

**FUNDAMENTALS OF HYDROTHERMAL PRETREATMENT OF SEWAGE & INDUSTRIAL
SLUDGES: FEEDSTOCKS FOR CLEAN ENERGY.**

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Keywords: Sludge rheology, heating value, gasification.

Sludge rheology and slurry solids loadings are significant from pumping and slurry heating value standpoints. In this paper, we discuss the fundamental aspects of hydrothermal pretreatment of sludge which impacts the physical and chemical characteristics of the sludge. The fundamental work served as a basis of the development of a continuous 5 ton/day Process Demonstration Unit.

INTRODUCTION

Texaco Inc. has investigated techniques to prepare dewatered sewage, industrial and biological sludges as feedstocks for gasification/oxidation processes, as part of its waste gasification program.^{1a} One of the most promising pretreatment methods has proven to be the hydrothermal treatment developed by Texaco R&D. A number of patents have been issued^{1b-d}. The objective of this paper is to present the fundamental aspects of hydrothermal pretreatment of sludge. Based on extensive bench-scale and pilot-scale runs, a demonstration plant was built to process 6 dry tons per day of centrifuged sludge cake. The results of the inaugural run are presented.

The Texaco Gasification Process produces synthesis gas, principally carbon monoxide and hydrogen, from carbonaceous feedstocks by partial oxidation. One hundred commercial plants have been licensed to use this technology over the last thirty years and the synthesis gas generated has been used for end-products ranging from hydrogen, ammonia and alcohol to electric power. The feedstocks have included natural gas, distillate oils, petroleum coke, and coal.

The proposed technical standards for the use/disposal of sewage sludge (40 CFR Part 503) cover the following options: incineration, agricultural and non-agricultural land application, marketing and distribution, monofilling, and surface disposal. Most large treatment plants would prefer incineration, land application, or marketing/distribution. However, the first option could be limited to plants with existing incineration facilities and the next two, the so-called "beneficial use" options, could be limited by land availability and assurances of pathogen reduction. Solids handling is a significant operating cost for municipal wastewater treatment plants. As an example, Greater Chicago spent over half of its 1990 operating and maintenance budget on solids processing and disposal. These costs will increase at all plants because new regulations and public concerns are limiting old options. Ocean dumping is banned, landfills are closing, and the public is demanding that sewage

sludge be put to beneficial reuse.^{3,4}

Obviously, there is a market for new sludge management technologies. Recently, wastes have been considered for gasification because they are a good source of hydrocarbons and cost less than traditional feedstocks. Gasification research and development is conducted by Texaco at its Montebello Research Laboratory in Los Angeles, California. Montebello was established in 1945 and has three 15 to 25 ton per day pilot units. In 1988, under a Hazardous Waste Reduction Grant from the State of California Department of Health Services, a demonstration at Montebello proved that low-Btu hazardous waste could be gasified safely with coal and with little impact on thermal efficiency.¹ The successful testing of hazardous wastes showed that gasification would be an environmentally-acceptable method of disposal for other high-volume, low-hazard wastes such as sewage sludge.

In order to maintain the highest efficiency in gasification there is a need to limit the amount of water carried in the feed. The high viscosity of partially-dried sludge limits its suitability as a feedstock, yet too much water in a less viscous slurry decreases its heat content. It was observed that even after complete drying, sewage sludge had a tendency to reabsorb water and did not form a good slurry for gasification. This phenomenon is known to occur with low-rank coals, so developments in this area were investigated. Several steam and hot water processes were developed to thermally dewater low-rank coal. The first of these was the Fleissner process patented in 1927.⁵ When coal is heated various oxygen functional groups are decomposed releasing carbon dioxide and water from the coal structure. The tendency to reabsorb moisture is reduced so that the slurring characteristics are similar to higher rank coals.⁷

EXPERIMENTAL

Bench-Scale Results/Discussion: Bench-scale and pilot tests were begun at the Texaco Research Center at Beacon, New York to investigate various techniques to improve the physical, chemical and transport properties of sludge.^{4,6} An indicator viscosity for all feedstocks was established at 1000 centipoise to allow comparisons of different pretreatment methods.

The Texaco Research Center at Beacon conducted extensive autoclave and other testings including pilot plant runs to demonstrate that hydrothermal pretreatment of sludge can significantly improve the physical/chemical properties of sludge. Hydrothermal treatment of sludge is somewhat similar to that of low-grade coals; however, there are significant differences between the pretreatment of coal and sludge. The viscosity of the product can be greatly reduced depending on the conditions used during pretreatment.

Figure 1 shows the influence of heat-treatment temperature on the

oxygen content of the sludge. The greater the pretreatment temperature the lower the sludge oxygen content. However, the overall solids loading for a pumpable slurry is increased as a function of pretreatment temperature. Figure 2 shows the similar trends for a different sludge. The sludge was mixed with coal after the former was hydrothermally pretreated (for the data shown in Figures 1 and 2).

Figure 3 shows the influence of sludge pretreatment on the various functional groups of (dried or hydrothermally treated) sludges. The treated sludge contains significantly lower oxygenated functional groups compared to the feed sludge. Similar results were also noted for an industrial sludge (Figure 4).

Figure 5 shows the typical "Coalification" curve as applied to sludge as a function of sludge pretreatment temperature. The sludge O/Cx100 versus atomic H/C ratio of various sludges are plotted in this Figure along with various other fossil fuels feedstocks. It is interesting to note that as the pretreatment temperature of sludge is increased, a pathway is followed by sludge which is similar to the pathway followed by geological maturation of various fossil fuels.

Process Demonstration Unit Results: Based on these results, it was decided that construction of a larger process demonstration unit was justified. Burns and Roe Industrial Services Company was retained to provide detail design and construction services for a trailer-mounted PDU with a capacity of 900 kg/h or 6 dry tons per day at 25% solids. The process is shown schematically in Figure 6. The effect of PDU Hydrothermal treatment on the viscosity of the slurry is shown in Figure 7. The dramatic effect is qualitatively similar to our pilot test results (not shown) and demonstrates that the pilot-scale and bench-scale results can be achieved in a commercial unit.

CONCLUSION

Hydrothermal Pretreatment Process, developed based on fundamental investigation, converts sewage and industrial sludges into attractive feedstocks for gasification/combustion and offers municipalities an environmentally-acceptable alternative to other disposal options.

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Figure 1. Relationship Between Heat-Treatment-Temperature and Slurry Solids Loading as a Function of Sludge Oxygen Content.

Sludge Oxygen Content Vs Solids Loading
Hydrothermal Treatment at Various Temp

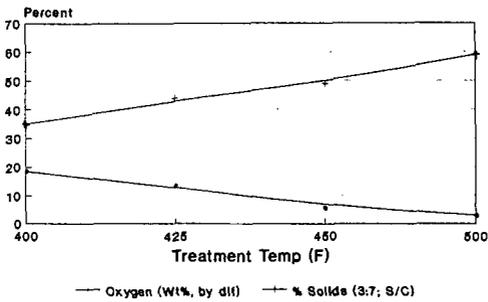
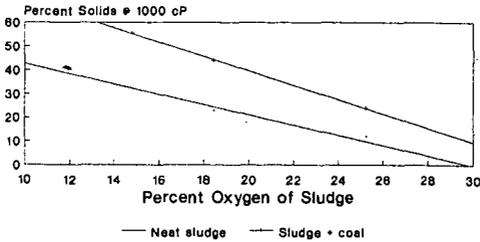


Figure 2. Relationship Between Slurry Solids Loading as a Function of Sludge Oxygen Content.

Slurry Solids Loading of Municipal Sludge as a Function of Oxygen Content.



Slurry viscosities at room temperature.
Municipal sludge to coal ratio 1:2.
Sludge sample from Passaic Valley, N.J.

Figure 3. FT-IR Analysis of a Municipal Sludge

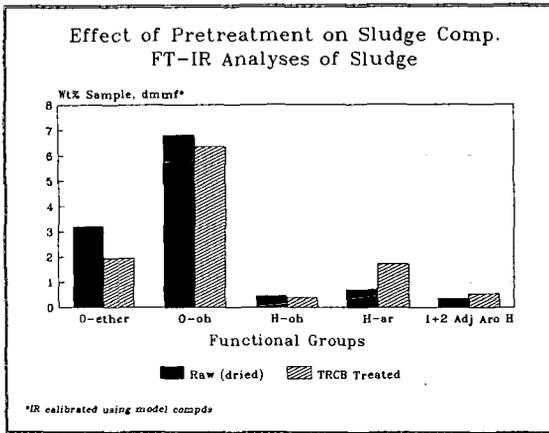


Figure 4. FT-IR Analysis of an Industrial Sludge

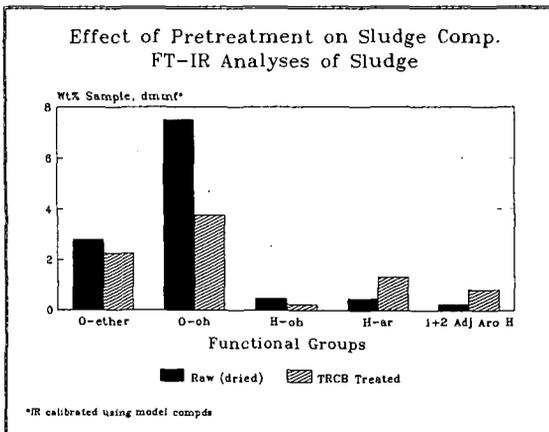


Figure 5. "Coalification" Curve: Atomic O/C Ratio Versus Atomic H/C Ratio

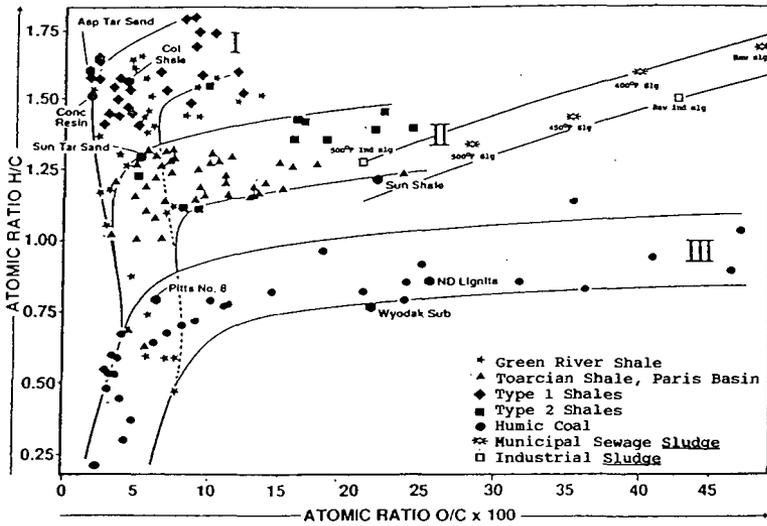


Figure 6.

Texaco Hydrothermal Treatment

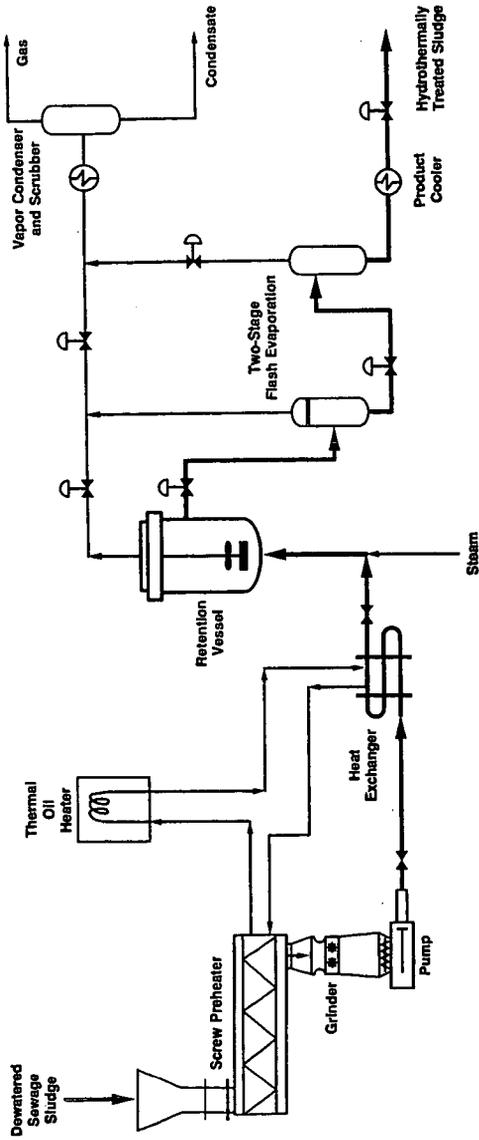
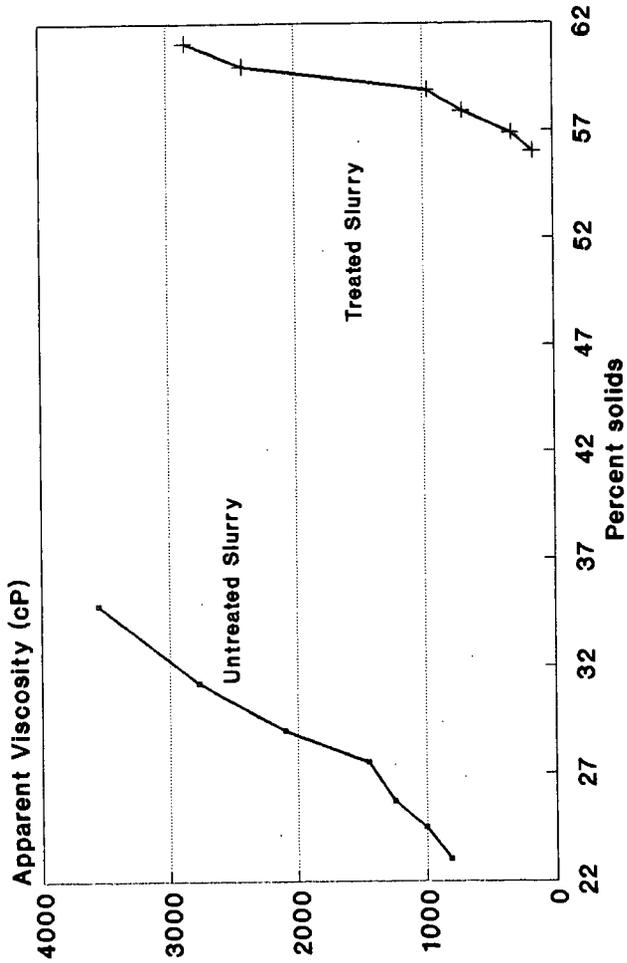


Figure 7.

TEXACO HYDROTHERMAL PDU RESULTS

Sludge:Coal 1:2; Slurry Rheology



COLIQUEFACTION OF WASTE PLASTICS WITH COAL

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Keywords: plastic wastes, coliquefaction, superacid catalysts.

ABSTRACT

Polyethylene (PE), poly(ethylene terephthalate) (PET), mixtures of PE and PET with different coals, and actual plastic wastes from such items as milk jug and soft drink bottles were liquefied in a tubing bomb reactor. Comparative experiments were performed at 400-450°C for times of 15-60 min. at a cold hydrogen pressure of 800 psi. The experiments used two types of catalysts: highly dispersed iron based catalysts and an HZSM-5 zeolite catalyst. Saturated oil, consisting of mainly straight chain alkanes and minor alkenes, and some light hydrocarbon gases were produced from liquefaction of both the plastic and the plastic-coal mixtures. Using PE, PET, and samples prepared from waste milk jugs and soda bottles alone with the HZSM-5 catalyst, 100% conversion with oil yields of 86 to 92% were obtained. Using coal/plastic mixtures with a highly dispersed iron catalyst, which gives excellent results for coal alone, somewhat lower conversions (53-91%) and oil yields (26-83%) were obtained. Further studies are in progress to explore the optimum conditions for direct liquefaction of plastic wastes and coal, and to examine the effect of a variety of potential superacid catalysts such as zeolite and highly dispersed sulfated metal oxides (e.g. $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{Fe}_2\text{O}_3\text{-ZrO}_2/\text{SO}_4^{2-}$).

INTRODUCTION

In recent years, disposal of plastic wastes has become an increasingly serious environmental concern. Due to an ever increasing volume of plastic products, sanitary landfills can no longer continue to be the major means for plastic wastes disposal. Plastics recycling appears to be a possible alternative solution and has potential for high growth. However, the recycling of plastics that takes place currently is not due to industry initiatives, but because of government edicts. In the United States, laws are in effect in states such as California, Oregon, and Wisconsin that require plastic bottles to be made of at least 25 wt% of recycled plastic. Similar laws in other states and federal laws are likely to follow. In Germany, the law requires that 80% of plastic wastes must be recycled by 1995. France has just recently passed a similar law.

In 1990, about 0.4 million tonnes of plastics in the form of soft drink bottles entered the municipal waste stream, of which 31.5% was recovered. However, out of seven million tonnes of total plastic wastes in the same year, only 3.7% was recycled (Figure 1)¹. Conventional plastic recycling always faces the problem of contaminated and mixed plastic scrap, which cause difficulties in the recycling. The potential exists for impurities to diffuse into products packaged in recycled containers. Aside from toxic concerns, these impurities could also damage the processing equipment. Further, the equipment conversion or replacement costs in order to use reclaimed plastics are high and may not be economical for a small plastic molding industry. In addition to all these obstacles in the way of using recycled resin in industry, the average price of virgin high-density polyethylene in the U.S. is currently 30 cents per pound, while the price of recycled high density polyethylene is 32-33 cents per pound². Conventional pyrolysis, as an alternative for plastic waste recycling, usually results in unsaturated and unstable oils of low yield and low value that can be used only for combustion.

Considering current conditions and expected future trends, of all the options that exist for plastics recycling, liquefaction of plastic and rubber wastes should be considered seriously for efficient and economical plastics recycling. Liquefaction of plastic wastes can not only provide a solution for plastics disposal, but can also generate an environmentally acceptable transportation fuel. The current rate of plastic waste materials that are disposed in the United States each year constitutes a potential hydrocarbon resource from which over 80 million barrels of oil per year could be produced. Moreover, coliquefaction of plastic wastes and coal could yield synergistic effects. Unfortunately, very few investigations have been conducted in this area and much work needs to be done to develop liquefaction strategies for recycling plastic wastes.

EXPERIMENTAL

In our preliminary experiments, a medium density polyethylene (PE), poly(ethylene terephthalate) (PET), mixtures of PE and PET with different coals, and actual plastic wastes from such items as milk jug and soft drink bottles were liquified in a one stage tubing bomb reactor in a fluidized sand bath using two different catalysts. This set of experiments is designed to investigate the effect of catalysts on the total yield and product distribution in the liquefaction process. The tubing reactor is first charged with feed materials and pressurized to 800 psi with hydrogen (cold). The reactor is then connected to an agitation apparatus and heated to desired temperature in a fluidized sand-bath while being agitated with a vertical motion at 400 cycles per min. during the reaction period. The liquefaction products from these experiments were determined by Soxhlet extraction with toluene, tetrahydrofuran (THF), and pentane. Comparative experiments were

performed for coliquefaction of mixtures of a medium density polyethylene (PE) and Blind Canyon coal and iron ion-exchanged Beulah lignite. The experiments used two types of catalysts: highly dispersed iron based catalysts and an HZSM-5 zeolite catalyst.

The quality of the oil products was examined using chemical analysis and gas chromatography. Extensive characterization studies are being carried out on the source materials, liquefaction products, and catalysts. A variety of analytical techniques are being used in these studies, including x-ray absorption fine structure (XAFS) spectroscopy, Mossbauer spectroscopy, x-ray diffraction (XRD), and transmission electron microscopy (TEM) for catalyst characterization.

RESULTS AND DISCUSSION

Saturated oils, consisting mainly of straight chain alkanes and minor alkenes, and some light hydrocarbon gases were produced from the liquefaction of both the plastic and the plastic/coal mixtures. The total conversion and oil yield for these experiments are listed in Table I. Using PE, PET, and samples prepared from waste milk jugs and soda bottles alone with the HZSM-5 catalyst, 100% conversion with oil yields of 86 to 92% were obtained. Using coal/plastic mixtures with a highly dispersed iron catalyst that gave excellent results for coal alone, somewhat lower conversions (53-91%) and oil yields (26-83%) were obtained. It is found that a mixture of iron ion-exchanged Beulah lignite³ and polyethylene (in a ratio of 25:75) exhibits higher conversion than mixtures of 50:50 and 75:25 of these two components, but lower than that for pure polyethylene. Catalytic liquefaction experiments were carried out both with and without the presence of the solvent. Polyethylene in the presence of HZSM-5 catalyst on the other hand, exhibited higher conversion than either the polyethylene alone or mixture of polyethylene and superfine iron oxyhydroxide, implying synergistic effects. The quality of the oil products was examined using gas chromatography in collaboration with the UK Center for Applied Energy Resources (CAER) and the results for oil and gases produced during liquefaction of polyethylene are shown in Figures 2 and 3, respectively.

Further detailed studies are in progress to explore and establish the optimum conditions for direct liquefaction of waste plastics and coal, including the effect of temperature, pressure, reaction time, and coal/waste plastic ratio. The effect of a variety of potential superacid catalysts such as zeolite and highly dispersed sulfated metal oxide (e.g. $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{Fe}_2\text{O}_3\text{-ZrO}_2/\text{SO}_4^{2-}$) is also being investigated.

Acknowledgement

The authors would like to thank Mr. Robert Keogh and Dr. Burt Davis for their generous collaboration during the experimental portion of this work at the UK CAER. We also would like to acknowledge the support provided for this work by the U.S. Department of Energy as a part of the research program of the Consortium for Fossil Fuel Liquefaction Science.

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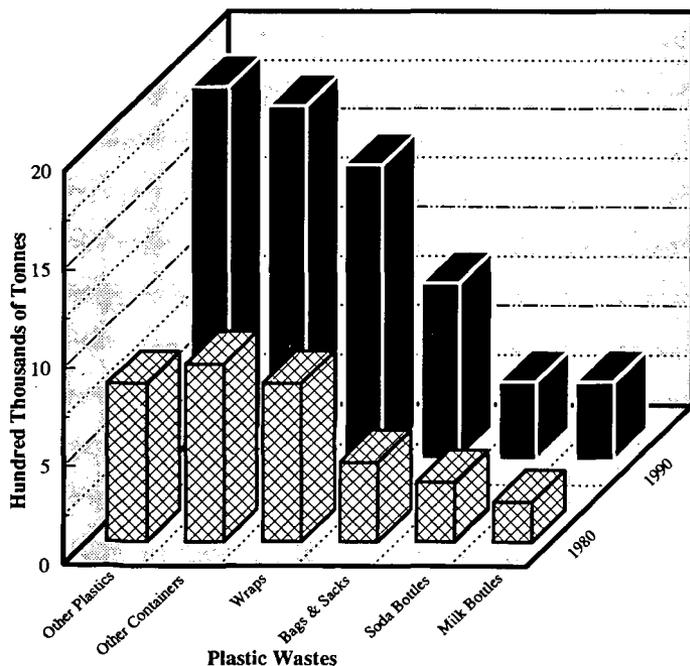


Figure 1. Characterization of Municipal Waste in the United States

Table I. Experimental results obtained from liquefaction of plastics, and colliquesfaction of plastic/coal mixtures.

Sample	Additives	Temperature(C)	Total Conv. %	Oil Conv. %
PET	HZSM-5	420	100	92
PE	HZSM-5	420	100	88
PET	HZSM-5	400	100	90
Milk jug	HZSM-5	420	100	86
Coke Bottles	HZSM-5	420	100	93
lignite:PE 1:3	Fe-exch.+DMDS	450	91	83
lignite:PE 1:2	Fe-exch.+DMDS	450	67	51
lignite:PE 1:1	Fe-exch.+DMDS	450	53	40
PE	Tetralin	450	100	33
BC Coal:PE 1:1	Tetralin	450	70	42
BC Coal:PE 1:1	30Å FeOOH+DMDS	450	48	26
PE	30Å FeOOH+DMDS	420	100	76

PE = polyethylene, PET = Polyethylene Terephthalate, DMDS = Dimethyl Disulfide
 BC = Blind Canyon coal, Fe-exch. = Iron ion-exchanged Beulah lignite

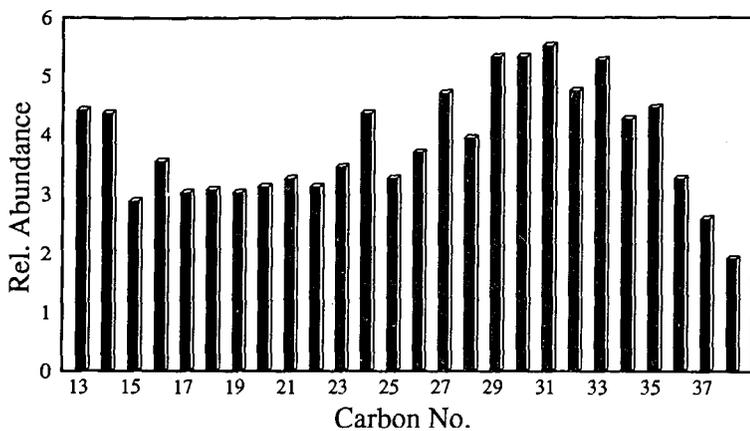


Figure 2. Pentane soluble products distribution of polyethylene

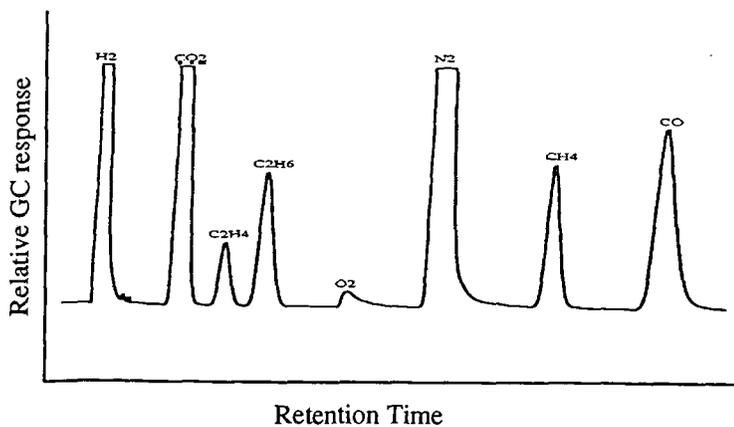


Figure 3. GC chromatogram of gaseous compounds produced during liquefaction of polyethylene

COLIQUEFACTION OF COAL AND POLYMERS TO LIQUID FUELS

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Coal is our most abundant fossil fuel, but presently supplies only about 24 percent of our total energy. Petroleum provides over 40 percent of our energy, but recently, over one-half of our petroleum demand has been satisfied by imports. This situation constitutes both a strategic and an economic problem which could be partially alleviated by liquefaction of coal. A serious environmental problem is the disposal of polymer wastes such as polyethylene, polystyrene, polypropylene and used rubber tires. Over 22 million tons of plastic wastes are disposed of annually in landfills⁽¹⁾ and over 75 percent of discarded used tires are similarly treated (242 million tires in 1992).⁽²⁾ Such waste polymers contain a large fraction of hydrogen which is needed to convert coal to high quality liquids. Coliquefaction of coal and waste polymers has the potential for supplying liquid fuels which could reduce our need on imported crude oil and refined products and at the same time, alleviate an environmental disposal problem.

Several others have studied the coliquefaction of coal with polymeric materials. Only a few will be mentioned here but they are significant relative to our research. W. Hodek combined coal with several plastic polymers with the idea of using coal as a hydrogen donor⁽³⁾. Using polyethylene, polystyrene, dechlorinated PVC, and "Trabant resin" in combination with coal, Hodek found coal to be a good hydrogen donor but the reaction rate was low. He also observed that some plastics formed condensation products in his experiments. Both Williams et al.⁽⁴⁾ and Farcasiu⁽⁵⁾ utilized rubber tire material to obtain liquid products. Farcasiu used tire rubber in combination with coal and found the quality of liquids produced from coal/polymer combinations higher than for products from thermal coal liquefaction in tetralin. Heptane soluble liquids (oil) represented over 80 percent of the products. This fraction was high in hydrogen (9.7 weight percent) and had low heteroatom content. Williams et al. used only pyrolysis to convert "automotive tyres" to products but nearly 60 percent of the charged rubber material was converted to gases and liquids. Temperatures were relatively high compared with conventional coal liquefaction processes (maximum yields were obtained at 720°C, the highest temperature studied). Molecular weights for the liquid "oil" fell between 100 to 1600 with the maximum number between 300 and 400. As with many pyrolysis processes, higher temperature treatments caused a shift in the molecular weights of the liquids to higher values.

Experimental

Coliquefaction experiments were conducted in tubing reactors (volume = 29 ml) which were heated in a fluidized sand bath. Reactions were conducted on dry coal and polymer mixtures or pure samples with shaking at 160 rpm and with hydrogen at 2000 psi. Pure polyethylene (PE), polystyrene (PS), and a commingled plastic mixture (mostly high density PE) obtained at a local recycling center were used with a high volatile bituminous coal (DECS-6-Blind Canyon, Utah, obtained from the Penn State Coal Sample Bank). Coal was ground to -100 mesh and plastics were ground to -8+25 mesh. In the case of commingled plastic, the bottles and containers were washed to remove contaminants and labels before size reduction by cutting and shaving. Final size reduction was done by grinding in a kitchen flour mill (stainless steel). Polyethylene and polystyrene were obtained from Aldrich Chemical Company. Analytical data for the coal and commingled plastic are given in Tables 1 and 2. In Table 3, trace element analyses for coal and commingled plastic waste (CPW) are given.

Table 1

Proximate Analysis of Coals and Plastic Waste
(weight percent, as received)

	Coals DECS-6	DECS-17	Commingled Plastic Waste
Fixed Carbon	47.31	44.9	0.45
Volatile Matter	42.4	45.0	99.7
Ash	5.6	6.3	1.8
Moisture	4.7	3.7	0.06

Table 2.

Ultimate Analysis of Coals and Commingled
Plastic Waste (weight percent, as received)

	<u>Coals</u>		<u>Plastic Waste</u>
	DECS-6	DECS-17	
Carbon	81.7	82.05	86.3
Hydrogen	6.2	6.2	14.0
Nitrogen	1.6	1.4	.05
Sulfur	0.4	0.44	0.22
Oxygen (by diff.)	10.1	9.94	--

Table 3

Trace Element Analyses for Coals and Commingled Waste Plastic
(ppm, wt. basis):

	<u>Coals (Blind Canyon, Utah)</u>		<u>Commingled Plastic</u>
	<u>DECS-6</u>	<u>DECS-17</u>	<u>Waste</u>
Cr	6.0	6.0	0.77
Cd	--	--	0.19
Cu	9.0	9.0	--
Ni	<2.0	--	0.4
Pb	--	--	3.2
Zn	4.	3.0	--

Results and Discussion

We have extensively studied the liquefaction of Blind Canyon coal, which has a low pyrite content. Hydroliquefaction of this and other coals of similar rank gives high yields of liquid products at temperatures near 400°C. At higher temperatures, liquid yields decrease as more gases are produced. To determine if coliquefaction could be accomplished experiments were done using different combinations of coal and polyethylene (PE) and coal and polystyrene (PS). In Figure 1 results for total conversion of PE and coal show that highest conversion was obtained at 400°C for PE but little difference was observed for coal/PE at 350 and 400°C. Polystyrene was easier to convert to liquids and gases than was PE as shown in Figure 2. Conversion of PS only at 400°C gave nearly 90 percent conversion. In contrast to polyethylene, polystyrene liquefaction gave highest yields at 300°C (Figure 3). Polystyrene conversion differed from polyethylene in another important respect; gas production. At 300°C a 50:50 mixture of coal and polystyrene gave a conversion of 71.5 percent with most of the product as a liquid (62.3% of the total sample weight). However, at 400°C the conversion dropped to 58%, but the drop in liquids was even greater (to 15%). Coal/polyethylene liquid yields were essentially identical at 350 and 400°C (33.1% and 33.3%, respectively).

Commingled plastic waste (CPW) contained some polystyrene, and other plastics, but the most abundant polymer in this waste was high density polyethylene (HDPE). CPW was composed of many large and small drink bottles, soap containers, prescription drug containers, etc. Colors included black, transparent, red, orange, green and blue. This material was by far the most difficult to convert to liquids soluble in THF. As shown in Figure 4 the conversion values for commingled plastic was much lower than for either PS or PE. From the trend shown at different temperatures it appears that higher temperatures may be required to obtain satisfactory liquid yields. Other results not shown in Figure 4 have been obtained for 50/50 coal/CPW at 450 and 500°C. At these higher temperature, total conversions were 28 percent with liquid yields of 23 percent at 450°C and 35 percent with a liquid yield of

26 percent at 500°C. CPW/coal/waste rubber tire material (WRT) were reacted at 450°C (33/33/33) and gave only slightly higher conversion and liquefaction (36 percent and 32 percent, respectively). Even higher temperatures and/or suitable catalysts will obviously be required to obtain higher conversion and liquefaction values.

From work by others using waste rubber tire material (WRT) it has been observed that high yields of liquids and gases can be obtained. We also reacted WRT with coal and with coal/CPW. Table 4 gives results at 350°C using a catalyst, ammonium tetrathiomolybdate (1% of total feed weight) for coal only and mixtures of coal and WRT. Although simple mechanical addition of the catalyst was no better than hydroliquefaction without catalyst, impregnation from aqueous solution improved the liquefaction (from 56% to 79% for 60/40 coal/WRT).

Table 4

Results for hydroliquefaction of Blind Canyon Coal (DECS-17) and Waste Rubber Tire Material Using 1% (weight % of total feed) Ammonium tetrathiomolybdate. (Temperature = 350°C)

% Coal in feed	% WRT in feed	Catalyst addition	Yields, (wt. %)	
			Liquids (THF Sol.)	Gas
100	0	none	36	
2				
60	40	Impregnated	79	2
50	50	Impregnated	65	2
50	50	Mechanically added	55	1
60	40	none	56	2

Reaction of coal and plastic materials, especially commingled plastic waste (CPW) has so far given only marginal results. Even for relatively long reaction times (1 hour) and temperatures up to 500° C liquid yields are less than we have obtained for hydroliquefaction of coals. Further work and characterization of the liquid products will be necessary to improve the conversion of coal/plastic streams to high quality liquid products.

Summary

Hydroliquefaction of coal, polyethylene, polystyrene and waste rubber tire material individually gives good conversion and liquefaction yields. Combinations of these materials gave less satisfactory results as far as liquid yields were concerned. Catalyst application (molybdenum) enhances the reaction to increase liquid yields and to produce higher quality liquids.

Acknowledgement

The financial support for this work by the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science and the University of Utah is gratefully acknowledged.

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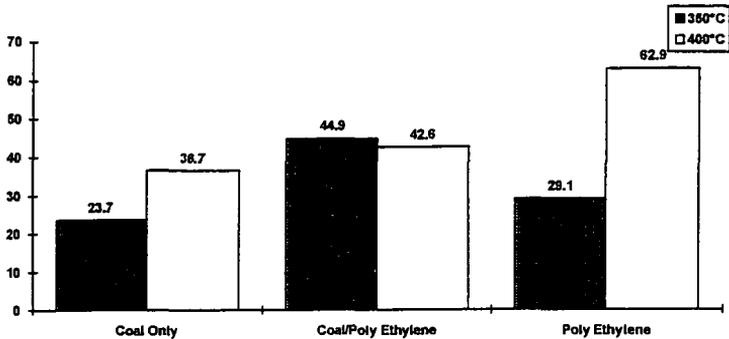


Figure 1. Coliquefaction yields for Blind Canyon Coal and PE (50/50) at two temperatures. Values are total conversion.

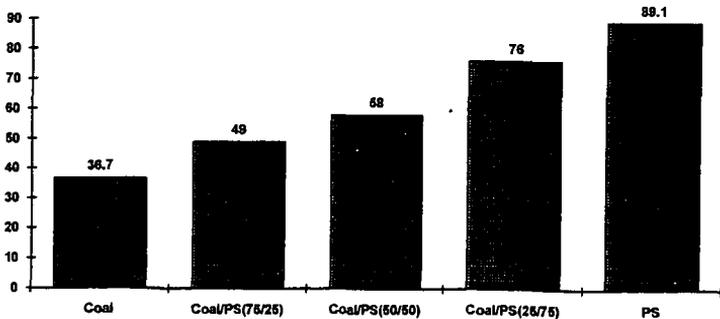


Figure 2. Coliquefaction conversion (liquids + gases) for Blind Canyon Coal and PS at 400°C (weight percent).

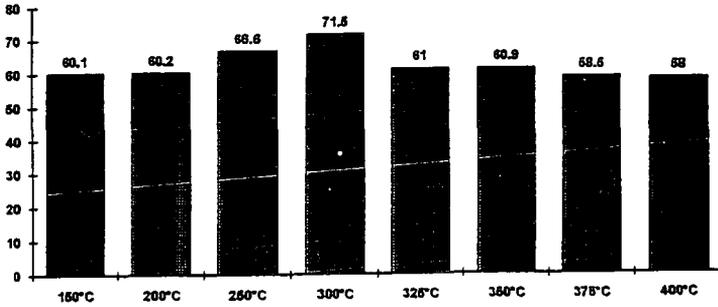


Figure 3. Coliquefaction yields (liquids + gases, weight percent) for Blind Canyon Coal and PS (50/50) different temperatures.

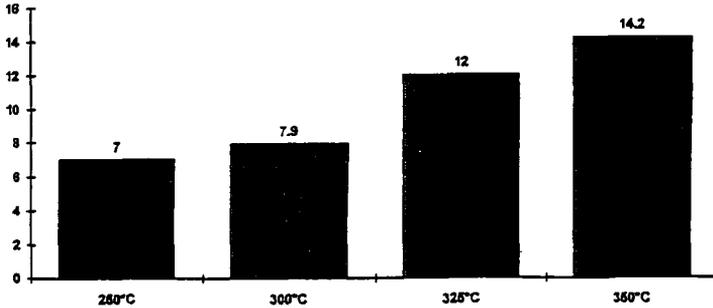


Figure 4. Coliquefaction yields (liquids + gases, wt percent) for Blind Canyon Coal and Commingled Plastic waste (50/50) at different temperatures.

MICROSCALE SIMULATION OF HIGH PRESSURE THERMAL AND CATALYTIC CONVERSION PROCESSES IN COAL AND WASTE POLYMERS WITH ON-LINE GC/MS

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Keywords:(on-line TG/GC/MS, coal, rubber, hydrolysis)

INTRODUCTION

Over 279 million automotive tires are discarded in the United States each year.¹ These used tires cause serious environmental problems since they are non-biodegradable, occupy considerable land-fill space, and emit noxious fumes when burned. One of the promising approaches to deal with used rubber is the co-processing of it with coal to produce hydrocarbon liquids for use as fuels and specialty chemicals. Recently there have been numerous studies on co-processing of tire rubber and coal since depolymerized rubber has good solvent properties and the carbon black which constitutes of about 20-30% of the rubber is a good catalyst for depolymerization and possibly enhanced coal liquefaction.^{2,3,4,5} Monitoring sample weight loss as a function of temperature with on-line analysis of the evolved products during the co-processing reactions is necessary to elucidate mechanisms and kinetics of the key conversion reactions. Due to the high pressure and high temperature required by some of the most interesting processes, it is difficult to continuously monitor the weight loss and reaction intermediates without interrupting the reactions.

On-line analysis techniques for high pressure conversion reactions have been reported previously,^{6,7} but these systems did not monitor total weight loss vs reaction temperature. They also were not applied directly to coal conversion studies because of the strong potential for plugging of sample orifices with pulverized coal.

Microscale simulation of coal conversion reactions has been performed by high pressure thermogravimetry with on-line combined gas chromatography and mass spectrometry (TG/GC/MS). It requires only a small sample size and can be operated at high temperature and pressure. The weight loss and low molecular weight products can be monitored vs reaction temperature. Analysis of pyrolysis and hydrolysis of coal, rubber and coal with tire rubber, with or without catalyst, by high pressure TG/GC/MS are reported here.

EXPERIMENTAL

High Pressure TG with On-Line GC/MS

The system as shown in Figure 1 consists of the high pressure TG instrument, pressure reduction line, vapor sampling inlet, short GC column and MS detector. A Cahn high pressure TG-151 was used as the reactor. The reactor vessel was made from a quartz tube which is corrosion resistant and has no known catalytic effect on the reaction. This reactor can be operated up to 1000 psi with temperatures up to 1000 C and heating rates ranging

from 0 to 25 C/min. The experiments in this study were operated at 900 psi with a heating rate of 10 C/min up to 600 C followed by a 10 min hold of the final temperature. The reagent gas was either helium or hydrogen. The quartz crucible used for holding the sample was modified as shown in Figure 1. The modified crucible with an open hole at the bottom greatly increased the sensitivity of the GC/MS detection since the vapor products go directly into the quartz sampling tube, which reduced the amount of sample necessary. The coal and tire rubber used were 60 mg each. The pressure of the reactor was kept constant by a back pressure regulator. During operation the reagent gas is flowing continuously through the reactor at 500 ml/min (ambient). A 1 m x 50 μ m i.d. fused silica capillary is used as a pressure reduction line, which carries vapor products to the ambient pressure sampling device. A novel automated vapor sampling (AVS) inlet developed at the University of Utah (U.S. Patent No. 4,970,905), provides automated, repetitive vapor sampling for the GC column. Samples were taken each 73 seconds. The AVS inlet was connected directly to a 2m x 150 μ m i.d. fused silica capillary column coated with methyl silicone (CP-SIL-5CB). The short column was operated isothermally at 90 C and provided rapid separation of the vapor products. The separated products were detected by a small quadruple MS system, the Hewlett Packard model 5971A MSD operating at 70 eV electron energy.

Materials

Blind Canyon (DEC-6), Utah coal (-100 mesh) from the Penn State sample bank was employed in this study. The proximate analysis of the coal is listed in Table I. The experimental procedure for impregnating coal with catalyst is described by Anderson et al.⁸ The catalyst used in the experiments was 1% Fe as iron chloride hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$] promoted with 0.05% Mo as ammonium tetrathiomolybdate [$(\text{NH}_4)_2\text{MoS}_4$]. The used tire rubber was scraped, cut into small pieces and then ground into fine particles in a cryogenic grinder with liquid nitrogen. The weight ratio of coal to rubber for the mixture was 1:1.

RESULTS AND DISCUSSION

The thermal decomposition of Blind Canyon coal, tire rubber and the mixture of coal and rubber was studied at high pressure under various conditions as seen in Table II. The thermogravimetric profiles are shown in Figure 2 indicating the different course of decomposition of the samples. The complex structure of coal resulted in continuous volatile product evolution up to the final temperature of the experiment (600 C) whereas the flat weight curves of rubber above 500 C suggest that only the relatively inert carbon black and inorganic filling are left and the organic components have been completely devolatilized. Although the volatile evolution of rubber is shifted to somewhat lower temperature in hydrogen atmosphere, the TG profile similarity in helium and hydrogen atmospheres is apparently due to the high inherent hydrogen content of rubber. The effect of hydrogen is clearly visible in the coal decomposition, where a significant increase in volatile product evolution can be observed above 500 C. Adding liquefaction catalyst to the coal and coal + rubber samples increases the total weight loss (Table II) by about 3-4% and the volatile evolution occurs at lower temperature. The effect of rubber on the coal decomposition is not apparent solely by looking at the thermogravimetric results.

Figure 3 shows the average mass spectra of the volatiles evolved from 350 to 600 C from coal and rubber as well as coal + rubber with and without catalyst in hydrogen

atmosphere. The spectrum of the high volatile bituminous coal is dominated by alkene (m/z 41, 55, 69, 83, etc.), and alkane (m/z 43, 57, 71, 85, etc.) fragment ion series as well as aromatic hydrocarbons (m/z 78, benzene; m/z 91, toluene fragment) and phenols (m/z 94, phenol; m/z 107, cresol fragment). The rubber spectrum shows the formation of unsaturated hydrocarbon ions from the butadiene segments of rubber (e.g., m/z 67, methyl butadiene fragment) and aromatic hydrocarbons originating from the styrene moieties (e.g., m/z 91, toluene fragment; m/z 104, styrene). It should be noted that the oil additive of rubber may also release aromatic products. The spectra of the coal + rubber mixture (ratio 1:1) resemble the rubber spectrum at first sight because the rubber releases higher amounts of organic volatiles than the coal. The evaluation of average mass spectra is further complicated by the formation of several common products from coal and rubber (e.g., alkyl aromatics and alkenes). In spite of these difficulties it can be seen that the intensity of several ions is not additive and the presence of catalyst changes the product distribution. More detailed information can be obtained about the effect, of the rubber and catalyst on the coal hydrolysis by using the time resolved data.

As discussed in the experimental section, samples were taken every 1.22 minutes from the volatiles evolved from the TG furnace and analyzed by MS after separation on a short GC column. The total ion intensity profile of coal obtained by this method can be seen in Figure 4a indicating that the maximum rate of decomposition occurs at 480 C. Enlarging one sampling period, the total ion curve shows the separation of several compounds within the 1.22 min interval (Figure 4b). Although the resolution is insufficient in the low MW range due to the relatively high column temperature (90 C), the extracted single ion chromatograms can be used for further analysis. Figures 4c and d show the abundance of characteristic alkene (m/z 55) and alkane (m/z 57) fragment ions revealing the increase of alkene/alkane ratio with decreasing carbon atom number. The intensity profile of a typical alkyl phenol fragment ion (m/z 107) indicates (Figure 4c) that not only different MW compounds (cresol vs. xylenol), but certain isomers (ethyl phenol vs. dimethyl phenol) can be separated on the short column.

The hydrolysis of tire rubber results in the formation of a large variety of products, as shown by the total ion current profile in Figure 5a. Figures 5b, c and d display the intensity profiles of three ions representing the three types of products. The butadiene segment of rubber releases primarily butene (m/z 56), exceeding the yield of butadiene, apparently due to the hydrogen atmosphere and high pressure applied. Styrene (m/z 104) is the major product of the polystyrene segments. Various alkyl, alkenyl, alkydicyl benzenes are released containing both building elements of the rubber polymer; m/z 117 (C₃H₅-benzene) represents a characteristic alkenyl benzene fragment ion in Figure 5d. M/z 104 ion is formed from several compounds beside styrene (Figure 5c). The evolution of styrene starts at lower temperature than the formation of other alkenyl benzenes as shown by the intensity profile of m/z 104 expanded to the whole temperature range in Figure 5c. Although the simple thermogravimetric curve does not reveal the complex reaction route, the different evolution profiles of products suggest a multiple step decomposition mechanism.

The most important products of the thermal decomposition of Blind Canyon coal were presented above. The next Figure (Figure 6) shows the effect of hydrogen reactant gas and a liquefaction catalyst on the evolution profiles of four characteristic products of coal. The TG curve of coal (Figure 2) exhibits two main decomposition regions in hydrogen atmosphere (350-520 C and above 520 C). The rate of volatile evolution up to 520 C is similar in

hydrogen and helium suggesting that hydrogen does not promote the devolatilization significantly in this temperature range. This assumption is confirmed by the intensity profiles of the individual ions in Figure 6. Although there are some variations in the evolution curves the overall difference does not seem to be significant in the lower temperature range. However, the formation of alkyl aromatic products (m/z 92, toluene and m/z 142, methyl naphthalene) is greatly enhanced at high temperature in hydrogen atmosphere. The liquefaction catalyst applied in hydrogen atmosphere increases the yield of each product. Some increase is observed in the high temperature release of alkyl aromatics in comparison with the uncatalyzed coal experiment in hydrogen. Furthermore, the catalyst promotes the formation of alkanes (m/z 43 propyl fragment of C_3-C_9 alkanes) and phenol (m/z 94) as well as methyl naphthalene at lower temperatures.

The mixture of coal and tire rubber (ratio 1:1) was used for simulation of their co-processing under high pressure in hydrogen atmosphere. Figure 7 compares the evolution profiles of m/z 92 and m/z 94 from coal, rubber and the mixture. The absolute intensities cannot be evaluated due to the different experimental conditions; therefore the intensities are scaled for equal height. The toluene evolution profile of the mixture (Figure 7a) appears to be the sum of the individual components. Other hydrocarbons exhibit similar behavior, however, it should be emphasized that this is not a quantitative comparison.

The spectra of both coal and rubber contain the m/z 94 ion, however, it represents two different compounds, phenol and heptatriene, respectively. Due to the chromatographic separation, the intensity profile of each product can be monitored separately in the mixture, as seen in Figure 7b. The heptatriene evolution occurs at about the same temperature from the rubber and the mixture. The rate of phenol formation from coal shows two maxima in hydrogen atmosphere (at about 450 C and 550 C). The presence of rubber significantly promotes the release of phenol in the lower temperature range (350-520 C).

CONCLUSIONS

Simulation of thermal and catalytic coal conversion processes was carried out in inert helium vs hydrogen atmospheres using a high pressure thermobalance coupled on-line to a GC/MS. The weight loss curves and the intensity profiles of products show that the volatile evolution of Blind Canyon coal significantly increases above 500 C in hydrogen atmosphere in comparison with helium due to the release of alkyl benzenes and alkyl naphthalenes. The Fe, Mo liquefaction catalyst increases not only the yield of alkyl aromatics, but enhances the formation of aliphatic hydrocarbons and phenols in the lower temperature range (350-520 C).

The presence of tire rubber appears to promote the phenol formation at 350-520 C, but the evolution profiles of other products seems to be additive in the mixture of coal and rubber. However, further experiments are required to reveal the effect of rubber on the yield of the individual products of coal.

ACKNOWLEDGEMENTS

We would like to thank Professor Larry L. Anderson and W. Tuntawiroon (University of Utah) for providing us with the samples of catalyst impregnated coal. We also acknowledge the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science and the State of Utah who financially supported this research.

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Table I. Proximate Analysis of Blind Canyon (DEC-6) Coal

	as received
Moisture (wt.%)	4.73
Volatile matter (wt.%)	42.40
Fixed carbon (wt.%)	47.31
Ash (wt.%)	5.56

Table II. Weight Loss Data from High Pressure TG

	Fe, Mo Catalyst	Reactant Gas	Weight Loss, %
Coal	No	He	36.6
Coal	No	H ₂	54.7
Coal	Yes	H ₂	57.9
Rubber	No	He	66.6
Rubber	No	H ₂	67.5
Coal + Rubber	No	H ₂	57.7
Coal + Rubber	Yes	H ₂	61.8

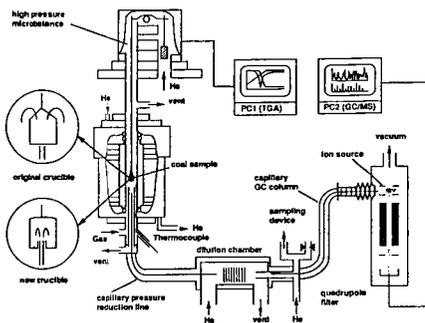


Figure 1. Schematic of the TG/GC/MS system.

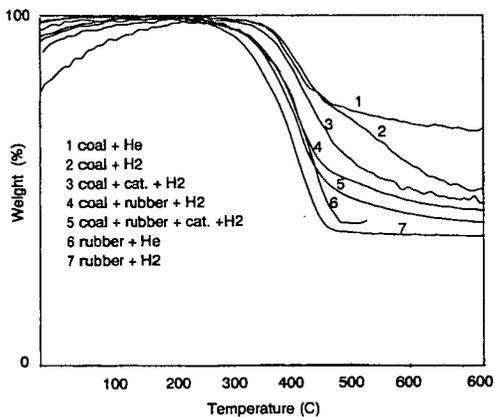


Figure 2. TG curves of coal and rubber under various conditions at high pressure (900 psi).

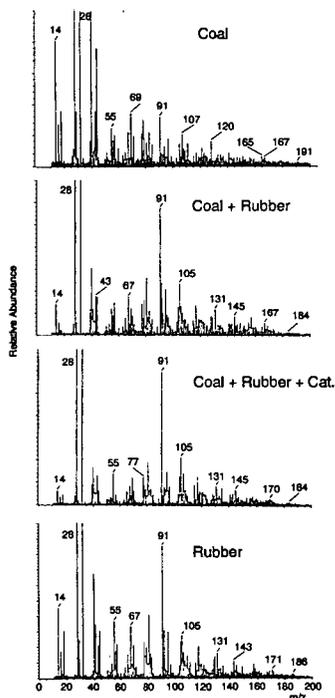


Figure 3. Average mass spectra of hydrolysis products of coal, rubber and coal + rubber with and without catalyst from 350 C to 600 C. (m/z 14, 28, 32, 40 are background peaks.)

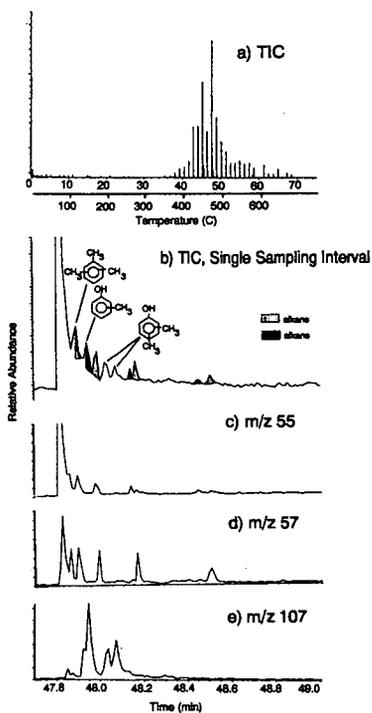


Figure 4. Thermal decomposition of coal in helium atmosphere. a) Total ion intensity; b) in a single sampling interval. Ion intensity of c) m/z 55, alkene; d) m/z 57, alkane; e) m/z 107, cresol fragment.

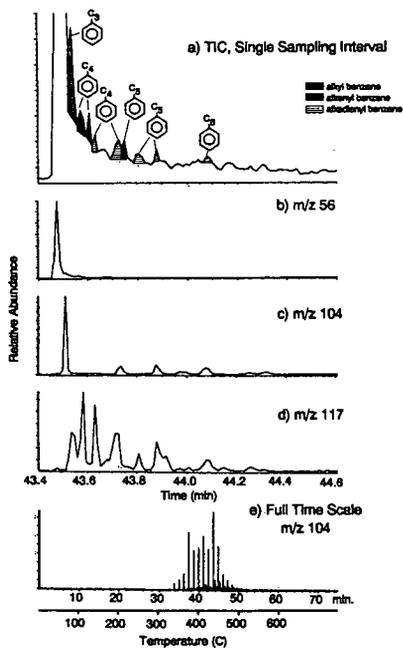


Figure 5. Decomposition of rubber in hydrogen atmosphere. a) Total ion intensity; ion intensity of b) m/z 56, butene; c) m/z 104, styrene; d) m/z 117, C₃H₄-benzene fragment; e) m/z 104 in the whole temperature range.

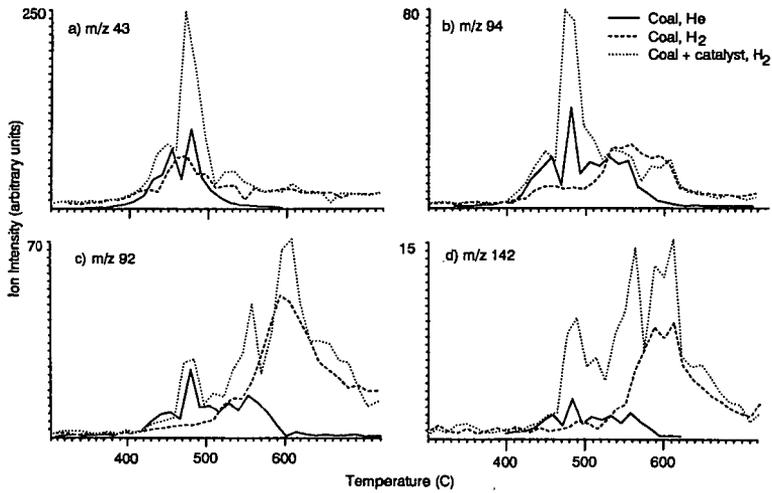


Figure 6. Effect of hydrogen and catalyst on evolution profile of coal decomposition products. a) m/z 43, propyl fragment, b) m/z 94, phenol; c) m/z 92, toluene; d) m/z 142 methyl naphthalene.

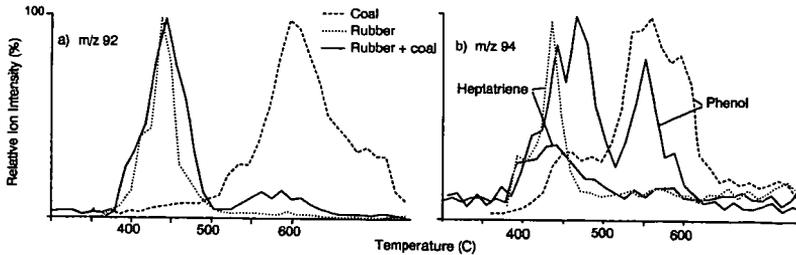


Figure 7. Evolution profile of a) m/z 92, toluene; b) m/z 94, phenol and heptatriene from the hydrolysis of coal, rubber and the mixture of coal and rubber.

A PROCESS TO RECOVER PLASTICS FROM OBSOLETE AUTOMOBILES BY USING SOLVENTS AT AMBIENT PRESSURE*

by

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INTRODUCTION

Recycling of the metal content of obsolete vehicles has been actively pursued since the 1950s [1]; today, obsolete automobiles are the single largest source of scrap iron. They contribute over 25% of the 36 metric tonnes (40 million short tons) of ferrous scrap recovered annually by the secondary metals industry and used in the production of finished steel products. They also contribute over one million metric tonnes (1.1 million short tons) of nonferrous metallic scrap a year for recycling. For each ton of metals recovered, about 500 lb of nonmetallic residue or waste is co-produced. Auto shredder residue (ASR) is a very heterogeneous mixture of solids and liquids. Table 1 lists most of the materials that are commonly present in the ASR. Figure 1 shows the relative concentration of the major constituents.

We have developed and tested in the laboratory a three-step process to separate thermoplastics, and other potentially recyclable products, from ASR [2]. The process involves a drying step followed by a mechanical separation step to concentrate the thermoplastics by separating the polyurethane foam and the fines, which are mostly metal oxides and other inert materials that are smaller than 0.62 cm (0.25 in.) in size. The concentrated plastics stream is then treated with organic solvents at ambient pressure and elevated temperatures to dissolve the desired plastics. The basic process is described in detail in Reference [2]. The salient features of the process are described below.

THE ARGONNE ASR-RECYCLING PROCESS

The Argonne process consists of three steps: drying, mechanical separation to concentrate the plastics, and solvent extraction of the plastics. The drying process is by indirect heating (i.e., steam coil) only. Flame or sparks could potentially set the material on fire. Drying at lower temperatures will minimize the evaporation of organic species along with the moisture, thereby avoiding a potential environmental problem that may require scrubbing or wastewater treatment.

The mechanical separation of polyurethane foam and fines (< 0.62 cm in size) from ASR is necessary for many reasons. First, the foam can be recovered as a potential product. Second,

* Work supported by U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, under Contract W-31-109-Eng-38.

the plastics in the remaining fraction can be concentrated (this results in smaller and less expensive equipment for the solvent-extraction operation and in lower solvent losses because fewer nonplastic materials that can absorb solvent [foam] or be wetted by it [dirt] will be present). Third, the presence of the fine, nonplastic particles will contaminate the extracted plastics unless excessive and costly filtration of the fine particles from the solution is performed. The mechanical separation was accomplished in the laboratory by using a fluidized column fitted with screens [2]. In the design of a 200-lb/day pilot plant, the plan is to use a trommel combined with a modified air classifier. Tests were conducted on several types of commercially available full-scale separation equipment. The trommel was selected because its of acceptable performance, moderate cost, and widespread use in the shredding industry.

An evaluation of the plastics-rich stream that remained after the separation of the foam and the fines, identified acrylonitrile-butadiene-styrene (ABS), polyvinyl chloride (PVC), polypropylene (PP), and polyethylene (PE) as potential candidates for recovery and recycling. ABS was targeted because of the high market value of the virgin resin and because of its good solubility characteristics in several mild organic solvents at low and moderate temperatures. PVC was selected because its chlorine content could be an obstacle if the stream is to be processed for its energy or chemical value (incineration, pyrolysis). In addition, reasonably clean PVC can also be used for making numerous products with flexible specifications. PVC, however, is susceptible to degradation upon thermal cycling; among the first signs of degradation is the appearance of a blackish color. PP was targeted for recovery because it is present in large quantities and its use by the automotive industry is on the rise. Moreover, because it is soluble only at high temperatures, it can be recovered with little contamination, except for the PP, which dissolves under very similar conditions. At this point, the economic values of PE and PP are not sufficient to justify their separation.

To minimize the contamination of the recovered plastics, the first step in the extraction process was to use a mild solvent (such as hexane) to extract the automotive fluids (see Table 1) without dissolving the targeted plastics. The "oils" recovered in the process have heating values between 16,000 and 178,000 Btu/lb. However, the hexane also extracts the PCBs that may be present in the ASR.

After the "oils" are extracted, the extraction of the plastics at ambient pressure was tested by using two methods. In the first method, selective solvents were used to extract individual plastics in series [2]. In the second method, a solvent was used to dissolve all of the plastics of interest, and then the mixed plastics were separated by using different solvents. Each method has advantages and disadvantages. For example, in the first method, the ABS and the PVC can be recovered without being exposed to the high temperature required for the recovery of PP and PE. However, the extraction steps occur in large reactors. In the second method, only one extraction has to be done in a large vessel. The separation of the mixed plastics can be conducted in smaller reactors. In addition, the second method enables more efficient cascading of the heat between the stages to minimize the energy requirement of the process. All of the plastics will, however, be exposed to the high temperature and will experience a higher number of thermal cycles. Therefore, the potential degradability of some of the products is higher. Products generated by both methods are under evaluation. The economics of both methods is also being studied.

Figures 2, 3, and 4 are the infrared spectra of recovered ABS, PVC, and PP/PE samples, respectively.

PROCESS ECONOMICS

Table 2 summarizes the key parameters used in and the results obtained from a preliminary economic study that we have recently completed. The results indicate that a three-year payback is realistically possible. This study assumed that the plant will charge no tipping fees for accepting the ASR and will pay no fees for the disposal of the nonmagnetic fines. It was, however, assumed that the recovered oil will be disposed of as a hazardous waste. No revenues were assumed for the material left after the extraction process is completed, even though it has a heating value of about 3,000-5,000 Btu/lb and is virtually dry, PCBfree, and nearly chlorine-free.

CONCLUSIONS

The work done so far on the process demonstrated that the process is technically feasible and potentially economical. The process uses all commercially available equipment, even though it can benefit from a better system for the mechanical removal of foam and fines. The economic competitiveness of the process is dependent on the market value of the recovered foam and the recovered plastics.

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Table 1. Composition of ASR

Recyclables	Energy Value*	Inerts
Thermoplastics	Gasoline	Glass
Foams	Brake fluid	Dirt
Fibers	Engine oil	Sand
Metal chunks	Transmission oil	Gravel
Rust	Grease	Moisture
Wires	Wood chips	
	Thermosets	
	Rubber	
	Tar	
	Paper	

* Heating value is about 2,500-7,000 Btu/lb.

Table 2. Economic Analysis of the Argonne
Plastics-Recycling Process

Item	Description/Value
Plastics product form	Pellet
Process type	Precipitation
Raw material source	ASR
Feed (MM PP)	183
Plastic output (MM PP)	25
Capital investment (MM)	7.5
Operating pressure (atm)	1
Costs (cents/lb)	
Variable	11
Fixed	8
Subtotal mfg. cost	19
Depreciation (20%)	5
Charge for ROI + wk cap	6
Netback Req'd (ex SAR)	30
Annual Realization (MM\$)	+1.6*
Payout time (yr)	3

* Value is determined on the basis of assumed values for the recovered materials of \$0.25/lb for foam and PVC, \$0.05/lb for PP&PE, and \$0.40/lb for ABS.

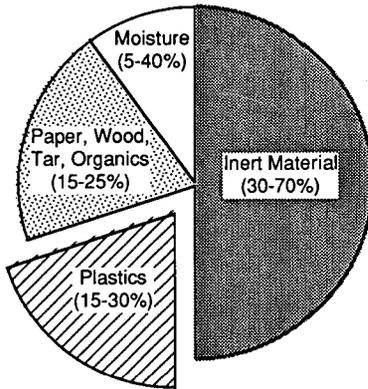


Figure 1. Approximate Composition of ASR

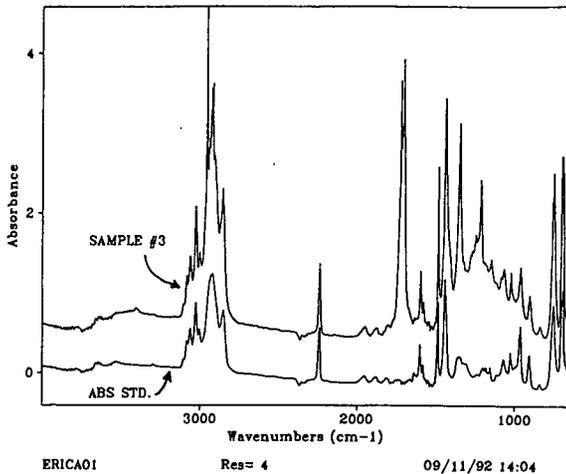


Figure 2. Infrared Spectra of Recovered ABS and Commercial-Grade ABS

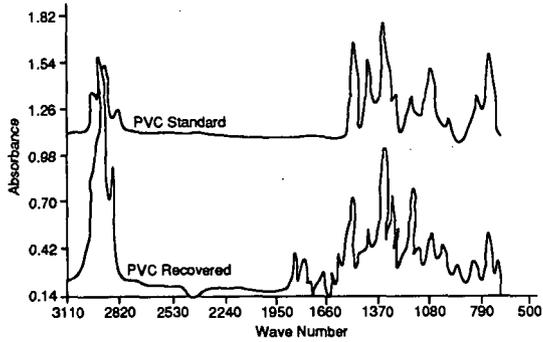


Figure 3. Infrared Spectra of Recovered PVC and Commercial-Grade PVC

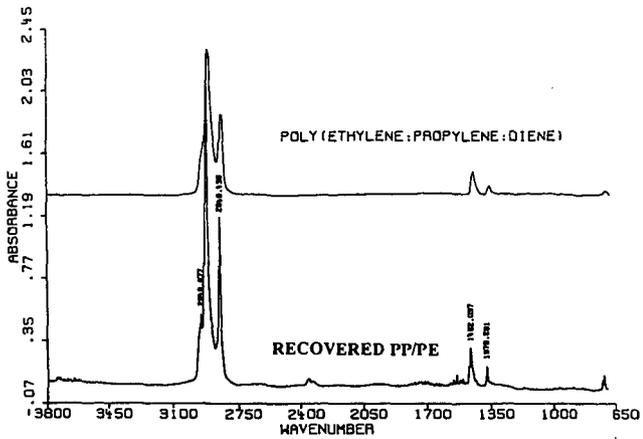


Figure 4. Infrared Spectra of Recovered PP/PE and PP/PE-Diene

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