruction mechanisms that affect the overall NO_x emission. It can be said that the principal mechanisms have been identified in most cases. The formation of thermal NO_x , Zeldovich NO_x , is initiated by the reaction between O radical with N_2 in air. Another source of thermal NO_x is known as prompt NO_x , where hydrocarbon radicals assist the decomposition of N_2 leading to the NO_x formation. The most important contribution to the overall NO_x emission in coal-fired plant comes from fuel nitrogen. About 75-90% of NO_x is due to this source when low NO_x burner is used. The fate of fuel nitrogen is illustrated in Fig. 2. The volatile nitrogen and char nitrogen are oxidized to NO, and the NO is reduced by various reductants including char. The formation of NO_x from coal nitrogen is quite complex and not yet fully understood. The reduction of NO_x over char surface takes place to a significant extent. However, the contribution of this reaction on the overall NO_x reduction is not yet clear. The reaction mechanism, especially in high temperature zone, is also not well understood.

Regulations for NO_x and N_2O will become more and more stringent in near future. Without knowing the detailed mechanism of the reactions occurring during coal combustion, it would be difficult to meet such regulations. The formation of NO_x from fuel nitrogen and the decomposition of NO_x over char surface should be elucidated. The N_2O formation and destruction mechanism is also important to find out the best way to reduce it. At present, there is no regulation on N_2O emission, but about 50 ppm of

N₂O is emitted from fluidized bed coal combustor.

The Scope of this Paper

Among all reactions occurring in coal-fired combustion system, the least clear parts are the char-related reactions. Formation of NO_x from char and the reduction of NO_x over char surface are understood only superficially. Therefore in order to get a clearer picture of these reactions, we have investigated the mechanism of C-NO_x reaction. For the purpose of simplification, we used PF char (phenol formaldehyde resin char) as a model of coal char. This does not have inherent nitrogen before the reaction. We have studied the reaction of PF char with NO, the reaction of PF char with N₂O, as well as the NO_x formation from coal char combustion. The computer simulation studies have also been carried out for these systems. In this presentation we would like to summarize our results and discuss the future direction related to this field.

The most unique feature of our study is that we have paid a special attention to the role of surface nitrogen species on char. Boldly speaking, combustion people are only interested in the formation of NO_x but not necessarily in the N₂ formation. This was deduced from the fact that many studies have used air as oxidizing gas. This is simply because air is used in practical combustion systems. Thus the formation of N₂ has been neglected and, as a result, the nitrogen mass balance has not been obtained. On the contrary, we are interested in the overall reaction pathways including the formation of N₂. Thus we used O₂-He mixture instead of O₂-N₂ mixture for the coal char combustion, and NO-He mixture for the study of C-NO reaction. Thus we could establish the accurate nitrogen mass balance. Through this attempt, the amount of nitrogen species on carbon surface during the reaction could be quantitatively determined. It is well known that such surface species play an important role in many carbon gasification reactions.

Reaction of PF Char with NO

We have studied the C-NO reaction from various aspects, and have made several new findings in these studies [2-5]. First, the accurate mass balance clearly showed the presence of nitrogen accumulated on carbon surface. Many studies had noticed the presence of such surface nitrogen species, but there had been neither direct evidence nor quantitative data. Not only from the mass balance, but also from the XPS analysis the presence of surface nitrogen species was confirmed very clearly. The reaction can be described as



where C(·), C(N) and C(O) denote the surface free site, nitrogen and oxygen complexes, respectively. Then, the N₂ formation mechanism from C-NO reaction was identified in step response experiments using isotope gases. The reactant gas was switched from ¹⁴N¹⁶O to ¹⁵N¹⁸O during the reaction with PF char, and the product gases were analyzed (Fig. 3). The appearance of ¹⁴N¹⁵N immediately after the introduction of ¹⁵N¹⁸O strongly suggested that the main route for N₂ formation is as eq 2.



This holds true in a wide range of temperature from 600 to 1000 °C. This study presented the elementary reaction step of N₂ formation for the first time. Before this study, it was thought rather ambiguously that N₂ is formed from two C(N) species.

Effect of O₂ on the Reaction of C-NO

In the coal combustion system, the NO reduction by char takes place more or less in the presence of O₂. The effect of O₂ on the C-NO reaction is very remarkable. For example, N₂ formation rate is significantly increased by the presence of O₂, and N₂O formation is greatly affected by O₂. Even though the reasons for these observations are not known, there has been almost no systematic study on the C-NO-O₂ system. We carried out step response experiments in the presence of O₂, and it was found that the main N₂ formation path is similar to eq 2 [6]. As for the N₂O formation during the C-NO reaction, many studies reported that there is no N₂O formation in the absence of O₂ [7]. On the contrary, we observed some N₂O formation in the absence of O₂. This finding is practically not so important, but from a fundamental point of view this is important for identifying the true reaction mechanism. We need to revise the former explanation for this reaction.

Simulation of C-NO Reaction by Molecular Orbital Theory

The chemisorption of NO molecule on carbon surface and the subsequent decomposition of the surface species were simulated by an *ab initio* molecular orbital theory (MO) [8]. For simplicity, single layer of polyaromatic compounds was employed as a model for carbon. The MO calculation of the system including both the model carbon and NO molecule was made, and its geometrical parameters were optimized. The adsorption of NO on carbon edge sites resulted in the formation of several types of stable NO containing complexes, C(NO). To elucidate the N₂ formation route from the

surface nitrogen complexes, one more molecule of NO was put on the N atom of the C(NO) species. The MO calculation predicted the formation of six-member ring complex including NNO bonding. The bond population analysis predicted that N₂ desorption from such complex is very probable. The N-O bond is so weak as seen in Fig. 4 that C(NN) complex will be formed. The C-N bond in the resultant species is much weaker than N-N bond, and it can be easily dissociated to release N₂ molecule. This reaction scheme is exactly the same as eq 2, which was experimentally implied.

Reaction of PF Char with N₂O

Compared with the reaction with NO, the reduction of N₂O by carbon and the formation of N₂O from coal char are investigated to lesser extent. These reactions are not important at high temperature combustion, but very important for low temperature process like fluidized bed combustion.

In the case of the reduction of N₂O by carbon, it has been assumed that N₂ is produced from N₂O without any bond breaking between two nitrogen atoms, although there was no direct evidence. We have carried out a step response experiment, and found the reaction mechanism being eq 3 as was expected. There is little N=N splitting during C-N₂O reaction [9].



In MO simulation study, the calculation predicted the release of N₂ and the formation of C(O) when N₂O was put on the carbon edge [8]. This is again in agreement with the experimental observation.

NO_x Formation from Coal Char Combustion

As a result of recent development in low NO_x burner, the contribution of coal nitrogen to NO emission is of significant importance. In particular, the char nitrogen is the major contributor to the overall NO emissions. Therefore many studies have been carried out in relation to this reaction, and the importance of secondary reactions is suggested [10]. However, few researchers have shown an interest in the quantitative analysis of secondary reactions. We have carried out the reaction of coal char with O₂ in a fixed-bed reactor until the complete conversion of char, and established the mass balance. Fig. 5 shows the result of isothermal reaction at 850 °C with different bed heights. Several common features are noteworthy; (1) as a total, the major product was N₂, followed by NO, with a very small amount of N₂O, (2) the ratio of NO/N₂ was very small at the beginning but became almost unity at the final stage of reaction, and (3) the ratio decreased with increasing bed height. All of these observations can be explained if the occurrence of secondary reaction on char surface is assumed. We would like to emphasize again the important role of surface nitrogen species in this reaction. NO is expected to be the primary nitrogen-containing product from char combustion. NO thus produced would react with the char in the downstream to produce C(N), which then react with another NO to produce N₂ as in eq 2. If the remaining char became less and less, NO would escape from the bed without being converted to N₂. Thus the fractional conversion of char nitrogen to NO increased with char burn-off. This is in contrast with the observation by De Soete who reported that the fractional conversion of char nitrogen to NO was approximately proportional to the carbon burn-off [11]. This is probably due to the difference in reactor type, but further work is required.

Future Subjects

We now realize that we do not know much about the char-related NO_x reactions. We have to further investigate what actually happens in combustor. Especially the reaction behavior of char rapidly heated to high temperature should be explored. Through these studies, we may be able to design a better combustor with a lower NO_x emission.

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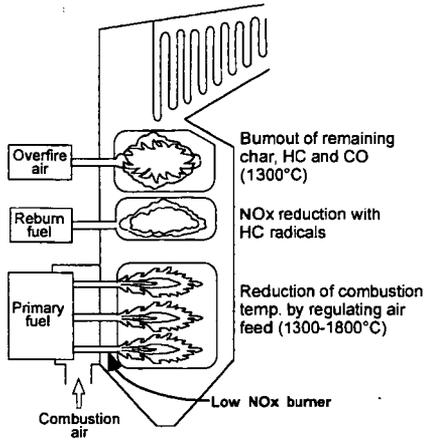


Figure 1. Advanced utility boiler with various measures for NO_x reduction.

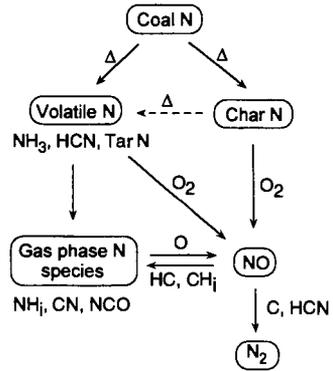


Figure 2. Reaction pathways to the formation of NO and N_2 from coal nitrogen.

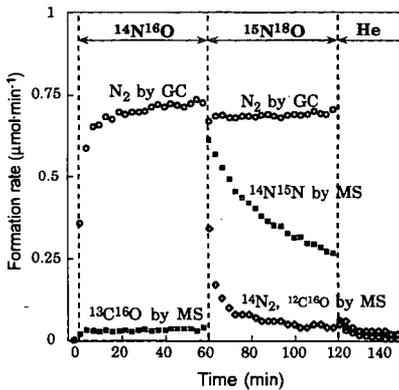


Figure 3. N_2 evolution profile during a step response experiment for C-NO reaction at 850°C .

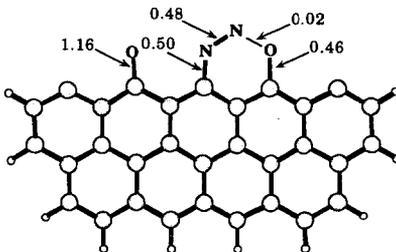


Figure 4. Stable structure of carbon with two NO molecules, suggested by MO simulation. Numbers indicate parameter of bond strength.

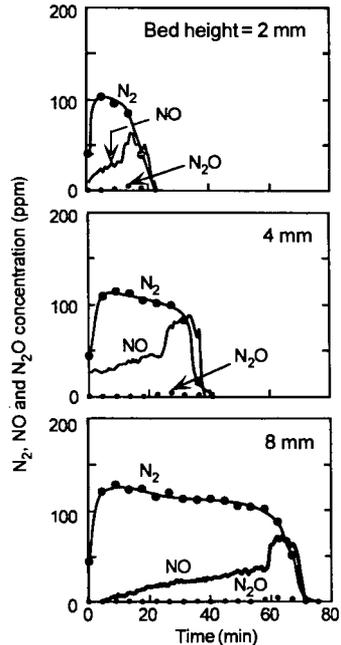


Figure 5. Effect of bed height on the gas evolution during O_2 gasification of coal char at 850°C .

CHARACTERIZATION AND REACTIVITY OF ORGANICALLY BOUND SULFUR AND NITROGEN IN FOSSIL FUELS

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Keywords: organic sulfur, organic nitrogen, characterization

Introduction

The chemistries of organically bound sulfur and nitrogen forms impact significantly on the reactivity of and utilization strategy for fossil fuels. Previous inability to speciate and quantify the chemical forms of these heteroatoms coupled with the lack of a suite of standardized, well preserved, well characterized coals of varying rank limited the gaining of understanding of important fundamental chemical mechanisms. Advances in X-ray instrumentation over the last decade, along with the establishment of the Argonne Premium Coal Sample Program have allowed the determination and quantification of organically bound sulfur and nitrogen forms in fossil fuels and has led to deeper understanding of their reactivities. This paper reviews recent technical advances in this area and highlights several areas where significant progress in chemical understanding has been achieved and speculates about future trends.

Organically Bound Sulfur Characterization

In the last decade, major advances have been made in speciating and quantifying forms of organically bound sulfur in fossil fuels, involving both reactive and direct measurements. One reactive method uses flash pyrolysis¹, while the direct measurements involve XPS², K-Edge X-ray Absorption Near Edge Structure Spectroscopy (XANES)^{3, 4} and L-Edge XANES⁵. The XPS and sulfur K-edge XANES methods were used to determine the forms of sulfur in the suite of Argonne Premium coals⁶, and the results from XPS and two different K-edge XANES methods are plotted together in Figure 1. The accuracy of the latter methods is reported to be ± 10 mole%. It was concluded that in low rank coals there are significant amounts of aliphatic sulfur (i.e., dialkylsulfides), and that levels of aromatic sulfur (i.e., thiophenes and diarylsulfides) increase directly as a function of increasing rank^{3, 4}. The X-ray methods have been used to follow the chemistry of organically bound sulfur under mild oxidation in air⁷, where it was shown that the aliphatic sulfur oxidizes in air much more rapidly than the aromatic sulfur, pyrolysis^{8, 9}, single electron transfer and strong base¹⁰ conditions. Recently, results from the XPS and K-edge XANES methods have been shown to compare favorably with those from flash pyrolysis¹¹, mass spectrometry¹², and temperature programmed reduction (TPR)^{13, 14}. This is a particularly important development since an approach to sulfur speciation using these techniques may be much more readily available than X-ray methods. In the future, speciation and quantification of organically bound sulfur by a pyrolysis GC/MS analysis or TPR approach may develop into a standard laboratory method.

Organically Bound Nitrogen Characterization

It is necessary to know how nitrogen is incorporated in the organic matrix, since it has been apparent for some time that nitrogen species play a role in coal asphaltene behavior¹⁵ and in coal conversion chemistry¹⁶. X-Ray Photoelectron Spectroscopy (XPS) was used to speciate and quantify accurately the forms of organically bound nitrogen^{17, 18}, including the basic pyridines and quinolines and the weakly acidic or neutral indoles and carbazoles. These measurements, done on a suite of UK coals containing 80wt% or more carbon, indicate that basic nitrogen increases as pyrrolic nitrogen decreases as a function of carbon content. The organically bound nitrogen forms in the Argonne Premium coal samples⁶ were determined by XPS¹⁹. The quantitative distributions of nitrogen types in Argonne Premium coals from XPS analyses are plotted in Figure 2 as a function of wt% Carbon. For fresh Argonne Premium coals, pyrrolic nitrogen was found to be the most abundant form of organically bound nitrogen, followed by pyridinic, and quaternary types. It is clear from Figure 2 that the distributions are rank-dependent, with the highest abundance of quaternary nitrogen in the lowest rank coals. The concentrations of this form decrease while pyridinic, or basic nitrogen forms appear to increase correspondingly as a function of increasing rank. The quaternary species were attributed to protonated pyridinic or basic nitrogen species associated with hydroxyl groups from carboxylic acids or phenols¹⁹. Similar distributions from XPS analysis of coal as a function of rank were independently confirmed³². The predominance of pyrrolic and pyridinic nitrogen forms in Argonne

Premium coal was verified by recent desorption high-resolution mass spectrometry both with whole coals and their pyridine extracts³³. The sensitivity of the XPS approach for amino nitrogen species in fossil material has been established^{28, 29}. Samples of recent sediments with up to 45% amino nitrogen²⁹ and pyrolysis tars of kerogen with up to 33% amino nitrogen²⁸ have been reported.

X-ray Absorption Near Edge Structure spectroscopy (XANES) has also been used for characterization of nitrogen forms in petroleum asphaltene^{20a} and Argonne Premium coals^{20b}. These early nitrogen XANES results are not in total accord with those from XPS. Pyrrolic nitrogen appears to be the major form of organically bound nitrogen measured by both techniques. However, the XANES results report, in addition to pyrrolic and pyridinic nitrogen, the presence of aromatic amines and also pyridone forms, the latter in amounts similar to pyridinic nitrogen. In addition, the XANES results do not report the presence of quaternary nitrogen. While the XPS results were largely confirmed by high resolution mass spectrometry³³, opportunities remain for further development of an XANES approach for nitrogen speciation.

Solid state ¹⁵N nmr offers much promise for characterizing nitrogen forms. The difficulties in developing a solid state ¹⁵N nmr technique for the characterization of nitrogen forms in coals have been discussed, and progress is being made²¹. An earlier attempt to characterize the nitrogen forms in three Penn State coal bank coals by solid state ¹⁵N nmr reported the observation of pyrrolic but not pyridinic nitrogen forms²². This appeared to be in contradiction with XPS and XANES data, however more careful work on Argonne Premium coals and their acidified derivatives showed the presence of pyridinic nitrogens. In the future, it is expected that the current hurdles will be overcome and that the technique will be used almost routinely for characterizing organically bound nitrogen forms.

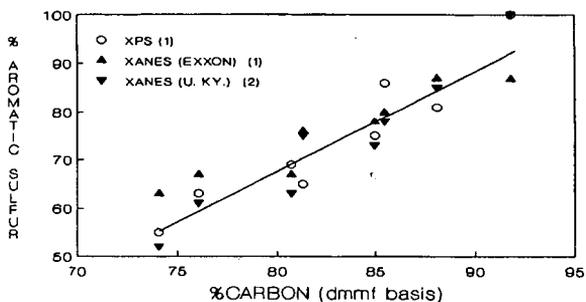
X-ray Photoelectron Spectroscopy (XPS) was used to help define the possible correlation between the functional forms of nitrogen in coals and the formation of NO_x precursors during combustion processes^{23, 30, 31}. These studies showed that the impact of structural variation in nitrogen forms initially present in coal was secondary to the effect of other coal combustion factors^{30, 31}. XPS has also been used to characterize the forms of nitrogen found on carbon surfaces after treatment with NO_x²⁴. XPS was used to identify and quantify the changes in organically bound nitrogen forms initially present in the Argonne coals in their tars and chars after pyrolysis²⁵. In that study, coals were pyrolyzed in a temperature programmed decomposition (TPD) apparatus²⁶ at 0.23°C per second up to a specified temperature then cooled. Several temperatures from 400-810°C were chosen. Tars and chars from each pyrolysis temperature were collected and analyzed for nitrogen forms distribution by XPS. The reproducibility and repeatability of the nitrogen curve resolution results (± 3 mole %) is the same as in a previous investigation of fresh Argonne premium coal samples¹⁹. Representative changes in the nitrogen forms in two Argonne coal chars as a function of temperature are shown in Figure 3. Some of the quaternary nitrogen species are lost at the very earliest stage of pyrolysis, however, the major changes occur over a relatively narrow temperature range (600-700°C). Above 600°C the loss of pyrrolic forms is accompanied by a rise in the relative number of quaternary nitrogen forms in the chars, as noted by Pels, *et al.*²⁷ and Kambara, *et al.*²³, and the quaternary and pyridinic nitrogen forms become the dominant forms in severely pyrolyzed chars. The significant disappearance of pyrrolic nitrogen in these high temperature chars confirms the suggestion of Pels, *et al.*²⁷, that pyrrolic nitrogen is partly converted into pyridinic nitrogen. Quaternary forms are proposed to arise from incorporation of pyridinic nitrogen into the growing polynuclear aromatic structures.

Future Outlook

In summary, methods are available today to get the kind of detailed information on important coal structural features that was not available just a few years ago. They are being applied to a standard suite of coals, and this represents an important advance in order to define the parametric variations as a function of coal rank. Exciting new opportunities now exist for elucidating and understanding the detailed chemistry taking place during conversion procedures by using these methods to characterize the reaction products as well as the starting coals. Mechanistic inferences and structure-reactivity relationships can be built based on this information.

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Figure 1. Organic Sulfur Speciation and Quantification by S-XANES (refs. 3, 4)

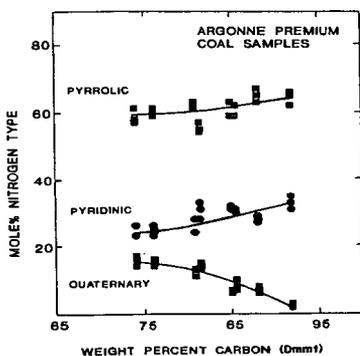


Figure 2. Organic Nitrogen Speciation and Quantification by XPS. (ref. 19)

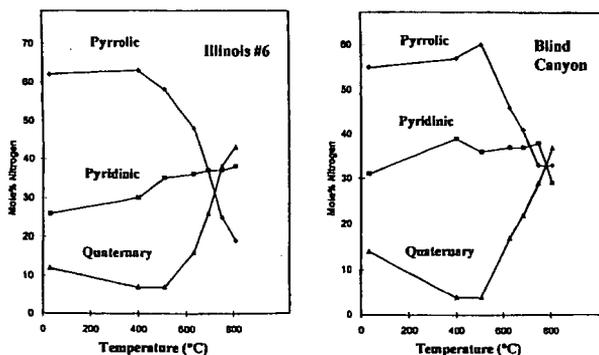


Figure 3. Tracking the Reactivity of Organically Bound Nitrogen Species (ref. 25)

Non-covalent Interactions in Coals

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ABSTRACT

The interactions between bituminous coals and organic molecules can be quantitatively described using only two terms: interactions dependent on polarizability and acid/base interactions, especially hydrogen bonding. Except for groups having an unpaired electron (the coal radical sites), the same two forces so dominate coal-coal interactions that it is not necessary to invoke any others. Except for radical sites, HOMO-LUMO gaps are so large that π - π and charge transfer interactions (aromatic "stacking" interactions) are improbable.

DISCUSSION

The aromatic groups in coals can interact with each other by London Dispersion Interactions which increase as their polarizability increases. Electrostatic interactions due to the existence of dipoles or quadrupoles are also important. Charge transfer interactions, in which electron density is transferred from a donor molecule to an acceptor are not important. It makes no difference if the electrons in question are non-bonding or π electrons, charge transfer is not important. The remainder of this article is a justification of the foregoing assertions. The terms π - π and "stacking" interactions occur frequently in the coal literature and are not often defined. They seem to be used to mean associative interactions between aromatic systems due to electron transfer. That is the meaning assumed in this article.

Using gas chromatography to avoid complications caused by diffusion into coals¹, the isosteric heats of adsorption of a variety of organic molecules on the surface of Illinois No. 6 coal were measured.² As expected, noble gases and saturated hydrocarbons gave adsorption heats that are a linear function of molecular polarizability confirming that their interactions with the coal surface are dominated by London Dispersion Interactions. Molecules (e.g. pyridine, THF) that are solely bases, that have no ability to donate an acidic proton, lie above the line defined by the non-polars. That excess interaction enthalpy for all 7 bases studied is equal to their heats of hydrogen bonding to p-fluorophenol. The isosteric heat of adsorption of those 7 bases on Illinois No. 6 coal is quantitatively explained by two terms, London forces and hydrogen bonding. There being no need to invoke others, normal scientific practice prohibits it. Contact angle studies also demonstrate that only two terms, dispersion and acid/base interactions, are necessary to describe fully interactions at coal surfaces.³

Is the situation the same when molecules are dissolved in (absorbed by) solid coals? The interactions of organic molecules when dissolved in coals can be monitored by studying volumetric solvent swelling.⁴ Swelling pyridine-extracted Illinois No. 6 or Pittsburgh No. 8 coals with non-polar solvents gives rise to a symmetrical bell-shaped curve when solvent-swelling ratios are plotted against solvent solubility parameters (see Fig. 1). Plotting the swelling caused by basic molecules using their non-polar solubility parameters generates a set points all lying above the line defined by the non-polars. Furthermore, the excess swelling (the amount by which the swelling by bases is increased above the non-polar line) gives good straight lines when plotted against the bases' heats of hydrogen bonding to p-fluorophenol.⁴ This behavior parallels that observed for adsorption and again only hydrogen bonds and London Dispersion Interactions are required to explain the interaction between dissolved molecules and bituminous coals.

The existence of bell-shaped plots of coal swelling by non-polar solvents and of acetylated coals by all solvents¹ is strong evidence against n - n and charge transfer (CT) interactions. This can be argued in two ways. First, the shape of the plot demonstrates that these systems are following regular solution theory. That theory assumes that there is an averaging of the interactions between the coal and the swelling solvent based on the assumption that only dispersion interactions are occurring.⁵ Coal-coal, solvent-solvent, and coal-solvent interactions are all assumed to be solely dispersion interactions. Specific complex formation and the interactions that would lead to them are excluded. Second, the solubility parameter of the coal is that value defined by the peak of the bell-shaped curve. The square of that

solubility parameter value is the cohesive energy density of the coal, a direct measure of the coal's self interactions. For all of the bituminous coals studied, these self interactions are of the same order as toluene's or chlorobenzene's, liquids which self interact by London dispersion interactions and electrostatic interactions due to π -dipole or π quadrupole interactions. These bell shaped curves provide evidence against a significant role for π - π stacking and CT interactions in coals.

A qualitative consideration of π - π stacking and CT interactions using perturbation molecular orbital theory⁶ provides a strong argument against their importance in coals. The benzene dimer is a convenient starting point and example. As a pair of benzenes approach each other in a face-to-face orientation, their interaction gives rise to new bonding and antibonding orbitals by overlap of the highest occupied molecular orbitals (HOMO). The energy difference between the HOMO and the lowest occupied molecular orbital (LUMO) is so large that no interaction between them occurs.⁶ The HOMO-HOMO overlap of the two benzene filled orbitals gives rise to new bonding and antibonding orbitals. Both are filled and the fact that the antibonding orbitals increase in energy more than the bonding orbitals decrease results in a repulsive interaction. The interaction of the two benzene π systems is repulsive. The antibonding destabilization is greater than the bonding stabilization. This is a 2-orbital 4-electron repulsive interaction. The benzene dimer is "T" shaped minimizing this repulsion and maximizing quadrupolar interactions.⁷ Theory and experiment agree.⁷

This model can be used to define those circumstances in which pair-wise interactions will be favorable due to electron transfer. First, if the HOMO-LUMO gap is small, then the HOMO and LUMO can interact. This interaction will give rise to a stabilization because only the bonding orbital will be occupied. This 2-orbital 2-electron interaction might be a charge transfer involving a non-bonding pair of electrons or a π - π interaction between an occupied and an unoccupied orbital. It makes no difference: the description is the same. To explore this possibility, the ionization energies and electron affinities of groups present in coals are tabulated in Table 1. The other possibility is a 2-orbital 3-electron interaction that will occur if a radical center is involved. Since the radical demands a half occupied "LUMO" or HOMO (called a SOMO), there is likely to be an orbital of similar energy available. It does not matter whether the interacting orbital is occupied or not. Both will give rise to a stabilization, greater in the case of a 1-electron 2-orbital interaction than in the case of a 3-electron 2-orbital interaction. The radical centers in coals may be the loci of strong interactions. This possibility is under investigation.

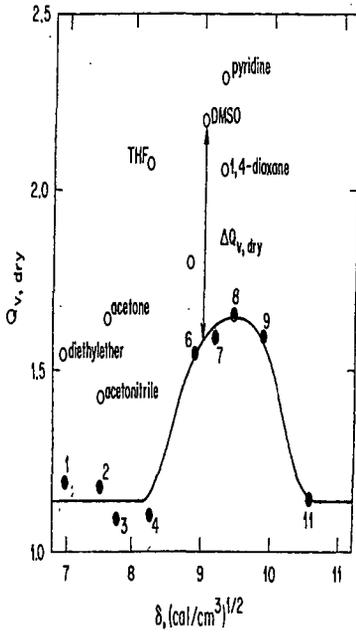
A consideration of the electron affinities (EA) and ionization potentials (IP) in Table 1 leads to the conclusion that π - π and CT interactions in coals are unlikely to be favorable. The HOMO-LUMO gaps are too large to allow CT to occur. This is supported by experiment. Consider first the interactions between several organics and tetracyanoquinodimethane (TCNQ), an electron acceptor with an EA about 50 kcal/mole more favorable than pyrene. The equilibrium constant for complex formation between pyrene and TCNQ is only 29 l/mole.⁸ With materials of lower electron affinity, the equilibrium constant will be even less. For the materials contained in the table, the HOMO-LUMO gap is so large that π - π and CT interactions are unimportant. The HOMO-LUMO gap remains large enough for all reasonably sized molecules to rule out stabilization by electron transfer interactions.

There are numerous experimental and theoretical studies of aromatic-aromatic interactions.⁹ To begin with theory, molecules as large as circumcoronene ($C_{54}H_{18}$) have been studied.¹⁰ Even here, the HOMO-LUMO gap is large enough so that the dominant attractive interactions are dispersion and electrostatic. The most favorable calculated geometry is not face-to-face but displaced and twisted. Effective theory has been developed and applied to numerous aromatic systems.^{7,9,11} It uses attractive dispersion and electrostatic (dipolar and quadrupolar) interactions and repulsions originating from π - π interactions.

There are numerous experimental studies of aromatic-aromatic dimers and multimers, most formed using molecular beam techniques.⁹ The geometries vary depending on the nature of the interactions and especially on any charge separation in the molecules. The range from "T" shaped, to a " π " shaped trimer¹², to face-to-face coplanar dimers^{13,14} where dipolar and quadrupolar interactions are most favorable in this geometry.¹⁵ In none of these is the primary interaction due to ground state electron transfer.

The principal attractive interactions between pairs of aromatic systems depends on the polarizabilities and dipole and quadrupole moments of the interacting systems. The filled orbital interactions are repulsive. This issue and others will be discussed in a full paper together with the evidence (or lack thereof) for π - π stacking and CT interactions in coals.

Figure 1. Volumetric swelling ratio (Q_v) for pyridine extracted Bruceton coal as a function of the solubility parameter of the non-polar solvents (\bullet) and the non-polar stability parameter of the polar solvents (\circ)



- 1) n-pentane, 2) n-heptane,
 3) methylcyclohexane, 4) cyclohexane,
 5) o-xylene, 6) toluene,
 7) benzene, 8) tetralin, 9) naphthalene,
 10) carbon disulfide, 11) biphenyl

=Table 1. Molecule Ionization Potentials (IP) and Electron Affinities (EA)

Molecule	IP (eV)	EA (eV)
Benzene	9.24 ^a	-0.72 ^b
Naphthalene	8.15 ^a	0.15 ^b
Anthracene	7.42 ^a	0.66 ^b
Phenanthrene	7.90 ^a	0.31 ^b
Pyrene	7.43 ^a	0.56 ^b
Pentacene	6.66 ^a	1.35 ^b
Coronene	7.36 ^a	
Phenol	8.51 ^c	-1.01 ^d
Aniline	7.7 ^c	-1.13 ^d
Pyridine	9.3 ^c	-0.62 ^d
Maleic Anhydride		1.33 ^e
TCNQ		2.84 ^e
TCNE		2.77 ^e
CS ₂		0.90

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NOVEL DIMENSIONS IN ON-LINE PROCESS SPECTROMETRY

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INTRODUCTION

The myriads of novel chemical processes the new millennium may be expected to bring to future generations will require increasingly sophisticated process characterization and monitoring techniques. Over the past decades the advantages of on-line, in-situ and/or real-time spectrometric techniques have been widely demonstrated. The main challenges for the new millennium will be: to achieve higher information yields and sample throughputs; to develop intelligent devices that interpret their own measurement data; to close the feedback process control loop; to probe harsh reaction environments in real-time; and to reduce total lifecycle costs for on-line spectrometry equipment.

INCREASING INFORMATION YIELD AND RATE

As discussed convincingly by Hirschfeld [1] and by Giddings [2], the most effective way to achieve higher information yields is to couple two or more compatible analytical techniques into a single "hyphenated" tandem method. Well documented examples include GC/MS, LC/MS, MS/MS, GC/IMS and GC/FTIR. (It may be noted that the term "hyphenated" - popularized by Hirschfeld - is somewhat of a misnomer since IUPAC nomenclature prescribes the use of forward slashes rather than hyphens to depict tandem instrument configurations). Hyper-hyphenated methods, featuring as many as four different analytical instruments in tandem have also been described, e.g. TG/GC/FTIR/MS [3]. Even more analytical dimensions can be added through "tandem-in-time" configurations such as in ion trapping MSⁿ methods, with n readily achieving values of 6 or 7 [4]. Also, it should be pointed out that as many as four useful analytical dimensions can be added by recording temporally [5] as well as spatially resolved spectra. An example of the use of time-resolved, on-line MS data to deconvolute a complex mixture of coal pyrolysis products, evolving from a small Curie-point pyrolysis reactor, into its main maceral constituent patterns, is shown in figure 1.

Unfortunately, our ability to add analytical dimensions has greatly outpaced our ability to process and interpret multidimensional data. Some progress is being reported in the development and application of principal component analysis techniques for three-way data matrices [6]. Also, the class of algorithms loosely described by the term ANN (artificial neural networks) is in principle capable of handling n-dimensional data outputs [7]. However, most of us are still struggling to comprehend multivariate data analysis results for two-way data matrices. Clearly, processing and interpretation of n-way data matrices is an area with much room for progress in the new millennium.

Whereas hyphenated methods are widely known for their ability to increase information yields, less well recognized is their potential for increasing analysis speed. At first sight it is counterintuitive that the coupling of two instruments in tandem could produce shorter analysis times. However, as pointed out by Giddings [2], to the extent that the information provided by independent, the resolving power of the tandem instrument equals the product of the resolving powers of the two modules. Since many analytical techniques can trade resolving power for speed the required minimum resolution for a given analytical application can often be reached with both modules operating in a high speed, low resolution mode, as illustrated in figure 2.

Interestingly, low resolution analytical modules also tend to be easier to miniaturize (or, perhaps more correctly stated, miniaturization tends to result in lower resolution) leading to the paradoxical conclusion that hyphenated methods may well lend themselves better to miniaturization and micro-miniaturization and, thus, to use as on-line analytical devices. The added complexity of the control electronics and software required to control hyphenated devices versus single stage modules may hardly increase the size and cost of large-scale-integrated electronic chips. In short, the future for hyphenated techniques in on-line process analytical applications is likely to be equally bright as in today's conventional analytical laboratory environment where the majority of new GC systems purchased is now equipped with an MS "detector".

PROBING HARSH REACTION ENVIRONMENTS

The suitability of stand-off spectroscopic techniques for probing high-temperature, high-pressure, high-radiation, highly corrosive and/or abrasive environments is widely known and is only limited

by the relatively low resolving power for complex chemical mixtures, by the availability of suitable window materials, and by the optical properties of the reactor contents. Since continuing progress can be anticipated in all these problem areas, the role and importance of stand-off spectroscopic process analysis techniques may be expected to help increasing over the next few decades.

Compared to stand-off techniques, the suitability of typical point detection methods (i.e. methods requiring physical transport of molecules, sampled at a given point in space and time, into the detector) for probing harsh reaction environments is less immediately obvious. Yet, the superior separation and identification capabilities of point detection methods such as MS (with or without chromatographic pre-separation) have time-and-again induced scientists and engineers to use MS-based methods in highly forbidding environments. An example of the use of on-line GC/MS for monitoring a 600 F flue gas stream, laden with abrasive ash particles, on the 7th floor of a rumbling, dusty coal combustor situated in a building subject to circadian temperature variations in excess of 50 F, is shown in figure 3.

Fortuitously, the use of rugged sample probes lined with fused silica, quartz or other refractory materials is often compatible with the required operating conditions for a given point detector, particularly in combination with highly flexible, readily heatable, capillary transfer lines. This approach enables successful coupling of GC/MS instruments to reactor environments with pressures in the several thousand psi range, including supercritical environments (see figure 4) and temperatures in excess of 1800 F [8]. Nonetheless, there is considerable room for further improvement in sample transport systems, e.g. capable of entraining fine particulate matter indigenous to the sample stream or produced with the help of ablative laser probes. Another, as yet unexplored, sampling strategy would be to enlist the support of "stand-off sampling techniques" for point detectors, e.g. by shooting fast traveling vortices, capable of entraining vapors as well as fine particulate matter, across reactors into the point detector inlet.

REDUCING INSTRUMENT LIFECYCLE COST

Most on-line spectroscopic techniques have a reputation for high capital equipment cost, very high maintenance cost and exorbitantly high operating cost (due to the need for highly trained operators). As a result most production managers are understandably reluctant to introduce novel spectroscopic techniques into existing process operations unless there are serious problems. Consequently, new opportunities for on-line spectroscopic techniques must primarily may need to be sought in the development and testing of novel processes and pilot plants.

Recent breakthroughs in the design of highly miniaturized and/or microfabricated MS analyzers promise to drastically change the instrument lifecycle cost equation for this type of analyzer within the next few years. Not only are these miniaturized MS analyzer modules (including ion source and detector) likely to become available commercially at a cost of less than US \$1,000 but — due to the difficulty of exchanging or cleaning the very small ion source or detector components — they are also meant to be disposable in case of failure or deterioration. The big advantage of this approach is its potential to greatly reduce overall maintenance cost.

Presently, no fewer than three such disposable MS devices are either already available (viz. Ferran's miniature quadrupole head [9]), or may become available soon (viz. a subminiature double focusing magnetic device and an FTICR type MS device; both expected to be introduced at the January 2000 ASMS conference in Sanibel). Present limitations include limited resolving power (i.e. the product of mass range and resolution), as well as relatively low sensitivity and/or speed. As discussed earlier, hyphenation (e.g. by adding a micro-GC preparation module) may eventually help overcome some of these limitations. A related area where major improvements will be needed to match these new developments in MS analyzer technologies is high vacuum pumping. Current high vacuum pump technology is expensive and difficult to miniaturize further.

Finally, the major cost of using on-line spectroscopic techniques, viz. the need for highly trained operators, is only going to come down when the above-mentioned multidimensional data processing and interpretation steps can be fully automated and integrated into the design of the spectroscopic instrument. In other words, development of sufficiently "smart" spectroscopic devices is likely to be the final hurdle on the way to broad acceptance of on-line spectroscopic technologies into the full scale process analysis marketplace.

CONCLUSION

Rapid development of MS-based and other miniaturized and micro-miniaturized, MS based on-line spectroscopic methods can be expected over the next few decades, eventually resulting in the presence of multiple, networked, disposable, hyphenated devices per reactor. The temporally and

spatially resolved information produced and processed by the network will allow an unprecedented degree of process control and quality assurance, as well as rapid troubleshooting capability if and when human intervention becomes necessary.

ACKNOWLEDGMENT

The technical and scientific contributions of many current and former UUCMARC staff members and students need to be acknowledged here. Without their dedicated and inspired work this forward looking article would have had little or no foundation. Together with the support of several sponsors, the contributions of some co-workers are specifically acknowledged in references 3, 5, 8 and 10.

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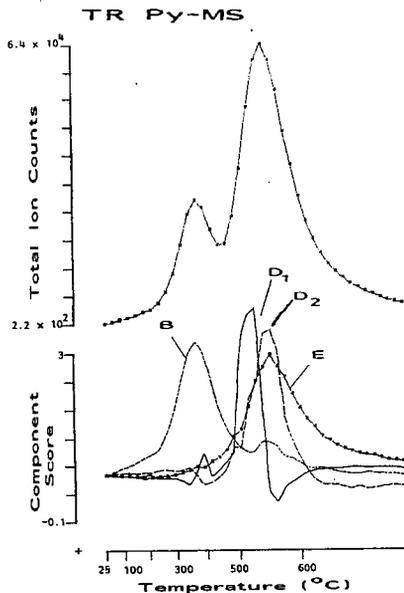


Figure 1. Example of the use of time-resolved mass spectral profiles to produce an additional analytical dimension. The total ion profile in (a), representing Curie-point pyrolysis products evolving from a coal sample, is being deconvoluted into four maceral-like components (b) by means of multivariate statistical analysis methods. For detailed information see reference 5.

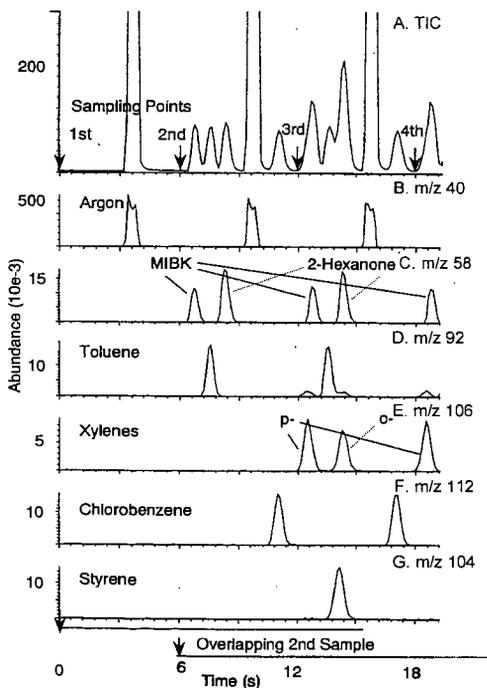


Figure 2. Example of fast, repetitive hyphenated (GC/MS) analysis demonstrating complete resolution of 9 components in 2-dimensional (GC/MS) space although the individual component techniques resolve only 5 (GC) and 7 components (MS), respectively. For detailed information see reference 10.

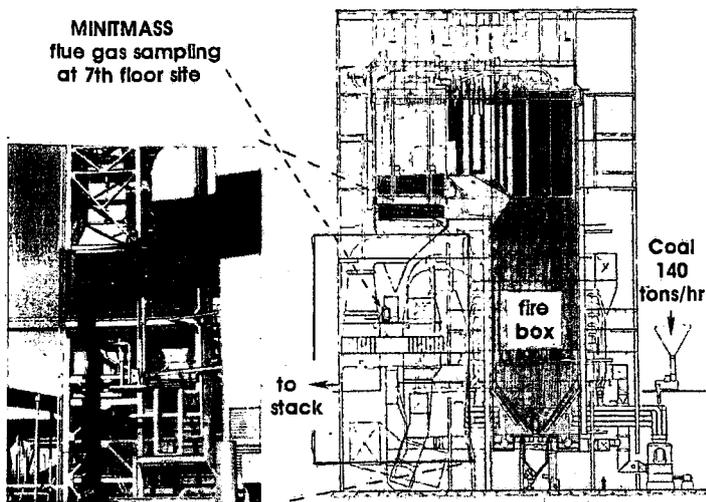


Figure 3. Example of operating a GC/MS instrument, nicknamed "minitmass," in a harsh industrial environment.

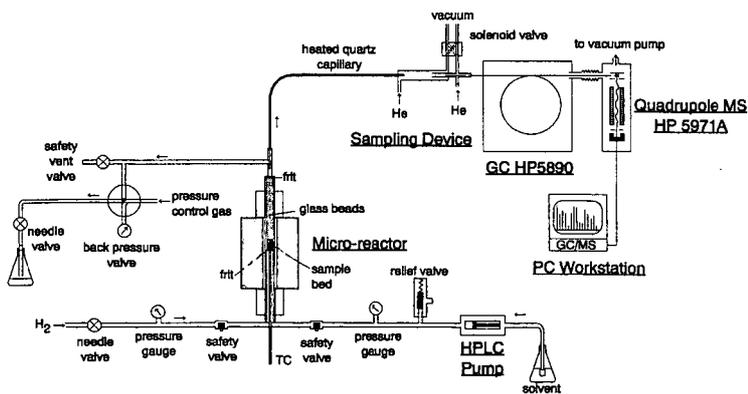


Figure 4. Example of an on-line GC/MS experiment coupled to a bench-scale high pressure reactor operating under supercritical conditions. For detailed information, see reference 8.

THE CHAMELEONIC CARBON SURFACES: ENVIRONMENTAL PROBLEMS AND SOLUTIONS

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KEYWORDS: Coal-derived carbons, surface chemistry, coal conversion

1. INTRODUCTION

Among the fossil fuels, the negative environmental impact of coal is typically larger than the impact of either petroleum or natural gas. Considerations of both conventional pollution (acid rain and smog) and global warming (presumably *caused* by CO₂ accumulation in the atmosphere) cast serious doubts on the continued massive use of coal in the 21st century. A simple back-of-the-envelope calculation illustrates the complexity of the problem. While bringing an economic boom to states such as Wyoming, the ongoing market switch from higher-rank, high-sulfur coals (ca. 200-250 lb CO₂/10⁶ BTU) to lower-rank, low-sulfur coals (ca. 300-350 lb CO₂/10⁶ BTU) is making the global warming problem even worse:

$$\frac{72\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{8000\text{BTU}} = 330 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

$$\frac{82\text{lbC}}{100\text{lbCoal}} \frac{44\text{lbCO}_2}{12\text{lbC}} \frac{1\text{lbCoal}}{14000\text{BTU}} = 215 \frac{\text{lbCO}_2}{10^6 \text{BTU}}$$

While the politics of this issue are daunting -- it remains to be seen how the world will prevent China and India from using coal to fuel their expected economic boom in the 21st century and whether the U.S. will find cost-effective alternatives to coal for electricity generation -- here we shall explore a new concept in carbochemistry (vs. petrochemistry), as an alternative "high-tech" way of continuing to use the world's vast coal resources. We are not advocating the return to carbochemistry of the 19th century, when coal was the source of organic chemicals which gave birth to chemical industry (1). Our main focus is on the fact that the 20th century has ushered in the "age of materials" (2, 3). We argue that a realistic path toward the appealing "natural capitalism" advocated by Amory Lovins for the 21st century (4) naturally includes an increasing role for coal-derived carbons. We are thus proposing a novel concept in coal conversion (see Figure 1): the production of high-value-added carbon materials from *all* of its fractions. The key distinguishing feature of *this* concept is not that coal will be the raw material for the production of low-cost, high-performance materials such as carbon fibers, even though "Natural Capitalism" advertises these products as a panacea (4). Rather, the novelty of the concept is illustrated in Figure 2. Previous coal conversion concepts were based on tailoring the process toward the manufacture of one or two products; the residue, often a very large fraction of the coal, was then used as a fuel or was discarded. For example, in "mild gasification" (actually coal pyrolysis), which was a popular concept a decade ago, coal-derived liquid fuels are the desired product but the residual char, used as fuel, can represent as much as 70% of the product. There will be no residue in the processes whose concept is being advocated here. As illustrated in Figures 1 and 2 and discussed in more detail below, the processing steps and the intermediate products will be optimized in such a way that each end-product will find a market where its properties will be in most cases superior or at least comparable to existing products. The principal markets (see Figure 1), which are expected to be big in the 21st century *and* are natural outlets for coal-based products, are specialty adsorbents, catalysts, electrodes and electrocatalysts. While the required properties for these materials differ in many important details, they have one important commonality: in addition to optimized physical surface properties (i.e., a specific pore size distribution), superior performance requires careful tailoring of their chemical surface properties (5).

2. COAL-TO-CARBON CONVERSION

This is envisioned as a fractionation process akin to that of coal liquefaction. Taking advantage of the vast industry experience, the products are grouped into preasphaltenes, asphaltenes, oils and (heptane-) insolubles. The conditions we advocate are typical to those often encountered in coal liquefaction, but there is no insistence on maximizing the yield of oils, and thus the expected costs (see Section 7) are not as vulnerable as those of coal liquefaction: $<<1000$ psi N_2 or H_2 , 620-670 K, using a process-derived solvent. The post-fractionation processing steps are discussed below. The feedback loop in Figure 1 illustrates the key issue: do the process conditions used and the selection of a particular coal result in an optimum yield and quality of the intermediate and final products? The affirmative answer to this question relies on our ability to practice molecular engineering by heat treatment of the fractions and chemical modification of the intermediate products (see Figure 1). This in turn gives us the ability to control crystallite alignment and property anisotropy development in the final products. The optimum yield issue is briefly addressed in Section 7. The quality issue is outlined in Sections 3-6.

3. SPECIALTY ADSORBENTS FROM COAL

Coal-derived activated carbons for air and water cleanup have become commodity products, at a typical cost of \$1/lb. There is now some irony in future developments: the research required for better products is hampered by this commodity status and by global-economy competition. And yet the increasingly stringent legislation on clean air and clean water do require vast improvements in the performance of activated carbons. The way out of the impasse is the development of specialty adsorbents. In recent years it has become obvious that in the use of carbons for water treatment in particular (e.g., removal of phenols), but also for removal of gases and vapors where at least interfering moisture effects are present (e.g., SO_x and NO_x removal from air, gas storage), the chemistry of the adsorbent surface is often the dominant factor (6, 7). Both the nature of the coal and the conditions of coal and carbon processing are highly adaptable to the production of a desired surface chemistry in the final product. Thus, for example, all the intermediate products except oils (see Figure 2) are suitable precursors for specialty carbon adsorbents. Their porosity and surface area development ("activation") may not require a preoxidation step (as is the case in conventional preparation of activated carbons from bituminous coals) and their chemical modification can make the surface either highly acidic (and hydrophilic) or highly basic (and hydrophobic).

4. CATALYSTS FROM COAL

Carbon materials are known to have unique properties in catalysis, both as supports and as catalysts in their own right (8, 9). Even though this is a relatively mature market, almost as mature as that of activated carbons, the opportunities for tailoring chemical surface properties for optimum performance are practically virgin territory. The issues here are similar to those outlined in Section 3: catalytic activity depends at least on the surface area of the catalyst, which in turn can be tailored by optimizing the surface chemistry and physics of the support. But it also depends on the electronic structure of the carbon, either directly (electron transfer in the catalyzed reaction of interest) or as a consequence of the often desirable catalyst/support interaction. Two examples will suffice to illustrate the tremendous opportunities here for coal-derived carbons. In the pharmaceutical and fine-chemicals industries, carbon-supported noble metal catalysts are widely used and yet poorly understood; in the processing scheme shown in Figure 2, each one of the products will have a unique combination of bulk (e.g., electronic) and surface properties, depending on the degree of carbon crystallite growth and alignment, which is controlled in turn by selecting the starting coal and the processing conditions. Even carbons produced by vapor cracking (e.g., P3 in Figure 2), used without surface modification, offer unique catalytic properties; a good example is the family of oxidative dehydrogenation reactions (e.g., of ethylbenzene), where carbon is now known to play a key role (8, 10) even though the (nominal) catalyst is alumina-based.

5. ELECTRODES FROM COAL

The necessary combination of optimized bulk *and* surface properties, which is generated naturally in the coal-derived carbons proposed here, is a *sine qua non* condition in high-performance electrodes. Here we have in mind not so much the conventional markets (e.g., steel and aluminum manufacturing); we see untapped opportunities primarily in the booming and yet very deficient market of rechargeable batteries (11) and supercapacitors. Because this is such an interdisciplinary application, with required inputs from coal and materials scientists, as well as from carbon scientists and electrochemists, successful development of (ash-free) superior products will be possible only through implementation of the *entire* spectrum of carbon characterization tools shown in Figure 1.

6. ELECTROCATALYSTS FROM COAL

This is the holy grail of energy science and technology. It is also the ultimate challenge for carbon science and technology and it is here that the proposed concept can provide the much needed breakthroughs. Carbon materials are currently used (12, 13) and misused (14) in several types and components of fuel cells. In the "hot" field of polymer-electrolyte-membrane fuel cells, for example, they are not only the electrodes and current collectors but also the diffusion layers and electrocatalyst supports. In each application, the right combination of porous structure, surface chemistry and proton and electron transfer characteristics is required. There is no better opportunity than that afforded by the concept proposed in Figures 1 and 2 to achieve this goal: a cost-effective, high-performance, even perhaps a non-noble-metal carbon-supported electrocatalyst for the reduction of O₂ (as well as hydrogen and/or hydrocarbons).

7. SUMMARY: TECHNO-ECONOMIC OPTIMIZATION

The oversimplified but illustrative equation presented below highlights the key advantage of the proposed concept (see Figure 2).

$$\text{Max} \frac{\$}{\text{yr}} = \frac{\text{OptlbP1}}{\text{yr}} \frac{\$}{\text{lbP1}} + \frac{\text{OptlbP2}}{\text{yr}} \frac{\$}{\text{lbP2}} + \frac{\text{OptlbP3}}{\text{yr}} \frac{\$}{\text{lbP3}} + \frac{\text{OptlbP4}}{\text{yr}} \frac{\$}{\text{lbP4}}$$

The aromatic character of coal makes it a natural, high-yield raw material for carbon products. And the chameleonic nature of the carbon surface, which can be tailored to produce a variety of either bulk-property-dominated materials (e.g., P3) or surface-active materials (e.g., P1, P2, P4), provides the desired flexibility in exploiting the emerging markets of the 21st century. Both the yields of the products (OptlbP/yr) and their quality or market value (\$/lbP) can thus be optimized and continually fine-tuned for maximum profit (Max\$/yr). This augurs well for an elegant scientific, technological and economic solution to the environmental problems of coal utilization.

ACKNOWLEDGMENTS

This study was made possible by an ORISE grant (Fossil Energy Faculty Research Participation) from the Department of Energy. LRR is grateful to the Fuels and Process Chemistry Division of FETC for their hospitality during his stay in Pittsburgh in August 1999.

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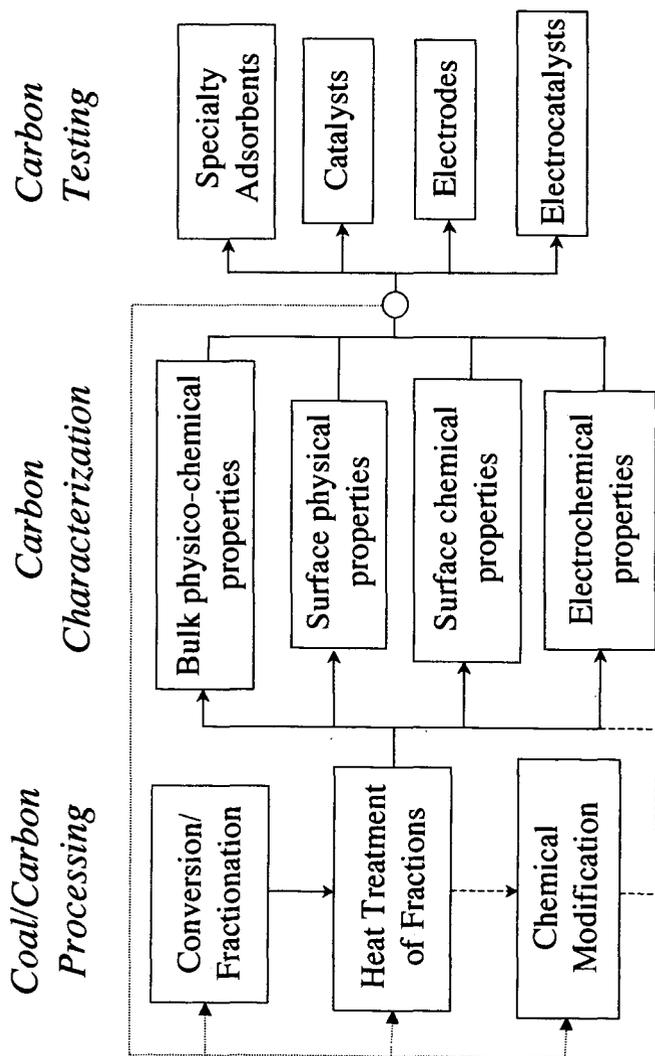


Figure 1
R&D flow diagram of an environmentally benign, technologically novel and economically flexible process of coal utilization by complete conversion to high-value-added carbon materials.

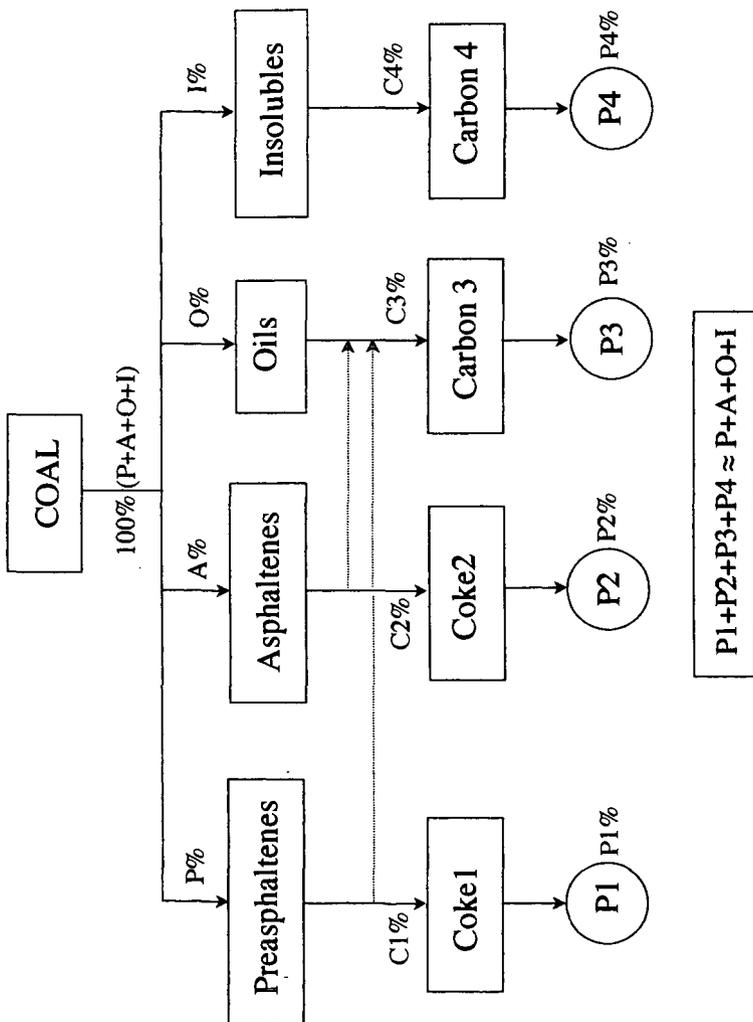


Figure 2. Optimization of the yields of end-products (P1-P4) in the complete conversion of coal to high-value-added carbon materials.