

DESULFURIZATION AND SULFIDATION OF COAL AND COAL CHAR

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Part I: Desulfurization of Coal and Coal Char at Various Temperatures and Pressures

Introduction

This work was undertaken to obtain a better understanding of the desulfurization of Illinois No. 6 coal and of char derived therefrom. In particular, the effect of temperature, pressure, and methane content of the gas on the rate of sulfur removal and the final sulfur content of the product was studied.

The desulfurization of high-sulfur coals, cokes, and chars has been the subject of many investigations in the past, those pertaining to the desulfurization of coke going back as far as the 1850's. In recent times the subject has gained importance because of the necessity of utilizing large reserves of high-sulfur coal and of reducing the emission of sulfur-bearing gases in plants using coal or coke.

Experimental

Illinois No. 6 coal or char derived therefrom was used in all experiments; the size of the particles was between 12 and 18 mesh (average particle diameter ≈ 1.3 mm). The coal was dried for 24 hours at 110°C before it was used. Two types of char were prepared by treating the dried coals in H₂ for 3 hours at 600 or 800°C. The total sulfur content and the amounts of the various forms of sulfur present in the coal and the char (prepared at 600°C) are given in Table I.

The desulfurization experiments, using either dried coal or one of the chars, were done in H₂, He, CH₄, and mixtures of H₂ and CH₄ for periods of time up to 3 hours at 600 and 800°C at pressures up to 10 atm. For each experiment 100 to 250 mg of sample, contained in a platinum or nickel basket, was suspended in the hot zone of a resistance furnace. The gas flow rate was 0.5 l(STP)/min in all cases. The samples were lowered into and pulled out of the hot zone as quickly as possible under a flow of He. At the end of an experiment the entire sample was analyzed for total sulfur by means of the combustion method(1).

In selected cases surface-area measurements on partially desulfurized samples were made using the BET method. Use was also

made of electron-probe analysis and optical microscopy, in particular in those cases where the form of the sulfur was of interest.

Results and Discussion

The results for the desulfurization of dried coal in H_2 , CH_4 , and He at 600 and 800°C are shown in Figures 1 and 2. In all cases a rapid loss of sulfur during the first 30 minutes is observed. This initial rapid desulfurization is due partly to the reduction of pyrite (FeS_2) to pyrrhotite (FeS) and partly to the loss of less stable organic sulfur.

The coal originally contained 0.52 percent sulfur as pyrite (Table I), present as particles with an average diameter 1 to 50 μ . Typical pyrite particles, as observed in the dry coal, are shown in Figure 3a and b. Electron-probe analysis showed that these particles have a composition approaching that of FeS_2 (Figure 3c).

The partial pressure of sulfur in equilibrium with FeS_2 and FeS is 1 atm at 690°C(2). Therefore, some decomposition of pyrite into pyrrhotite is expected in an inert atmosphere at 600°C. This is shown in Figure 3d, e, and f for a coal which was treated for 10 min in He at 600°C. The composition of the large porous particle in Figure 3d was found to be close to that of pyrrhotite, as shown by Figure 3e, whereas the two smaller particles in Figure 3d had a composition between pyrite and pyrrhotite (Figure 3f).

Figure 3g is a micrograph of char prepared at 600°C, the chemical analysis of which is shown in Table I. This char served as the starting material for subsequent desulfurization experiments. The porous particles, in the center of the micrograph, are pyrrhotite formed by the complete reduction of pyrite, as evidenced by the x-ray spectrum in Figure 3h. This observation is in keeping with the chemical analysis in Table I which showed that no pyritic sulfur was present in this char.

It is interesting to note that the observed gasification in CH_4 is the same at 600 and 800°C, whereas in He or H_2 the gasification is about 20 percent higher at 800°C than at 600°C. It is generally accepted that the carbonization of coal takes place in two stages(3). In the temperature range 350 to 550°C the so-called primary devolatilization (not involving CH_4) takes place. The secondary gasification, involving mainly the release of CH_4 and H_2 , begins at about 700°C. In the presence of CH_4 , secondary gasification is therefore inhibited at 800°C and involves mainly the primary devolatilization equal to that observed at 600°C.

Although two types of char were used in the desulfurization experiments, only the experimental results pertaining to the char prepared at 600°C are presented here. The results obtained for the

char prepared at 800°C are similar and will not be presented in detail.

The effect of pressure and composition of the H₂-CH₄ mixture and temperature on the rate of desulfurization of char, prepared at 600°C, is shown in Figures 4 to 6. Lower sulfur contents and higher rates of desulfurization are favored by an increase in PH₂ and temperature. The presence of CH₄ inhibits desulfurization.

In gas mixtures containing more than 25 percent CH₄, gasification ceased after about 30 min of reaction time to reach a plateau (Figure 5). The gasification corresponding to this plateau is shown as a function of the percentage of CH₄ in the gas in Figure 7. For the char prepared at 600°C, gasification during desulfurization at 800°C (T_g) decreased considerably with increasing CH₄ percentage in the gas. Gasification for the char prepared at 800°C was only slightly dependent on the amount of CH₄ in the gas, irrespective of the temperature of desulfurization.

As seen from these results, desulfurization of coal char takes place in two distinct stages. The first stage shows a simultaneous rapid desulfurization and gasification. During the second stage sulfur is removed more slowly, practically independent of the extent of any further gasification. The observed initial rapid loss of sulfur together with the initial rapid gasification suggests that there may exist a relationship between the initial fractional removal of sulfur, $(\Delta S/S_0)_i$, and that of carbon, $(\Delta C/C_0)_i$.

The data in Figure 8 show the relative sulfur removal after about 15 minutes reaction time as a function of the relative carbon loss incurred during this time. A similar relationship was observed for the char prepared at 800°C. It is seen from Figure 8 that for each desulfurization temperature (T_g) the data points corresponding to various experimental conditions (e.g., total pressure, CH₄ content) form a curve, indicating a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$.

Further examination of the data in Figure 8 shows that the same functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ exists, irrespective of the temperature at which desulfurization took place. This is shown in Figure 9 where the open circles represent all the data points in Figure 8. Also shown in Figure 9 are the results obtained for the char prepared at 800°C, which show a similar relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$; however, the slope is steeper than observed for the char prepared at 600°C. The higher the char preparation temperature, the more gasification and desulfurization has taken place during charring. Therefore, it should not be concluded that it is generally more advantageous to use a char, prepared at a higher temperature, for subsequent desulfurization.

Also included in Figure 9 are the data from Jones, et. al. (4) who desulfurized a char derived from Illinois No. 6 coal,

prepared at 870°C. The desulfurization temperature varied between 704 and 1010°C, the pressure between 1 and ~8 atm, and they used H₂ as well as equimolar mixtures of H₂ and CH₄. Although their data show some scatter, it is concluded that there exists a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$. The data of Batchelor et. al.(5) who used a char, prepared at 500°C, from a Pittsburgh seam coal, are also shown in Figure 9. Desulfurization took place in H₂-H₂S mixtures (P_{H₂} between 1 and 11 atm) at temperatures varying between 650 and 880°C. Also for these data, a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is observed. It may thus be concluded that the functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is dependent only on the temperature at which the char was prepared. Subsequent desulfurization of a given char can only be achieved at the expense of loss in carbon, the extent of which is determined by the appropriate functional relationship depicted in Figure 9.

After the initial rapid drop in sulfur content of the char, a more gradual decrease is observed, Figures 4 to 6. Assuming that for this stage of the process the desulfurization reaction may be described by a first-order reaction relative to the sulfur content of the char, then

$$\frac{dS}{dt} = -k_S S \quad 1)$$

where S is the concentration of sulfur at time t and k_S a rate constant. Integration of Equation 1 gives

$$\log \frac{S}{S_0} = -k_S t \quad 2)$$

where S₀ is the sulfur concentration after 15 minutes of reaction time, after which desulfurization proceeds more gradually.

Because of the scatter in the experimental results, it was not considered warranted to treat the results obtained for the two chars separately. Figure 10, depicting the first-order plots, therefore represents the averages for both types of char. It is seen that log(S/S₀) is a linear function of time within the scatter of the data.

The rate constant k_S, obtained from the slopes of the lines in Figure 10, is shown in Figure 11A as a function of the concentration of H₂ in the H₂-CH₄ mixture for the desulfurization experiments at 5 atm pressure at 600 and 800°C. Although the equilibrium concentrations of CH₄ in H₂-CH₄ mixtures at 5 atm pressure are 56 percent and 16 percent at 600 and 800°C, respectively(2), no measurable weight increase of the char was recorded after treatment in CH₄ at 800°C. This indicates that CH₄ did not dissociate to any measurable extent under the present experimental conditions. Therefore, it may be assumed that the partial pressure of H₂ prevailing during the desulfurization experiments in H₂-CH₄ mixtures was the same as that in the ingoing mixture.

On this basis, Figure 11B was plotted, supplemented with some data obtained from desulfurization experiments in 100 percent H_2 at 1 and 5 atm pressure. It is seen that the rate constant pertaining to the second stage of desulfurization in 100 percent H_2 is the same as that in H_2 - CH_4 mixtures, although in 100 percent H_2 gasification continues in the second stage (Figures 4 to 6). This suggests that desulfurization and gasification are interrelated in the initial stages only; in the second stage desulfurization takes place at a rate independent of gasification.

To explain these observations, it is suggested that the initial loss of carbon—which is accompanied by a simultaneous loss of (mainly organically bound) sulfur—creates new pores providing better access for the reducing gas to the pyrrhotite particles embedded in the char. This is supported by the observed change in surface area of the char during desulfurization. The initial surface area of char prepared at $600^\circ C$ is about $2\text{ m}^2/\text{g}$. The change in surface area is most pronounced during the first hour of desulfurization, particularly at $800^\circ C$, Figure 12. The pore surface area increases with increasing temperature and pressure and, hence, the amount of gasification.

A char, prepared at $600^\circ C$ and subsequently desulfurized for 2 hours in 5 atm H_2 at $800^\circ C$, was analyzed for the various forms of sulfur present in the product. The analysis showed that of the total sulfur content of 0.16 percent, about 0.11 percent was present as pyrrhotite and about 0.05 percent as organic sulfur. The micrograph in Figure 13a for this partially desulfurized product shows three types of particles: bright, greyish colored, and two-phase particles partly bright and partly grey. The composition of the greyish particles varies somewhat but nominally approaches that of pyrrhotite (Figure 13b and c). The bright particles are iron (Figure 13d) formed by the complete reduction of pyrrhotite.

It is concluded from these observations that most of the sulfur is in the form of pyrrhotite during the later stages of desulfurization. The overall rate of desulfurization during this stage is thus expected to be mainly governed by the slow reduction(6) of pyrrhotite in H_2 .

Conclusions

It was found that the desulfurization of coal char in mixtures of H_2 and CH_4 takes place in two distinct stages. In the first stage rapid desulfurization is accompanied by gasification. These two processes were shown to be interrelated, the relationship being dependent on the char preparation temperature only. The second stage of desulfurization was found to proceed at a much slower rate and is being controlled by the slow reduction of pyrrhotite to iron.

References: listed at end of part II.

Table I

Forms of Sulfur (in Wt.%) Present in Dried
Coal and Char Derived Therefrom (3h, H₂, 600°C)

<u>Form of Sulfur</u>	<u>Dried Coal</u>	<u>Coal Char</u>
Pyrite	0.53	-
Sulphate	0.12	0.005
Sulphide	0.005	0.13
Organic	1.27	0.61
Total	1.93	0.75

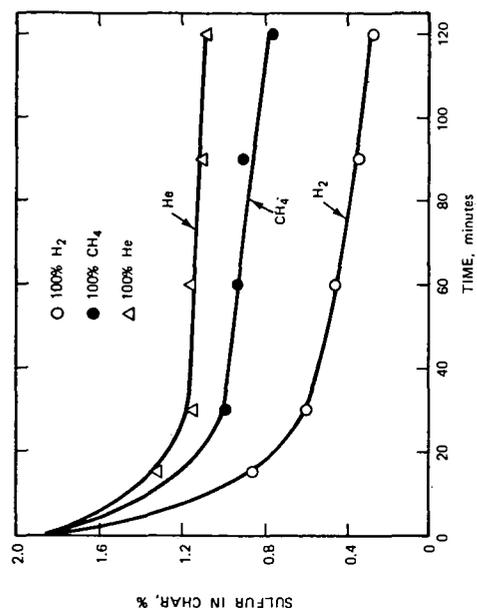
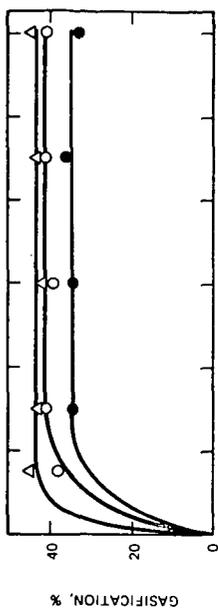


Figure 2. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H₂, CH₄, AND He AT 800°C AND 1 ATM PRESSURE

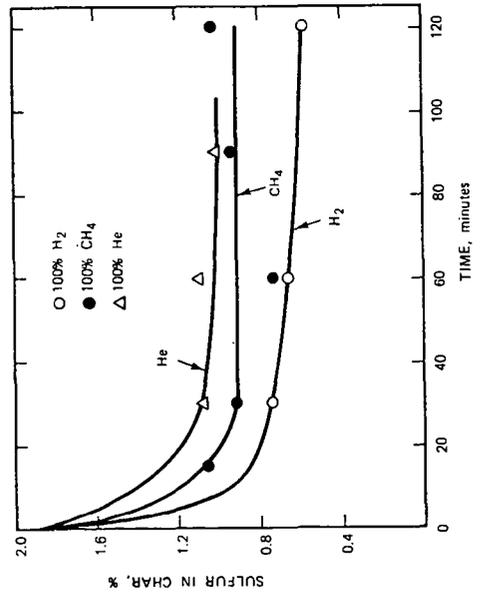
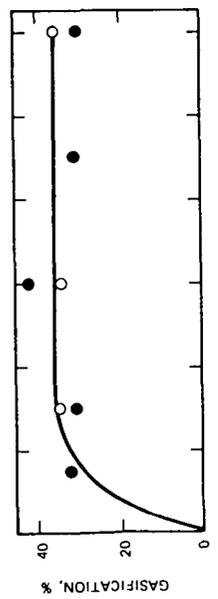


Figure 1. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H₂, CH₄, AND He AT 600°C AND 1 ATM PRESSURE

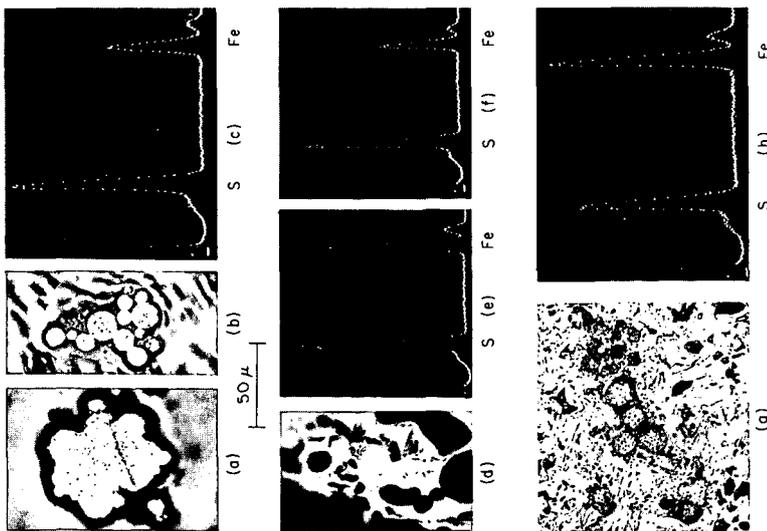


Figure 3. MICROGRAPHS AND ELECTRON PROBE ANALYSIS FOR COAL AND CHAR
 TOP: ORIGINAL DRY COAL;
 MIDDLE: COAL TREATED IN He AT 600°C FOR 10 MIN;
 BOTTOM: CHAR (3h. IN H₂ AT 600°C).

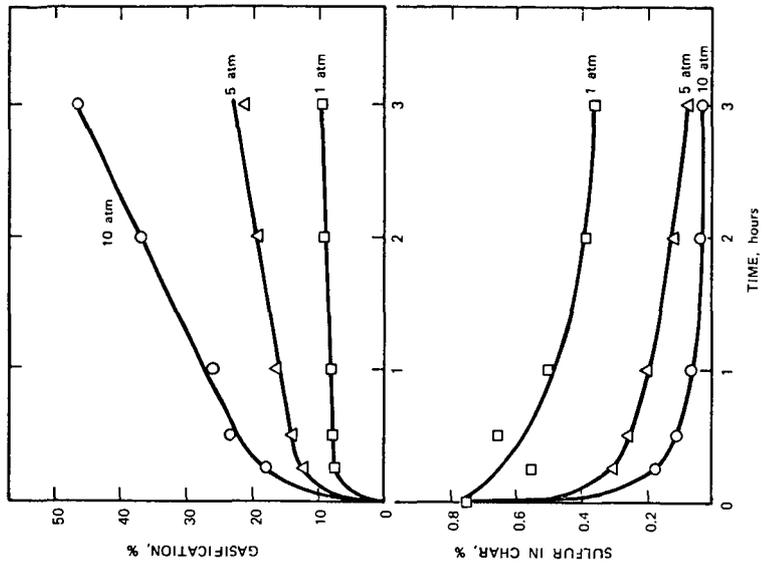


Figure 4. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H₂ AT INDICATED PRESSURES AT 800°C

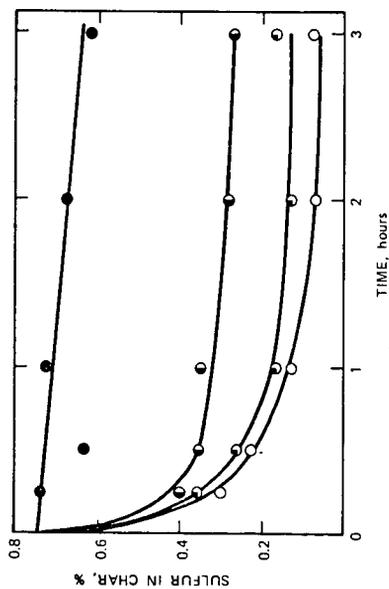
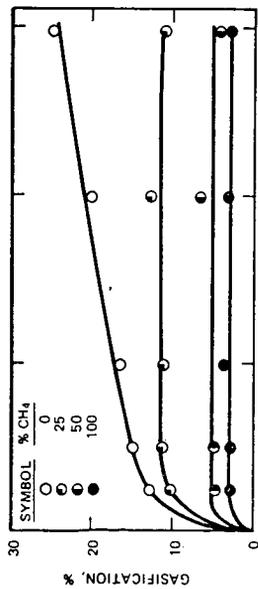


Figure 5. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H₂-CH₄ GAS MIXTURES OF 5 ATM AT 800°C

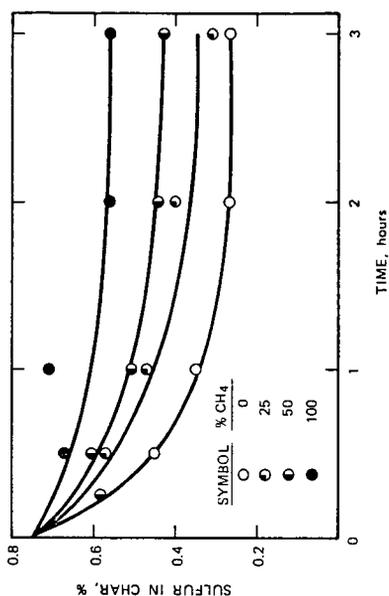
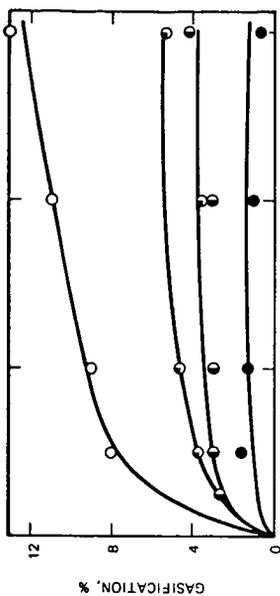


Figure 6. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H₂-CH₄ MIXTURES OF 5 ATM AT 600°C

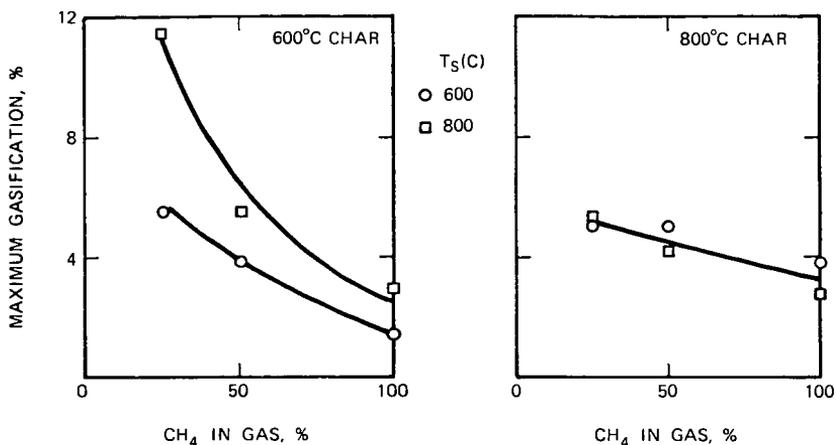


Figure 7. FINAL LEVEL OF GASIFICATION AS A FUNCTION OF THE AMOUNT OF CH₄ IN H₂-CH₄ MIXTURES FOR TWO TYPES OF CHAR, DURING DESULFURIZATION AT 600 AND 800°C (T_S)

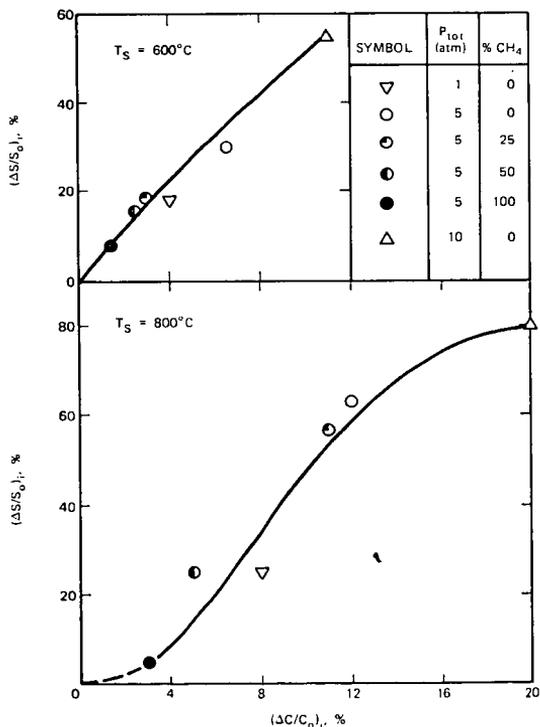


Figure 8. RELATION BETWEEN INITIAL LOSS OF SULFUR AND CARBON (AFTER 15 MINUTES REACTION TIME) FOR A CHAR PREPARED AT 600°C AND SUBSEQUENTLY DESULFURIZED UNDER INDICATED CONDITIONS AT T_S = 600 OR 800°C

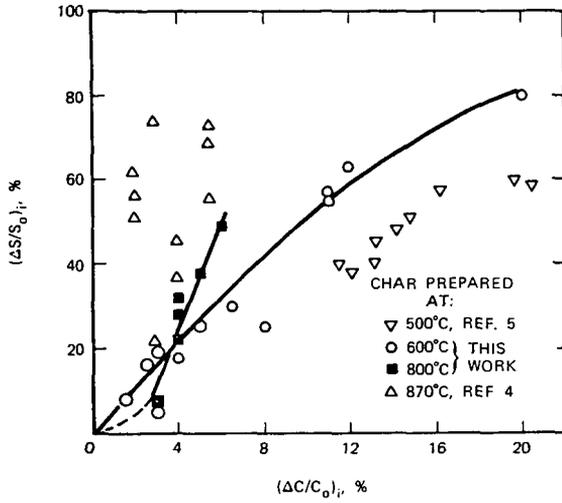


Figure 9. GENERAL RELATIONSHIP BETWEEN INITIAL LOSS OF SULFUR AND CARBON FOR TWO TYPES OF CHAR, SHOWING THAT THE DATA FOR VARIOUS EXPERIMENTAL CONDITIONS FOR A GIVEN CHAR ARE REPRESENTED BY THE SAME FUNCTION

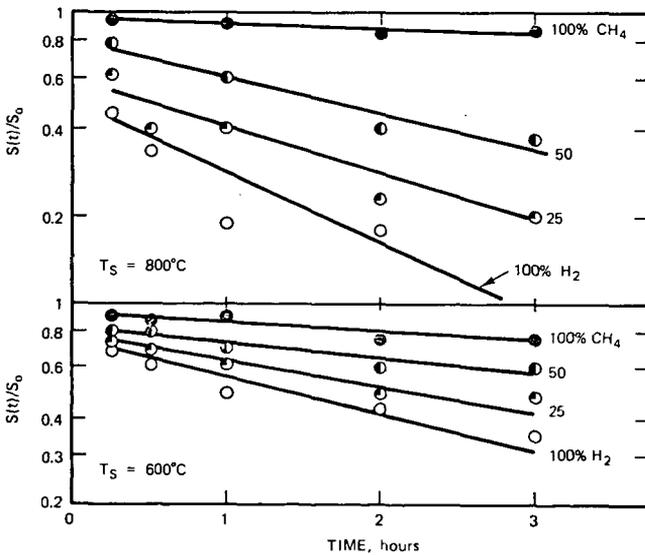


Figure 10. DESULFURIZATION OF CHAR IN MIXTURES OF H₂ AND CH₄ AT 5 ATM AND INDICATED TEMPERATURES, AS A FIRST-ORDER REACTION

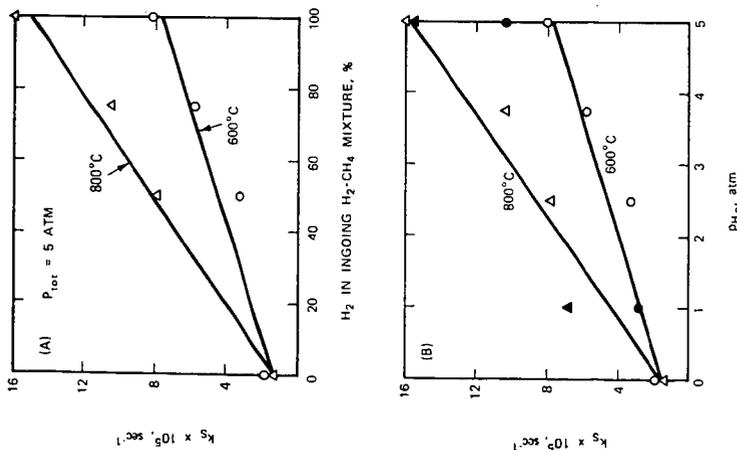


Figure 11. FIRST-ORDER RATE CONSTANTS FOR DESULFURIZATION AT INDICATED TEMPERATURES SHOWN AS A FUNCTION OF (A) H_2 CONTENT OF GAS MIXTURE (5 ATM) (B) PARTIAL PRESSURE OF H_2 (SOLID SYMBOLS REPRESENT DATA FOR 100% H_2)

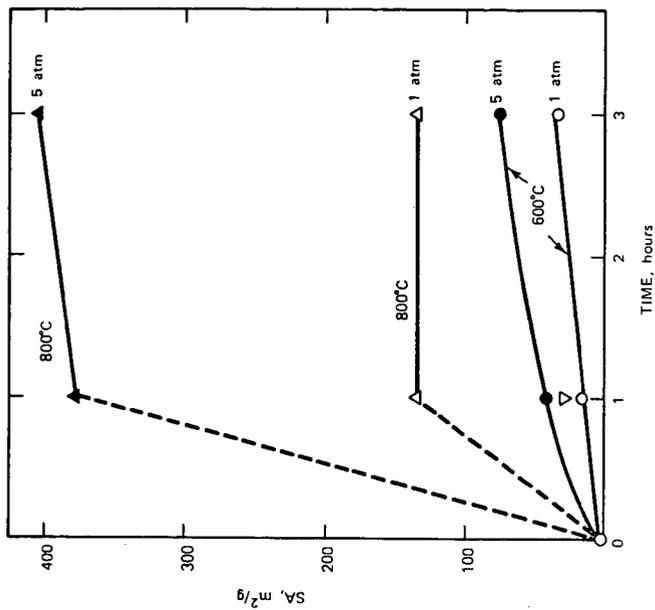


Figure 12. SURFACE AREA (SA) OF CHAR AFTER TREATMENT IN H_2 AT INDICATED TEMPERATURES AND PRESSURES

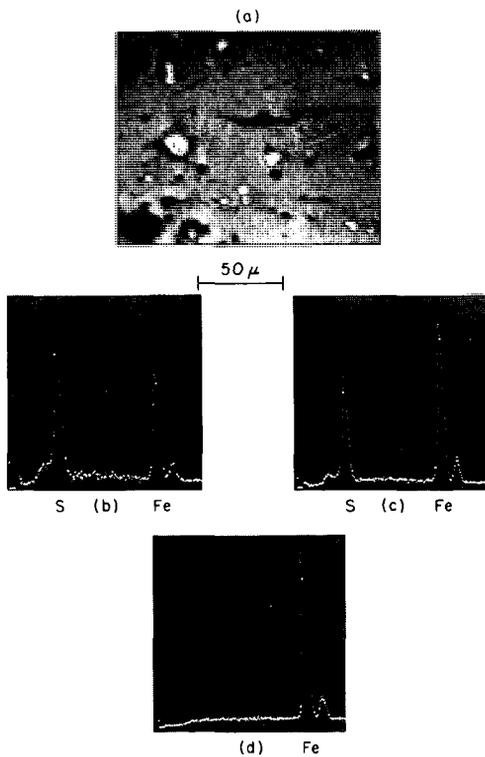


Figure 13. OPTICAL MICROGRAPH AND ELECTRON ANALYSIS OF CHAR, TREATED IN $p_{H_2} = 5$ atm, 800°C FOR 2 HOURS, SHOWING THE PRESENCE OF PYRRHOTITE AND REDUCED IRON

Part II: Sulfidation of Coal Char and Synthetic Chars

Introduction

Desulfurization of coal and coal char in hydrogen results in evolution of H_2S . Depending on the process, the H_2S is either entirely or partly removed and recirculated. The work, described in Part II, was undertaken to obtain a better understanding of the interaction between chars and gas mixtures containing H_2S .

A literature survey indicated that no investigations have been made of the sulfidation of carbonaceous materials, including chars, in gas mixtures of H_2 and H_2S such that the sulfur potential was systematically varied.

Experimental

Char from two different sources, prepared under a variety of conditions, was used in this work. The preparation conditions are summarized in Table II.

The preparation of char from Illinois No. 6 coal was described in Part I (Experimental). Char from ash-free filter paper (0.008% ash) was prepared by charring the paper, contained in a high-purity alumina boat, in an atmosphere of dry He at 600 or 900°C for 3 hours. After the paper was charred, the boat was pulled to the cool end of the reaction tube where it slowly cooled. Subsequently, the char was quickly transferred to a desiccator where it was stocked. The chars that were further treated in He at 1250 and 1500°C for 24 and 96 hours, respectively, were taken from this stock.

The sulfidation experiments were done in a vertical furnace with the H_2 - H_2S mixture entering at the bottom of the reaction tube. The H_2/H_2S -ratio in the gas was adjusted by using the usual arrangement of capillary flow meters. In most of the experiments a gas flow rate of 30 cm^3 (STP)/min was used.

For each sulfidation experiment about 100 mg of char was placed in an alumina tray. In most cases the sulfidizing treatment was one hour, after which the sample was quickly pulled up to the cool top of the reaction tube, while the He was kept flowing. The cooled sample was then transferred to a desiccator. Sulfur in the char was analyzed by the combustion method(1).

In some selected cases about 750 mg of char was sulfidized, and afterwards analyzed for oxygen by the neutron-activation method. The surface areas of the chars used were determined by the BET method.

Results and Discussion

The partially desulfurized coal char (Table II) was sulfidized at 600, 800, and 900°C in H_2 - H_2S containing 0 to 100 percent H_2S . The results are given in Figure 14, in which the sulfur content of the char after one hour reaction time is plotted versus the percentage of H_2S in the gas at the experimental temperature, denoted by $(\%H_2S)_T$. Similar results were obtained after sulfidation for 4 hours.

In calculating $(\%H_2S)_T$ from the percentage of H_2S in the ingoing gas (at room temperature), due allowance should be made for the partial dissociation of H_2S at higher temperatures. The equilibrium H_2S percentage of the gas at the reaction temperature was calculated from the available thermodynamic data (2).

The present results may be compared with those obtained by Polansky, et. al. (7) who treated coke in H_2S - N_2 mixtures containing 4.2 and 8.8 percent H_2S . Their results show no pronounced difference in the extent of sulfur absorption at 800 and 900°C.

Of special interest is the absorption of sulfur at 900°C in H_2 - H_2S mixtures, containing less than 2 percent H_2S , by previously desulfurized coal char (from Illinois coal). This coal char was produced by desulfurization of a char that originally contained 0.13 percent sulfur as pyrrhotite; this is equivalent to about 0.23 percent iron. Upon sulfidation of this desulfurized coal char, pyrrhotite is expected to form when the sulfur potential is sufficiently high. This is illustrated in Figure 15, where a sudden rise in the amount of sulfur absorbed is observed when $(\%H_2S)_T > 0.3$. This is in good agreement with the value calculated from the thermodynamic data for the iron/pyrrhotite equilibrium (2) at 900°C. The increase in sulfur content at the "break point" in the absorption curve is about 0.20 percent, in good agreement with the estimated amount of iron present in the char.

The sulfur absorption curves, depicted in Figure 14, have the general character of absorption isotherms. However, proper interpretation of these results is hindered by the presence of impurities in the coal char. It was therefore decided to study the sulfidation of essentially impurity-free carbons and synthetic chars.

Sulfidation of Synthetic Carbons and Chars

Granulated samples of high-purity electrode graphite and pyrolytic graphite were equilibrated with a 50 percent H_2 , 50 percent H_2S mixture at 1000°C for 1.5 hours; there was no detectable sulfur absorption in either form of graphite. In another experiment samples of electrode graphite and pyrite were placed in separate

parts of an evacuated silica capsule and annealed for 20 hours at 650°C. This corresponds to a partial pressure of sulfur vapor of about 0.14 atm, as estimated from the thermodynamic data for the pyrrhotite/pyrite system(2). After this treatment, no sulfur was detected in the graphite.

The present observations are in general agreement with those of Wibaut and van der Kam(8) who found that even at sulfur pressures above atmospheric, no detectable sulfur was absorbed by either diamond powder or Ceylon graphite.

The results obtained for the synthetic chars are given in Figures 16 and 17 for 600 and 900°C, respectively. In most experiments the reaction time was 1 hour; however, some samples were sulfidized for longer times (up to 3 hours). These samples absorbed essentially the same amount of sulfur as those sulfidized for 1 hour. Moreover, it was observed that equilibrium could be reached from both sides. For example, it was found that filter-paper char (prepared at 900°C) which was first sulfidized in a 50 percent H₂, 50 percent H₂S mixture at 600°C to a final sulfur content of ~1 percent could subsequently be partially desulfurized in a 90 percent H₂, 10 percent H₂S mixture to yield a final sulfur content of 0.4 percent. This is essentially the same as the sulfur content after direct sulfidation of the char in the same gas mixture. Similar observations were made at 900°C, indicating that the absorbed sulfur is in equilibrium with the gas and that the process of sulfur uptake is reversible.

The surface areas of the chars (Table II) are indicated in Figures 16 and 17. It is seen that a char with a larger surface area has, in general, a larger capacity for sulfur absorption. The results obtained for coal char are also shown in Figures 16 and 17 for easy comparison. Coal char and filter-paper char (prepared at 600 and 900°C) have about the same surface areas and are seen to absorb similar amounts of sulfur.

The results of x-ray analysis of the various chars used in this investigation were compared in a qualitative way with the data reported by Turkdogan et al.,(9) as shown in Table III together with estimated mean crystallite sizes. It was mentioned before that graphitized electrode graphite, which has a mean crystallite size of 500 Å, did not absorb sulfur, whereas the nongraphitized chars did. Thus, it is concluded from these results that the ability of a given char or carbon to absorb sulfur is in the first place determined by its state of crystallinity. In poorly graphitized or nongraphitized carbons, the amount of absorbed sulfur increases with increasing pore surface area.

In view of the strong affinity between sulfur and oxygen, an attempt was made to investigate the effect of oxygen on the sulfur absorption by char. The initial oxygen content of synthetic chars is shown as a function of the surface area in Figure 18. It is seen that the initial oxygen concentration is a strong function of the surface area and hence the temperature at which the char was prepared (Table II).

To study the change in oxygen concentration after sulfidation of the chars, a series of special experiments was conducted; the results are summarized in Table IV. It is interesting to note that the oxygen content after sulfidation was independent, within the analytical error, of the ratio $(\text{PH}_2\text{S}/\text{PH}_2)_T$ in the gas. An increase in the sulfidation temperature resulted in a lower oxygen content in the char, particularly if the char had a larger surface area (Figure 18).

In all cases investigated, it was found that the chars with large surface areas contained more oxygen. Because of the interdependence of surface area and oxygen content, it is difficult to separate their effects on the capacity of a given char for sulfur absorption. However, some indication of the influence of oxygen on the sulfur absorption may be obtained from the results shown in Table IV. For instance, the surface areas of filter-paper char prepared at 600 and 900°C were 330 and 272 m²/g, respectively, a difference of about 20 percent. After sulfidation at 600°C in a gas of high sulfur potential, the oxygen contents of these chars differed by about a factor of two, yet the difference in sulfur absorbed was not more than about 10 percent. These findings indicate that the influence of oxygen on the sulfur absorption is probably secondary.

In this context the work of Hofmann and Ohlerich(10) should be mentioned. They treated sugar charcoal in dry O₂ at about 500°C to obtain a char containing about 10 percent oxygen as surface complexes. Upon sulfidation of this oxygenated char in S₂ at 600°C, they found that the amount of sulfur taken up was equal to that absorbed by a char which was not previously activated in oxygen. Hofmann and Ohlerich concluded, as did Hofmann and Nobbe(11), that the amount of sulfur absorbed by char is dependent only on its surface area.

Some of the filter-paper chars used in this work were analyzed for hydrogen and nitrogen. The results are summarized in Table V, which shows that the major impurities in filter-paper char are oxygen and hydrogen. The oxygen and hydrogen contents decrease with increasing temperature of char preparation, while the nitrogen content remains essentially constant.

The shape of the curves in Figure 19, in which the amount of sulfur in some synthetic chars is shown as a function of $(\text{PH}_2\text{S}/\text{PH}_2)_T$, strongly suggests absorptive behavior. Hayward and

Trapnell(12) give examples of typical absorption isotherms and note that chemisorption normally gives rise to isotherms of this general form.

Although a treatment of the present results in terms of idealized absorption isotherms is open to criticism, an attempt will nevertheless be made to treat the results accordingly. It will be shown that such a treatment leads to results which may be considered reasonable.

Assuming that the chemisorbed sulfur forms an ideal monolayer and that each chemisorbed species occupies a single site, application of the ideal Langmuir isotherm gives(12)

$$a = \frac{\theta}{B(1 - \theta)} \quad 1)$$

where a is the activity of the chemisorbed species, θ the fractional coverage, and B a temperature-dependent parameter containing the heat of chemisorption of sulfur. The fractional coverage $\theta = v/v_m$, where v is the volume of chemisorbed sulfur (STP) per gram of char and v_m the volume giving a complete monolayer of sulfur on the surface of the char. The surface area, $S \text{ m}^2/\text{g}$, is related to v_m by the following expression:

$$S = \frac{v_m}{22414} NA \cdot 10^{-20} \quad 2)$$

where N is Avogadro's number and A the cross-sectional area of an adsorbed species in A^2 . The volume, v , of the chemisorbed sulfur is obtained from the measured sulfur concentration as follows:

$$v_s = \frac{22414}{3200} (\%S) \quad 3)$$

Substituting for the sulfur activity $a = (p_{\text{H}_2\text{S}}/p_{\text{H}_2})_T$, $\theta = v/v_m$, and making use of Equations 2 and 3, the following expression is obtained from Equation 1.

$$\frac{1}{(\%S)} (p_{\text{H}_2\text{S}}/p_{\text{H}_2})_T = 1.87 \frac{A}{S} \left[\frac{1}{B} + (p_{\text{H}_2\text{S}}/p_{\text{H}_2})_T \right] \quad 4)$$

The experimental results plotted in accordance with Equation 4 are given in Figures 20 and 21 for 600 and 900°C, respectively. The slope of each line should be proportional to $1/S$; in fact, this is shown to be the case in Figure 22, in which $\log(\text{slope})$ is depicted as a linear function of $\log S$ with a theoretical slope of -1. From the intercept of this line with the ordinate the value of A ,

the cross-sectional area of a chemisorbed species, is calculated to be 17 \AA^2 . This value is to be compared with cross-sectional areas ranging from 10 to 50 \AA^2 as estimated from physical absorption data for a variety of gases(12).

According to Equation 4, the intercepts of the lines in Figures 20 and 21 with the ordinate should be proportional to $1/S$. This is shown to be the case in Figure 23, in which \log (intercept) is depicted as a function of $\log S$ with a theoretical slope of -1 . From the intercepts of both lines with the ordinate, together with the previously determined value of A , the temperature-dependent parameter B is obtained. This parameter is proportional to e^q/RT , where q is the heat of chemisorption of sulfur on char. From the temperature dependence of B , the value of q is estimated to be about -10 kcal/mole , a reasonable value when compared with the heats of chemisorption of other gases on carbon, as listed by Hayward and Trapnell(12).

The foregoing analysis, although of necessity oversimplified, shows that the absorption of sulfur by synthetic chars is most likely mainly governed by chemisorption. It is thus expected that the surface area is an important parameter in determining whether a given char or carbon is able to retain significant quantities of sulfur. This is in agreement with earlier work by Hofmann and Nobbe(11) and by Polansky, et al.(7).

However, the surface area is not the only parameter to be considered. For instance, electrode graphite in the unoxidized state has a surface area of $1 \text{ m}^2/\text{g}$ (9), approximately the same as filter-paper char prepared at 1500°C (Table II). Yet, no take-up of sulfur by electrode graphite was observed after sulfidation in 50 percent H_2 , 50 percent H_2S at 1000°C . The mean crystallite size, together with the X-ray analysis, of electrode graphite(9) shows that its nature is graphitic and therefore more ordered. Blayden and Patrick(13) concluded from their work that so-called disordered carbons with small carbon layers (equivalent to mean crystallite size) and many defects are better able to absorb sulfur than the more crystallite and graphitic carbons. The present findings are consistent with this viewpoint.

Conclusions

In the absence of impurities such as iron, the ability of chars or carbons to absorb significant amounts of sulfur in a sulfidizing gas such as a H_2 - H_2S mixture depends on the state of crystallinity of the carbonaceous material. The sulfur absorption decreases with increasing crystallite size. In general, carbons having a mean crystallite size of about 15 \AA or less absorb significant amounts of sulfur when treated in H_2 - H_2S mixtures. For carbons with a given crystallite size, the higher the pore surface area the higher is the amount of sulfur absorbed.

Sulfur absorption in high-purity chars, obtained from ash-free filter paper, increased with increasing sulfur activity and pore surface area of the char. This is in accord with the Langmuir relation for chemisorption on single sites in an ideal monolayer.

It is concluded from the present experimental results that sulfur is not accommodated in the three-dimensional lattice of the carbon but is chemisorbed on the surface. However, such chemisorption takes place only on the pore walls of nongraphitic (poorly crystalline) carbons, of which chars are good examples.

Acknowledgment

The author wishes to thank J. R. Cauley of this laboratory for his assistance with the experiments.

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Table II

Source, Conditions of Preparation, Initial Sulfur (S_i) and Oxygen (O_i) Contents and Surface Area (SA) of the Various Chars Studied

Source	Preparation Conditions	Properties of the Char		
		SA, m ² /g	S_i , %	O_i , %
Illinois Coal	5 atm H ₂ , 800°C for 3 h	400	0.05	-
Ash-free Filter Paper (0.008% ash)	1 atm He, 600°C, 3h	330	0.00	4.0
	1 atm He, 900°C, 3h	272	0.00	1.4
	1 atm He, 600°C, 3h+	30	0.00	0.34
	1 atm He, 1250°C, 24h			
	1 atm He, 600°C, 3h+	3	0.00	0.14
1 atm He, 1500°C, 96h				

Table III

Qualitative Comparison of the Crystallinity of Filter-Paper Chars Used in This Work With the Crystallinity and Mean Crystallite Size of Some Carbons Investigated by Turkdogan, et al. 9)

Type of Char and Preparation Temp., °C	Crystallinity from Turkdogan's Work	
	Qualitative Comparison From X-ray Analysis	Mean Crystallite Size, Å
Filter paper (600)	Between coconut charcoal and "vitreous" carbon	~10 - ~16
Filter paper (900)		
Filter paper (1250)	Approaching vitreous carbon	~16
Filter paper (1500)	Same as vitreous carbon	~16

Table IV

Oxygen and Sulfur Contents of Filter-Paper Chars After Sulfidation at 600 and 900°C for 1 Hr in Gases of Various Sulfur Potential

Sulfidation Temperature, °C	Preparation Temperature, °C	O _i , %	$\left(\frac{\text{PH}_2\text{S}}{\text{PH}_2}\right)_T$	Sulfidized Char	
				% O	% S
600	600	4.0	0.05	1.7	0.80
			61.5	1.6	9.50
	900	1.4	0.05	0.8	0.20
			61.5	0.8	8.40
1250	0.34	0.05	0.2	0.03	
		0.14	0.1	0.02	
900	600	4.0	0.05	0.7	0.90
			7.6	0.6	7.50
900	900	1.4	0.05	0.9	0.40
			7.6	0.6	5.80
1500	0.14	0.05	0.1	0.01	
		7.6	0.1	0.25	

* O_i = initial oxygen content of the char.

Table V

Chemical Analysis of Filter-Paper Char in Relation to Preparation Temperature

Char-Preparation Temperature, °C	Composition, weight percent			
	Carbon	Oxygen	Hydrogen	Nitrogen
600	93.9	4.0	1.9	0.02
900	97.0	1.4	0.6	0.06
1250	99.6	0.34	0.2	0.04

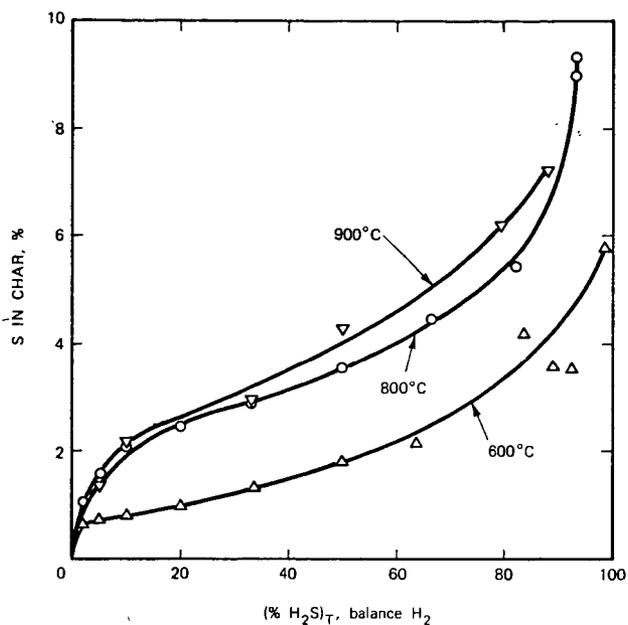


Figure 14. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR FROM ILLINOIS NO. 6 COAL AT INDICATED TEMPERATURES

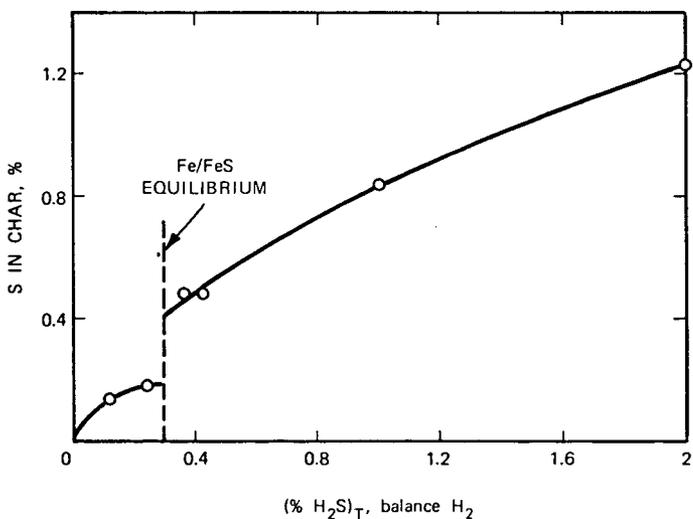


Figure 15. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR AT 900°C IN H₂-H₂S MIXTURES FOR LOW PERCENTAGES OF H₂S

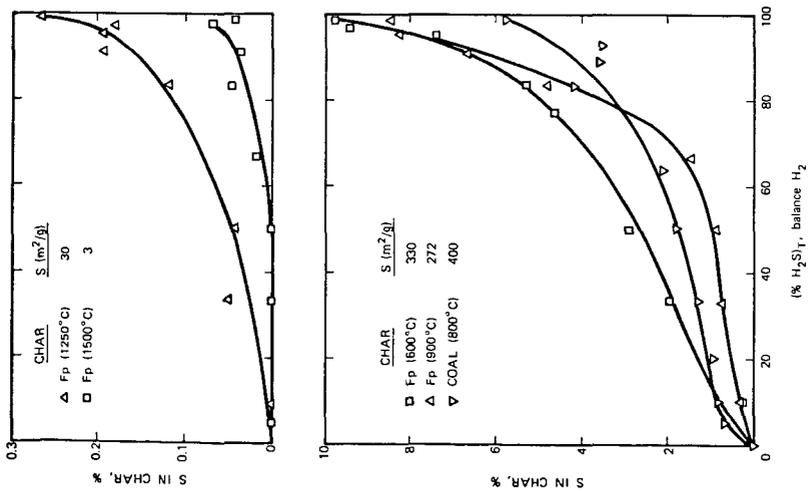


Figure 16. SULFIDATION AT 600°C IN H₂-H₂S MIXTURES OF VARIOUS CHARs, HAVING INDICATED PORE SURFACE AREA (S)

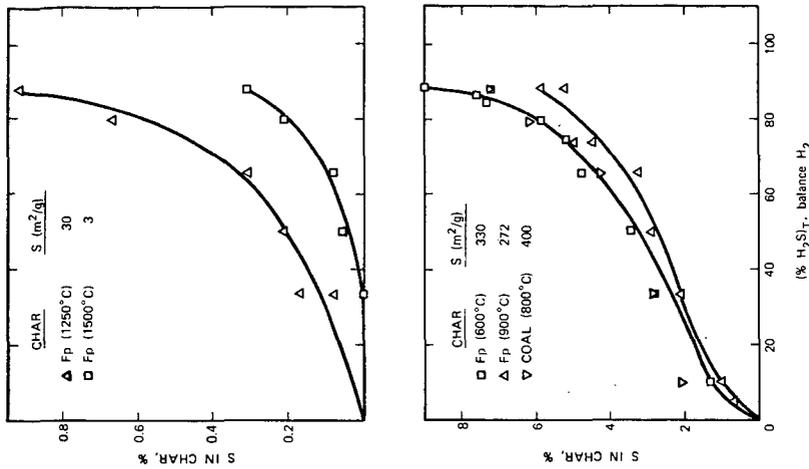


Figure 17. SULFIDATION AT 900°C IN H₂-H₂S MIXTURES OF VARIOUS CHARs, HAVING INDICATED PORE SURFACE AREA (S)

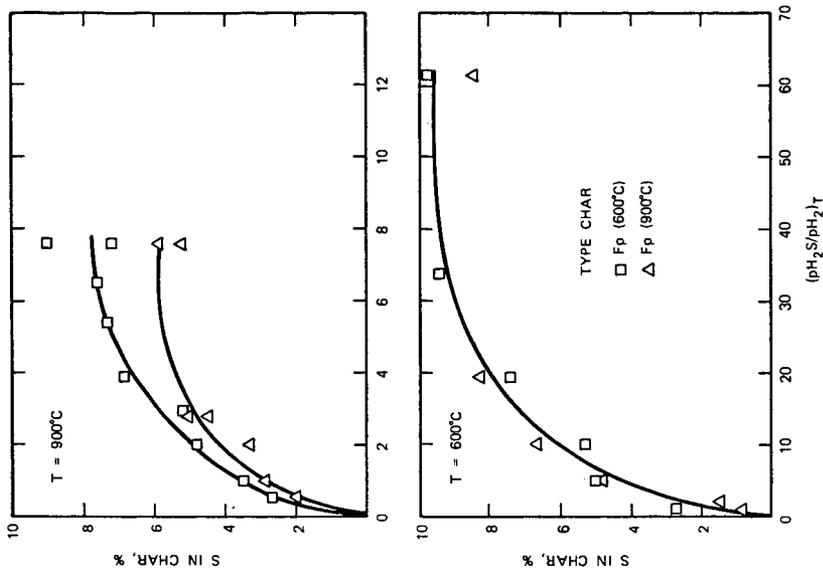


Figure 19. SULFIDATION OF VARIOUS CHARS AT 600 AND 900°C, SHOWING CURVES TYPICAL FOR CHEMISORPTION

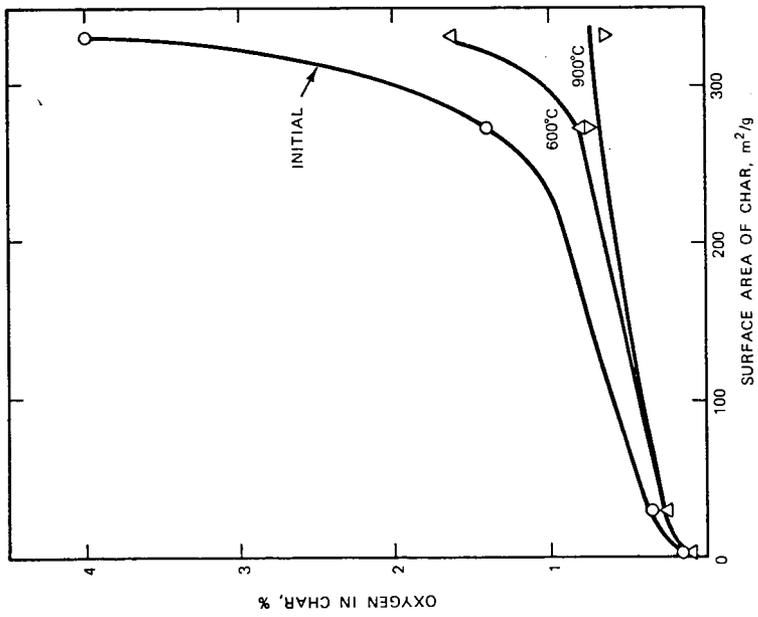


Figure 18. OXYGEN CONCENTRATION IN SYNTHETIC CHARS AS A FUNCTION OF SURFACE AREA: INITIAL, AND AFTER SULFIDATION AT 600 AND 900°C

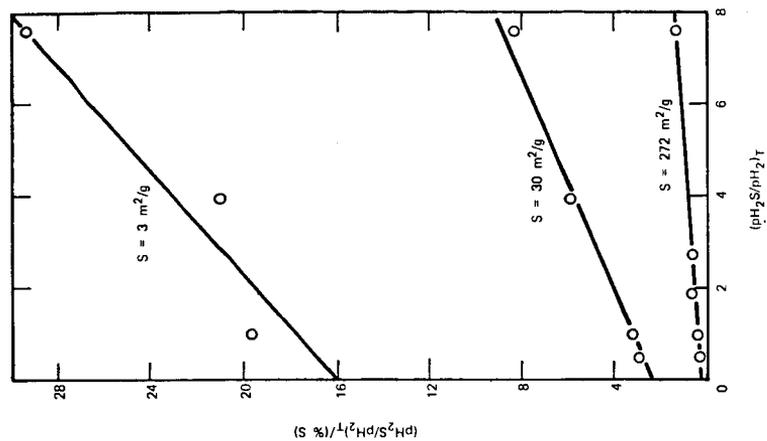


Figure 21. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 800°C ON CHARs HAVING INDICATED SURFACE AREAS

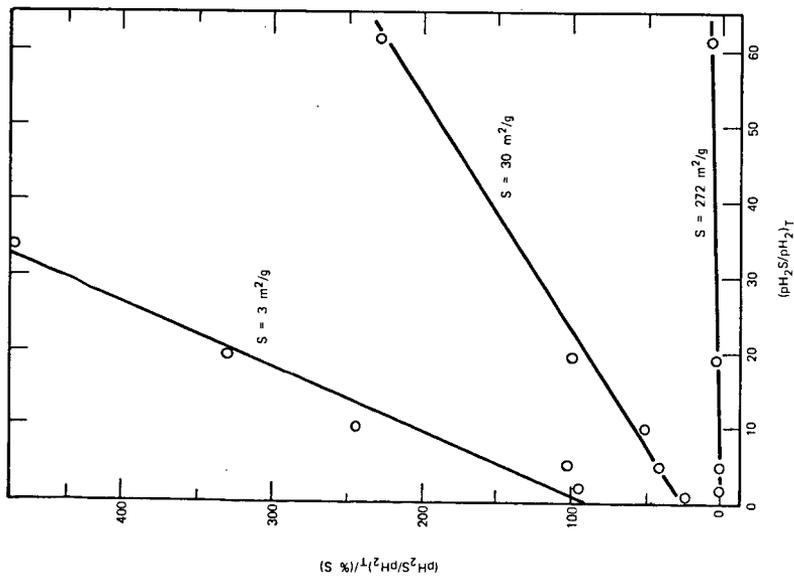


Figure 20. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 600°C ON CHARs HAVING INDICATED SURFACE AREAS

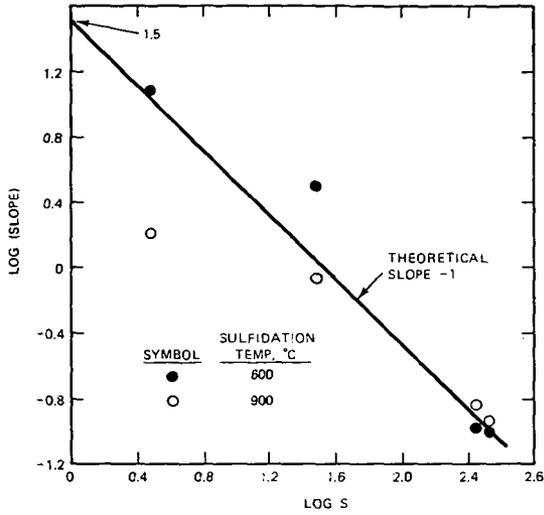


Figure 22. SLOPE OF CHEMISORPTION ISOTHERMS AT 600 AND 900°C AS A FUNCTION OF THE SURFACE AREA OF THE CHAR

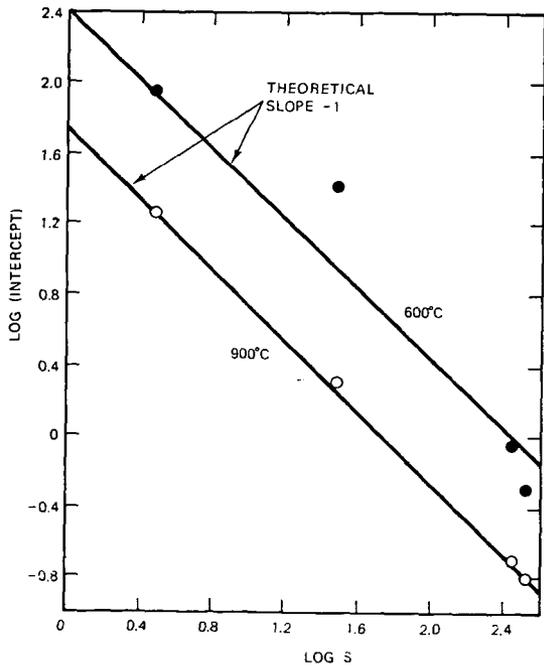


Figure 23. INTERCEPT OF CHEMISORPTION ISOTHERMS WITH ORDINATE AS A FUNCTION OF SURFACE AREA OF THE CHAR, SULFIDIZED AT INDICATED TEMPERATURES

FLUID-BED CARBONIZATION/DESULFURIZATION
OF ILLINOIS COAL BY THE CLEAN COKE
PROCESS: PDU STUDIES*

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Introduction

The CLEAN COKE Process combines both fluid-bed carbonization and hydrogenation/liquefaction to convert high-sulfur coal to low-sulfur metallurgical coke, chemical feedstocks, and to a lesser extent, liquid and gaseous fuels. The overall processing scheme, which has previously been described in detail (1), is illustrated by the sketch in Figure 1.

Briefly, run-of-mine coal is beneficiated and classified by conventional means and split into two feed portions: a sized fraction suited for fluid-bed processing and a fines fraction suited for high-pressure hydrogenation. The sized feed is dried and subjected to a mild surface oxidation in a nonpressurized bed fluidized with air-enriched flue gas. The dry, preoxidized feed is then carbonized in two stages, at 820°F (440°C) and 1400°F (760°C), in fluid-bed reactors operated at pressures up to 150 psig, to produce low-sulfur char, tar, and gas rich in methane and hydrogen. The fines fraction of the beneficiated coal, combined with run-of-mine coal, is dried, pulverized, and slurried with a process-derived oil. The slurry is then pumped to a pressure reactor and liquefied at 850 to 900°F (455 to 480°C) and a pressure of 3000 to 4000 psig to produce liquids and C₁-to-C₄ hydrocarbon gases. Liquids from both operations are distilled to produce a light chemical oil, a middle oil for recycle to the hydrogenation reaction, and a heavy oil. The heavy oil, a soft pitch, is combined with the carbonization char and processed to make a low-sulfur metallurgical formcoke, currently in the form of pellets. Similarly, product gases from all operations are combined and processed to produce hydrogen for the hydrogenation operation, fuel, ethylene and propylene, sulfur, and ammonia. A detailed description of yield of chemical products and process economics has been presented previously (2).

This paper presents the results obtained from sustained operation of the carbonization PDU (process-development unit). These results confirm and extend the data obtained previously in bench studies (3). All tests were run with Illinois No. 6 seam coal con-

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taining 2 to 2.5 percent sulfur after preparation. From this were produced chars containing, generally, 0.6 to 0.7 percent sulfur; char containing as little as 0.2 percent sulfur was produced under the more severe reaction conditions. Reaction conditions investigated for their effect on char sulfur content included residence time, temperature, pressure, and H₂S concentration in the fluidizing gas. Data are also presented to show the weight distribution of materials into and out of the PDU system. The scale of the tests discussed in this paper is best illustrated by a description of the design and operation of the carbonization PDU.

The Carbonization PDU

Figure 2 is a photograph of the carbonization PDU, in which the fluid-bed reactor occupies the second level; feed vessels are on the top level; the char receivers are at floor level. Two other vessels visible at floor level in the picture are liquid catchpots attached to the gas-to-gas heat exchanger (on the right) and the water-cooled exchanger (on the left). Construction details of the fluid-bed carbonizer are illustrated by the diagram in Figure 3. The vessel, including top and bottom closures, is 9 feet 3 inches tall and is fabricated from 1-inch-thick Incoloy Alloy 800 to permit operation at 1500°F (815°C) and 150 psig. The lower 36-inch section of the reactor is the 10-inch-ID fluid-bed area; the expanded upper 36-inch section has a 20-inch ID, to facilitate deentrainment of fine solids from the fluidizing gas. Feed enters the fluid bed by gravity flow through the feed pipe, positioned about 1 inch above the gas-distributor plate; char exits the fluid bed through the overflow pipe at 30 inches above the distributor plate. The vessel also contains an internal cyclone, which removes char fines from the exiting gas and returns them to the fluid bed.

The major components and stream flows of the complete PDU are illustrated in the simplified diagram in Figure 4. Feed is metered by rotary feeders from either of two lock hoppers to the fluid-bed carbonizer, from which product char overflows and falls into one of the two receivers, also lock hoppers. Residence time in the reactor is controlled by varying the solids feed rate.

Gas derived from carbonization of the feed is recycled through the system to fluidize the bed. Carbonization gases, along with recycle gas, leave the fluid bed, pass through the internal cyclone in the expanded section, and leave the vessel. The gas then passes through an external cyclone and into the gas-to-gas interchanger (shell and tube design), where it is partially cooled by heat exchange with clean recycle gas returning to the main gas heater. In the interchanger, the carbonization gas is also contacted with a spray of wash oil to remove tar mist and char dust, which collect in the interchanger pot. The gas then passes to a water-cooled exchanger for final cooling to about 110°F (45°C), after which it passes in series through a wash-oil scrubber and a caustic scrubber for final

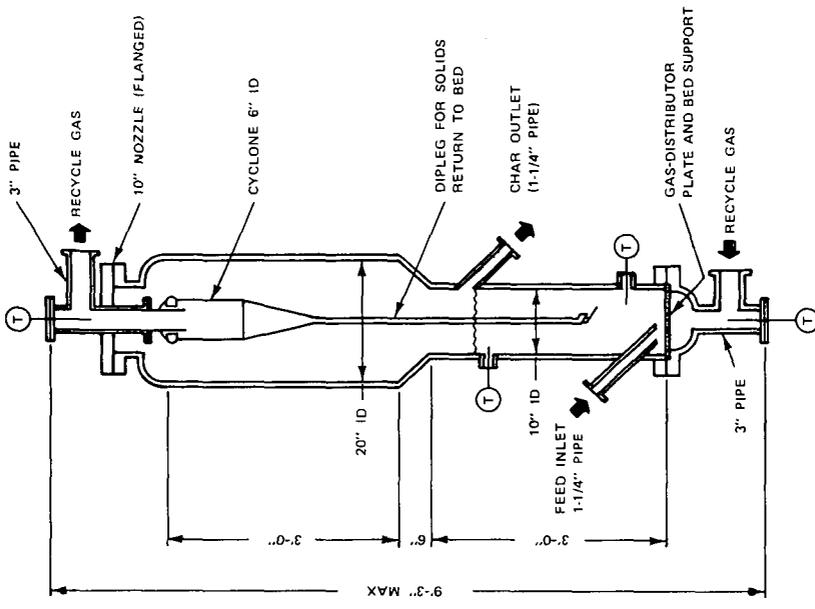


Figure 3. FLUID-BED CARBONIZER

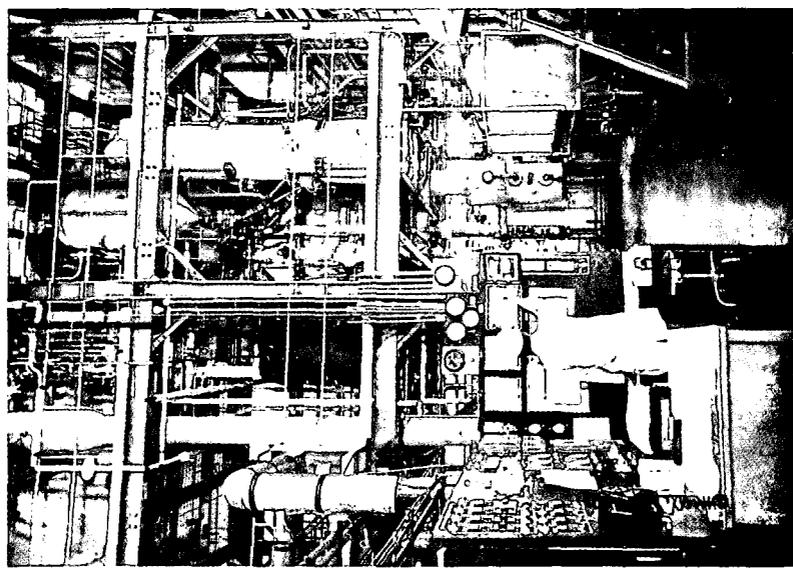


Figure 2. CARBONIZATION PDU FOR CLEAN COKE PROCESS

cleanup of tar mist, char dust, and acid gases—particularly H_2S . The clean gas is then recycled by a compressor through the shell side of the interchanger to the main electric heater, where it is reheated to the temperature desired to maintain the fluid bed at design temperature. Actual temperature of gas from the heater varies with operating conditions in the reactor, but the temperature of gas exiting the heater is on the order of $100^\circ F$ ($55^\circ C$) higher than bed temperature. Net product gas is vented by a pressure regulator-controller through a wet-test meter and sampled for analysis.

The function of the water-injection system, Figure 4, is to maintain a concentration of about 8 volume percent water vapor in the recycle gas while the gas is in contact with the hot alloy-metal surfaces of the main gas heater during second-stage carbonization. The presence of 8 volume percent water vapor, along with 50 ppm H_2S , prevents formation of carbon deposits on the hot metal surfaces, which attain temperatures above about $1500^\circ F$ during second-stage carbonization. Previous experience has shown that, without the water vapor, carbon deposits grew to sufficient size to significantly impede gas flow through the heater. Moreover, the carbon resulted in catastrophic carburization of the metal and destroyed the original recycle-gas heater. With water vapor and H_2S present, carbon formation is controlled, at least up to metal wall temperatures of $1550^\circ F$ ($845^\circ C$). Water is injected as a liquid into the interchanger shell-side gas inlet, where it is vaporized by external electric heaters. Most of the injected water condenses in the wash-oil quench in the interchanger pot and in the gas cooler. The remainder of the water condenses into the caustic-scrubber solution.

It should be noted that the wash-oil spray system is operated in different modes for the two stages of carbonization. For first-stage carbonization at $820^\circ F$, wash-oil quench of the gas occurs at the top of the interchanger to provide a washed-tube flow, which prevents plugging of the tubes by tar/char agglomerates. For second-stage carbonization at 1300 to $1400^\circ F$ (705 to $760^\circ C$), wash-oil quench of the gas occurs below the interchanger tube bundle. In this mode, tube-exit gas temperature is controlled at about $900^\circ F$ ($480^\circ C$) to prevent condensation of tar within the tubes.

Fresh wash oil, at about 2 gallons per hour, is metered continuously into the wash-oil scrubber to maintain a low concentration of tar and char fines in the oil system. Overflow from the level-controlled scrubber flows into the gas-cooler pot, from which the wash oil is pumped to the spray nozzle in the gas/gas interchanger. Wash-oil blowdown, including dissolved tar and suspended water and char, is removed from the interchanger pot. Wash-oil blowdown is screened to remove plus 50-mesh solids, heated to boil off contained water, and flash-distilled to separate heavy oil boiling above $540^\circ F$ ($280^\circ C$), which is used as part of the binder for coke production. The flash distillate is processed through a continuous distillation column at atmospheric pressure to separate a chemical oil distilling

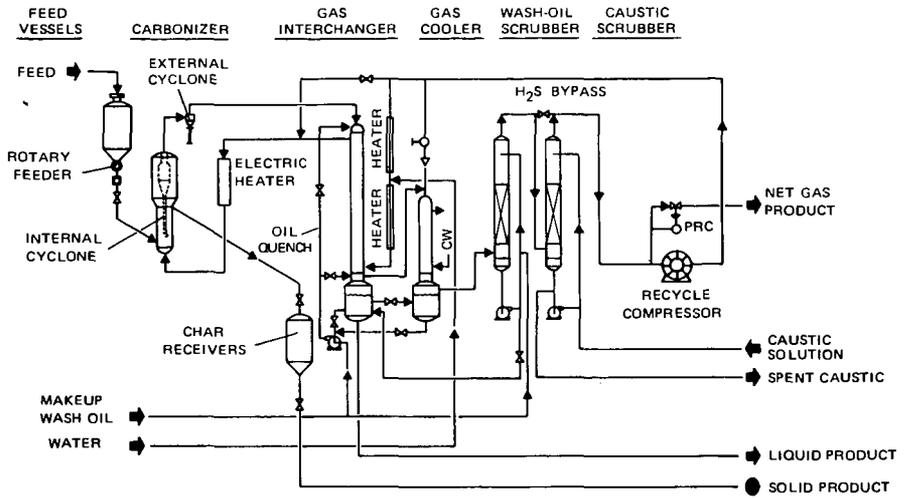


Figure 4. SCHEMATIC OF CLEAN COKE PROCESS CARBONIZATION PDU

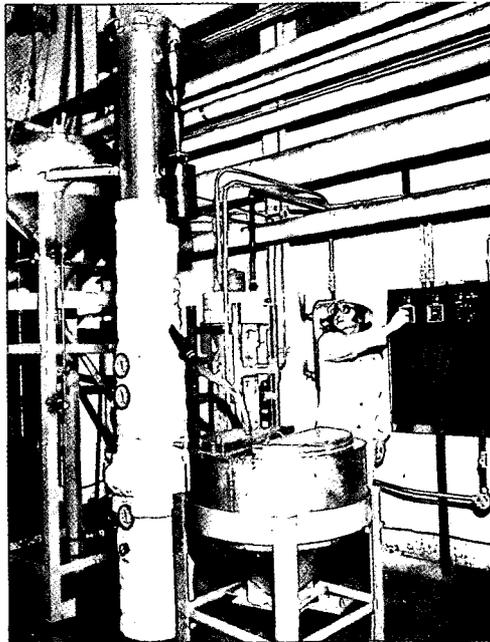


Figure 5.
CONTINUOUS 10-INCH
COAL OXIDIZER

to 445°F (230°C) as overhead and fresh wash oil as bottoms. The wash oil consists essentially of mono- and dimethylnaphthalenes, acenaphthene, and quinoline bases.

The final system is caustic scrubbing, which is used to control H₂S concentration in the recycle gas. Normally, H₂S concentration in the gas is maintained in the range 50 to 100 ppm, which aids in controlling carbon deposition from the catalytic decomposition of the carbon components in the gas. Control of H₂S concentration may be effected by means of partial bypass of gas around the caustic scrubber and by varying the rate of metering fresh caustic solution (about 7% NaOH) into the scrubber. Generally, the PDU operators prefer to use the latter method.

The Continuous Coal Oxidizer

An important adjunct to the carbonization PDU, the continuous coal oxidizer dries and preoxidizes the sized coal feed. The need for preoxidation of Illinois coal was discussed in the previous paper (3) on bench-scale studies, which showed that a mild surface oxidation of the coal diminishes its caking tendency sufficiently to prevent its agglomeration when it is heated at 800°F (425°C) in first-stage carbonization. Mild surface oxidation in this use refers to oxidation so slight that petrographic examination reveals virtually no change in the surface of the treated coal (4).

In practice, sized coal feed is heated at 350°F (177°C) for a 20-minute residence time in a bed fluidized with air at atmospheric pressure. The continuous coal oxidizer, shown in Figure 5, is similar in design and operation to the carbonizer reactor. The unit consists of a 10-inch-ID carbon-steel fluid-bed reactor with a coal-feed and product-overflow system and an electrically heated air supply. As in the PDU, the fluid bed of the coal oxidizer is heated to and maintained at design temperature by the heated fluidizing air. This unit is capable of oxidizing up to 1 ton of coal per 24 hours of operation, and it is normally operated at a coal feed rate of about 60 pounds per hour.

Heated air is used in the existing coal oxidizer for convenience only. In a larger operation, the oxidizer can be operated with waste flue gas containing about 2 percent oxygen to achieve adequate preoxidation of the feed coal.

Because the effluent gas from the coal oxidizer contains only moisture and dust from the fluid bed, waste-gas cleanup is accomplished by a small external cyclone and dust filters in the vent system. The yield of dry, oxidized coal is essentially a function of moisture content in the coal charged, which is generally about 8 percent by weight.

Experimental Results From First-Stage Carbonization

Carbonization of the oxidized coal in the PDU is conducted in two separate stages to avoid agglomeration of feed in the fluid bed. Initial carbonization is effected at temperatures in the range 800 to 840°F (425 to 450°C) to partially devolatilize the coal and produce a semichar, which can be fed subsequently into a fluid bed at 1400°F without agglomeration. The operating limits on temperature for the first stage were determined by bench-scale studies on the agglomeration problem. A nonagglomerating semichar was obtained at 800°F and incipient agglomeration was observed at about 850°F.

Although the primary function of first-stage carbonization is reduction of the agglomerating property of the coal, about two thirds of the carbonization tar is produced in this stage. Gas production is low in the first stage, amounting to about 15 weight percent of the total gas produced. Analysis of the recycle gas shows its composition (in mole %) to be methane, 71; ethane, 13; carbon monoxide, 10; hydrogen, 2; and C₂-to-C₄ hydrocarbons, 4.

Tests were made in the PDU to study the effect upon volatile-matter and sulfur contents in the semichar of bed temperature, residence time, system pressure, and H₂S concentration in the recycle gas. The variation in volatile-matter content with temperature and residence time is illustrated in Figure 6, which shows that volatile-matter content varies inversely with temperature and residence time and is independent of pressure over the range 15 to 160 psia. In the figure, a few data points from a 1-inch continuous bench-scale unit were included to extend the pressure range to 15 psia. Generally, about half the volatiles were eliminated from the coal in first-stage carbonization, and all the semichar products were processed through second-stage carbonization without agglomeration.

Response of sulfur content to residence time and temperature of first-stage carbonization is shown graphically in Figure 7. Sulfur content of the semichar product also varies inversely with temperature and residence time and is independent of pressure over the ranges studied; conditions included temperatures of 800 and 840°F, residence times of 20 to 80 minutes, and pressures of 80 to 160 psia. In these tests, H₂S concentration was controlled in the range 50 to 100 ppm. However, a test was run at 800°F, 52 minutes residence time, 120 psia, and H₂S concentrations varying from 300 to 2000 ppm. The semichar product from this test contained 1.77 percent sulfur, which is in the range normally attained with low H₂S concentration in the recycle gas.

Temperature and residence time thus appear to be the only variables having an effect on volatiles and sulfur remaining in the semichar product. The data in Figures 6 and 7 indicate that, at the temperatures deemed feasible, first-stage devolatilization/desulfurization is essentially complete in about 20 minutes residence time. To provide a consistent data base for process design, first-stage car-

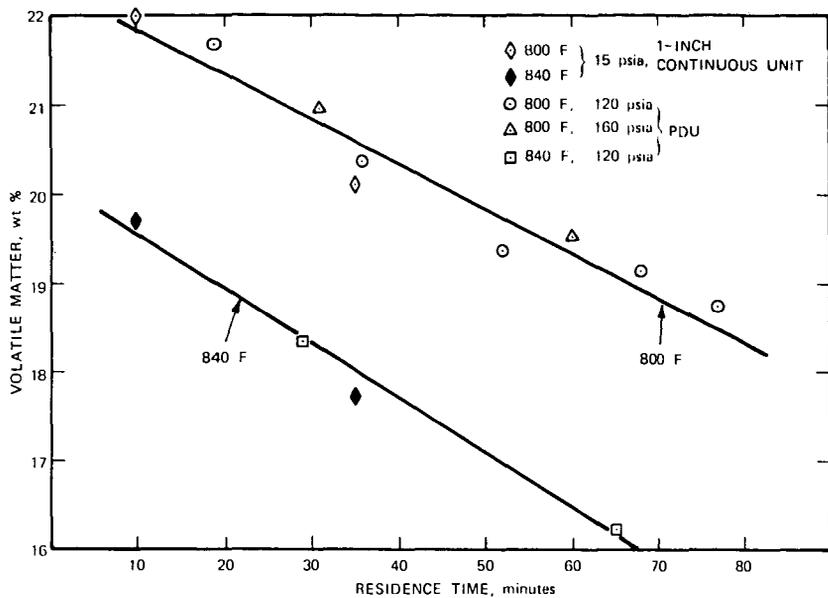


Figure 6. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON COAL DEVOLATILIZATION

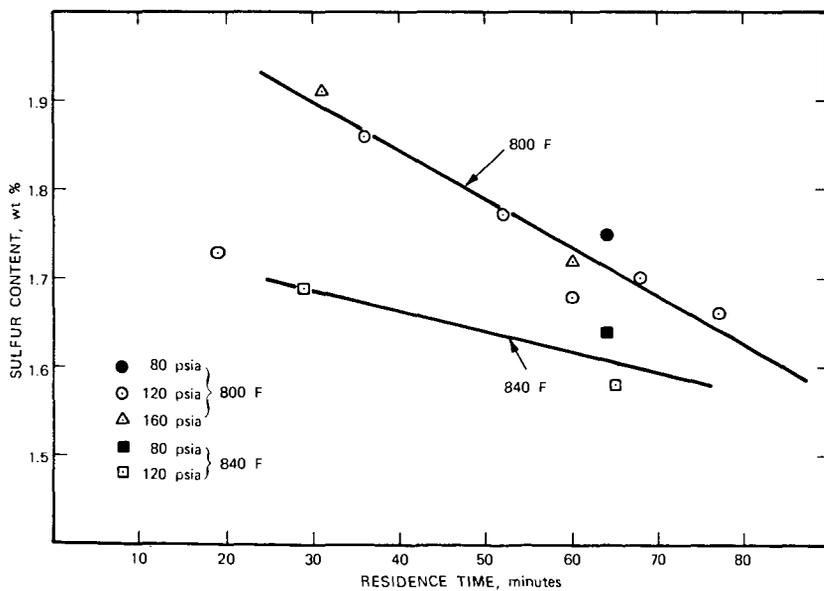


Figure 7. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON SEMICHAR SULFUR CONTENT

bonizations in the PDU are now routinely run at 820°F, 25 minutes residence time, 165 psia, and 100 ppm H₂S in the recycle gas. Under these conditions, coal containing 35 percent volatile matter and about 2.2 percent sulfur is converted to semichar containing 20 percent volatile matter and 1.7 to 1.8 percent sulfur.

Experimental Results From Second-Stage Carbonization

Tests were made in the PDU to study effects of temperature and residence time in the fluid bed upon sulfur content of the char produced in second-stage carbonization. The ranges for these variables were 1250 to 1410°F (675 to 765°C) and 40 to 200 minutes. System pressure was generally 165 psia, although other tests were run at pressures of 80, 120, and 150 psia. Concentration of H₂S in the recycle gas was controlled in the range 50 to 100 ppm, but concentrations as high as 1000 ppm H₂S were studied in special tests.

Results from the studies of temperature and residence-time effects are shown graphically in Figure 8, which for clarity were limited to data obtained at temperatures of 1250, 1325, and 1400°F. Sulfur content of the semichar feed for the test series ranged from 1.65 to 1.80 percent and averaged about 1.70 percent. The quantity of char produced at a single set of conditions was usually about 600 pounds, and more than 1600 pounds of char was produced during the longest test. Sulfur content of the char products ranged from 1.1 percent at the mildest conditions to 0.2 percent at 1400°F and 190 minutes residence time.

Temperature exerted the greatest effect on desulfurization of the char, as indicated in Figure 8; a temperature increase of 75°F provided a lower char sulfur content than increasing residence time threefold or even fourfold. For example, 40 minutes residence at 1400°F was the equivalent of 157 minutes at 1325°F in producing char containing 0.64 percent sulfur. It is apparent from the data that desulfurization of the feed occurred rapidly during the initial period of heating and devolatilization. Chars having sulfur contents in the range 0.7 to 0.8 percent were obtained in 40 to 50 minutes residence time at fluid-bed temperatures greater than about 1300°F. Desulfurization below about 0.8 percent sulfur proceeded at a much slower rate, and the rate then appeared to be almost completely linear with time.

All the data in Figure 8 were obtained at a system pressure of 165 psia, except for the one point, indicated on the 1325°F line, which was obtained at a pressure of 100 psia. This point was included to show that the effect of pressure over the range 100 to 165 psia is not discernible in the sulfur content of the char from the continuous fluid-bed reactor. Other tests in the PDU gave similar results; for example, at 1370°F and about 90 minutes residence time, the sulfur contents of the char products were 0.67 and 0.66 percent at pressures of 120 and 150 psia, respectively.

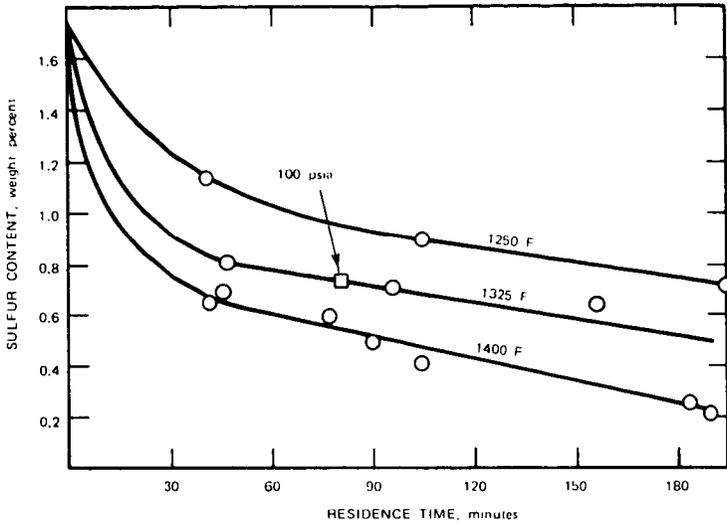


Figure 8. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON CHAR SULFUR CONTENT (165 psia)

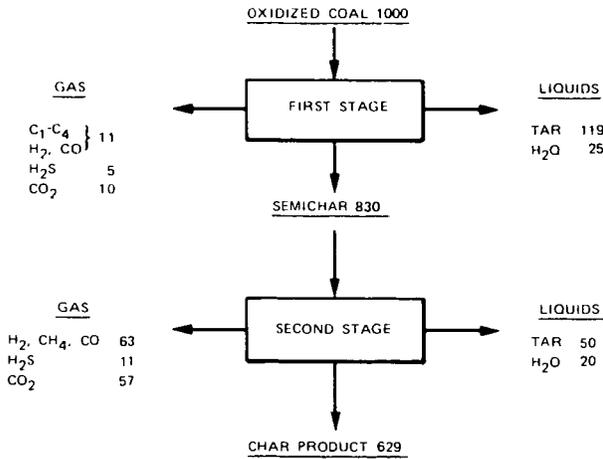


Figure 9. MATERIAL FLOW AND WEIGHT DISTRIBUTION DURING STAGED CARBONIZATION

The inability to demonstrate a pressure effect in the continuous reactor of the PDU results from the interdependence of variables in the system. For example, intentionally changing the pressure results in automatically changing the mole fraction of hydrogen in the gas, which changes the hydrogen-to-sulfur ratio in the fluid bed. In addition, a greater volume of lower-pressure (lower density) gas must be recirculated through the bed to maintain the same degree of fluidization, and lower-pressure gas must be hotter to effect the desired heat transfer to maintain bed temperature. Because of this, char particles near the bottom of the bed are contacting hotter gas and are momentarily heated to temperatures greater than the average bed temperature. These competing forces combine to mask the pressure effect in the continuous reactor. However, the effect of increased pressure is known to be beneficial in decreasing the sulfur content of the product char. This has been demonstrated by numerous investigations and by our bench-scale tests in batch reactors (3), which were suited for studying the pressure effect separately from the other variables.

An important dependent variable, for which a continuous reactor is best suited, is average sulfur content of the bed. In a batch unit, the sulfur content of the bed declines throughout the reaction time, but in a continuous unit, the average sulfur content of the fluid bed remains essentially constant, because of the continuous addition of sulfur with the feed, and is dependent upon the sulfur content of the feed and upon the feed rate. This factor contributes significantly to the observed benefit of very long residence times, which were achieved in the PDU by greatly reduced feed rates. The consequent reduction in rate of sulfur addition to the bed resulted merely in a lower average sulfur content in the bed. From these considerations, it may be concluded that the important variables in desulfurization of char in the PDU are temperature and average sulfur content of the bed, provided there is a significant concentration of hydrogen in the fluidizing gas.

Composition of the fluidizing gas was not a controllable variable, except for H_2S concentration, because process-derived gas was recycled in the system. The gas was composed almost entirely of methane, hydrogen, and carbon monoxide. Carbon dioxide was present only in tenths of a percent because of caustic scrubbing to control H_2S concentration. At 165-psia pressure, hydrogen concentration in mole percent varied from the low 20's at 1250°F to the low 40's at 1400°F; methane concentration ranged from the low 70's to the mid 50's; carbon monoxide concentration was nearly independent of reaction temperature but varied from a high of about 6 percent at the shorter residence times to about 2 percent at the longer times. Hydrogen concentration was also sensitive to residence time, and increased 3 to 5 percentage points between the shortest and longest times.

The effect of several H_2S concentrations in the recycle gas was studied in tests conducted at 1400°F, Table I. The tests were

run primarily to generate data relevant to the design of larger fluid-bed reactors, in which bed height would be significantly greater than the 30-inch bed height in the existing PDU. Concentration of H₂S increases in the fluidizing gas as it passes up through the bed, and at bed depths envisioned for reactors designed for 100 tons or more of feed per day, average H₂S concentration within the fluid bed might easily reach 1000 ppm.

Table I

Effect of H₂S Concentration in Fluidizing Gas on
Char Sulfur Content
(1400°F, 165 psia, 190 minutes residence time)

<u>H₂S Concentration, ppm</u>	<u>Char Product, wt % S</u>
50-100	0.21
500	0.71
1000	0.69

The data in Table I show a significant deterioration in char sulfur content from 0.2 percent to 0.7 percent, when the H₂S level in the gas entering the fluid bed was increased from the normal 50 to 100 ppm to the 500-ppm level. Interestingly, increasing the H₂S level to 1000 ppm did not have any perceptible additional effect. However, design for larger scale fluid-bed carbonizers will have to provide for minimizing the average H₂S concentration within the fluid-bed region.

To provide an indication of the reproducibility of data points, Table II presents analyses of the consecutive receivers of char produced during 10-day runs at 1400°F, 165 psia, and residence times of 46 and 190 minutes. The total quantities of feed for the tests were 2170 and 875 pounds, respectively. The data show excellent reproducibility, considering that observed variations in the products are the cumulative effects of variations in the semichar feed and process conditions, plus the repeatability of sampling and analysis.

Of interest also are the incremental changes in concentration of the various forms of sulfur originally present in the raw coal. These changes are illustrated by the analytical results in Table III for the feed and products involved in the CLEAN COKE Process. Forms of sulfur are shown simply as organic and inorganic, because the inorganic sulfur was nearly all pyritic and contained at most 0.05 percent sulfate sulfur. Coals from several mines in central Illinois were evaluated and all samples were quite similar. However, only coal from No. 24 mine of the Old Ben Coal Mining Company was processed

in the carbonization PDU, and the data in Table III were obtained with this coal.

Table II

Uniformity of Product Char From Carbonization PDU
(1400°F, 165 psia)

<u>Receiver</u>	<u>Char Sulfur Content, wt %</u>	
	<u>46 min</u>	<u>190 min</u>
1	0.69	0.26
2	0.70	0.21
3	0.68	0.18
4	0.61	0.18
5	0.68	0.18
6	0.66	0.25
7	0.68	--
<u>8</u>	<u>0.71</u>	<u>--</u>
Average	0.68	0.21

Table III

Incremental Change in Forms of Sulfur

<u>Processing Step</u>	<u>Sulfur Forms, wt %</u>	
	<u>Organic</u>	<u>Inorganic</u>
As-mined coal	1.00	2.50*
Cleaned and sized carbonization feed	1.13	1.00
Semichar (First-stage product)	0.91	0.81
Char (Second-stage product, 1400°F)	0.13	0.08

* Inorganic sulfur is pyritic sulfur plus about 0.05% sulfate sulfur in the as-mined coal.

Typically, the run-of-mine coal sample contained about 1 percent organic sulfur and 2 percent or so inorganic sulfur. Conventional

wet cleaning of this coal by gravity separation and tabling operations removed inorganic sulfur selectively and produced a clean coal feed, which contained about 1 percent inorganic and 1.1 percent organic sulfur. Devolatilization and desulfurization in first-stage carbonization at 820°F removed about one third of the sulfur in each form, and the ratio of organic to inorganic remained about the same in the semichar product as in the feed coal. (The coal-drying and preoxidation treatment did not affect either the amount or the forms of sulfur.) Final devolatilization and desulfurization in second-stage carbonization at 1400°F removed about 90 percent of each form of sulfur in the semichar feed, and the lowest sulfur char made contained only slightly more organic than inorganic sulfur.

It is also of interest that both forms of sulfur contributed substantially to the production of H₂S during carbonization. This fact is illustrated by the data in Table IV, which show the quantity of sulfur in each form that was converted and the quantity recovered as H₂S in the caustic scrubbing solution.

Table IV
Conversion of Forms of Sulfur to H₂S

	<u>Distribution of Sulfur, pounds</u>			<u>Recovered as H₂S</u>
	<u>Organic</u>	<u>Inorganic</u>	<u>Total</u>	
Coal feed	26.6	31.7	58.3	--
Converted sulfur (at 820°F)	8.4	12.3	20.7	18.2
Semichar feed	18.2	19.4	37.6	--
Converted sulfur (at 1400°F)	12.8	12.2	25.0	23.8
Char product	5.4	7.2	12.6	--

The pyritic sulfur converted contributed about two thirds of the H₂S produced by first-stage carbonization at 820°F, and the inorganic sulfur remaining in the semichar contributed about half of the H₂S produced during second-stage carbonization at 1400°F. Assuming that all the reacting inorganic sulfur is converted to H₂S, Table IV data show that about 70 percent of the organic sulfur reacting at 820°F was converted to H₂S and about 95 percent was converted to H₂S at 1400°F. Thus, it is apparent that reaction conditions in both stages are adequate to convert both types of sulfur compounds to easily recoverable H₂S. The remainder of the sulfur liberated from the coal during

pyrolysis is recovered as organic compounds in the liquid products, which contain 1.1 to 1.3 percent sulfur.

Material Flow During Staged Carbonization

Material flows and weight distribution through the two stages of carbonization of oxidized Illinois coal are shown in the simplified flow diagram of Figure 9. The products of first-stage carbonization of the coal are, in weight percent, semichar, 83.0; tar, 11.9; water, 2.5; fuel gas, 1.1; and acid gases, 1.5. The products of second-stage carbonization of the semichar (at 1400°F and 77 minutes residence time) are, in weight percent of the coal, low-sulfur char, 62.9; tar, 5.0; water, 2.0; process gas, 6.3; and acid gases, 6.8. The yield of CO₂ shown in Figure 9 is actual, but the high value results from the use of aqueous-caustic scrubbing to control H₂S levels in the carbonization PDU. Removal of CO₂ in the scrubber prevents this component from reaching a normal steady-state concentration in the recycle gas. In a larger system using conventional means for H₂S recovery, such as the use of Benfield scrubbers,* CO₂ would not be continuously removed from the gas, and its concentration in and yield from the process gas are expected to be substantially less.

Conclusions

The carbonization PDU of the CLEAN COKE Process has proved to be a valuable research tool in demonstrating, on a substantial scale, the efficient desulfurization of Illinois coal in a continuous, pressurized, fluid-bed carbonizer. After conventional cleaning and sizing, coal was processed during sustained operation of up to 10 days through two separate stages of carbonization, which together removed more than 90 percent of the coal sulfur and produced char containing as little as 0.2 percent sulfur. First-stage carbonization at a temperature of about 820°F served primarily to produce a nonagglomerating semichar feed for high-temperature carbonization, but the first-stage carbonization removed about one third of the sulfur from the coal and produced about two thirds of the total tar. Second-stage carbonization removed up to 90 percent of the remaining sulfur and produced low-sulfur char, hydrogen-rich fuel gas, and tar. Both forms of sulfur, organic and inorganic, were shown to be removed with equal facility by the carbonization process.

In addition to the data on desulfurization and process yields and chemistry, the PDU has provided much useful engineering information, which was needed for the design of a 100-ton-per-day pilot plant. The pilot-plant process-design work is currently in progress, and continued testing in the PDU will generate data needed for the design. Concurrently, studies are in progress on carbonization of high-sulfur

* Use of trade names or company names is for identification only and does not imply endorsement by ERDA.

coals from other major seams of national interest. Coal from the Kentucky No. 9 seam is being processed at present, and this will be followed by testing of a Pittsburgh seam coal.

Acknowledgments

The information contained in this paper and generated in the carbonization PDU would not have been possible without the design modifications and engineering assistance of Mr. George A. Ryder and Mr. John Stipanovich of the Chemical Engineering Design group. Their contributions to the success of the PDU program were invaluable and are sincerely appreciated.

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HYDRODESULFURIZATION OF COALS

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Introduction

The Institute of Gas Technology (IGT) is engaged in a program funded by the U. S. Environmental Protection Agency (EPA) to determine the operating parameters of the primary reactors in a patented process — the IGT Flash Desulfurization Process — to desulfurize coal by a combination of chemical and thermal means. The process is directed at the production of solid fossil fuel that can be directly consumed in existing equipment in an environmentally satisfactory manner.

Laboratory, bench-scale, and continuous PDU-sized equipment are being utilized in the project. The coal sample is subjected to the selected conditions of temperature, heat-up rates and residence time in a reducing atmosphere. After treatment, the material is chemically analyzed to determine the degree of sulfur removal. Results from tests with four different, high-sulfur coals (from abundant, Eastern seams) show good sulfur reduction; calculated sulfur-dioxide emissions of the treated material are below the present Federal EPA standards of 1.2 lb/10⁶ Btu for direct combustion of the solid fossil fuel product.

Coals Tested

Several coals were screened for sulfur content, seam location, and quantity available. Subbituminous coals and lignites were eliminated because of low initial sulfur content. Four bituminous coals were selected for testing:

- 1) Western Kentucky No. 9, 3.74% sulfur (run-of-mine)
- 2) Pittsburgh seam (West Virginia mine), 2.77% sulfur (highly caking)
- 3) Pittsburgh seam (Pennsylvania mine), 1.35% sulfur (high ash content)
- 4) Illinois No. 6, 2.43% sulfur (washed)

The coals were selected without regard for the relative pyritic and organic sulfur contents, because a universal coal desulfurization process should be capable of minimizing any sulfur type in the coal.

Pretreatment

The coals selected are all of the caking type and require an oxidative pretreatment prior to hydrodesulfurization. Pretreatment tests were conducted in a batch reactor to determine the proper pretreatment conditions for each coal. Temperatures, oxygen rates, fluidization velocities, and residence times were varied. These tests indicated that a temperature of 750°F and a gas velocity of 1 ft/sec were necessary. The degree of pretreatment required was not the same for each coal; residence time and oxygen consumption were adjusted to yield a non-caking material from each feedstock.

Approximately 25 to 30% of the coal sulfur is removed during pretreatment. This sulfur becomes primarily SO₂ in the low-Btu pretreatment off-gas. Approximately 8 to 12% of the coal is consumed during pretreatment, generating steam for the rest of the system and a low-Btu off-gas that can be consumed on-site to provide process steam or to generate power.

Pretreatment not only prevents caking, but also improves the sulfur removal in the subsequent hydrotreating step. Figure 1 represents two series of tests made with Western Kentucky No. 9 coal. One test series was made with crushed and screened coal and the other used crushed, screened, and pretreated coal as feed for hydrodesulfurization. The results show that the 70% sulfur removal achieved with untreated coal feed was increased to 95% by using a pretreated feed.

Hydrodesulfurization Results

Preliminary desulfurization evaluation of each coal was made in a thermobalance, a laboratory device that can continuously weigh a sample exposed to a controlled environment of temperature, pressure, and contacting gas composition. A total of 122 thermobalance tests have been performed in this program.

Samples for thermobalance tests were prepared using +40 mesh pretreated coal. This feed is placed in the sample basket and then lowered into the heated zone. Heat-up rates of 5° to 20°F per minute were used, to terminal temperatures of 1000° to 1500°F. Soaking times at the final temperature were varied from 0 minutes to 5.5 hours. The treated coal was analyzed for sulfur-by-types including pyritic, sulfide, sulfate, and organic. The small sample size did not permit more complete characterization.

Figure 2 presents the sulfur removal attained in the thermobalance tests for the four coals.

For all the coals, the pyritic sulfur has been 97 to 100% decomposed at 1300° to 1500°F, and the organic sulfur has been reduced by 80 to 88% at 1500°F. The total sulfur reduction is 90 to 95% at 1500°F. The calculated SO₂ emissions for combustion of the product, of all tests at 1400°F or above, would be below the present Federal EPA New Source Performance Standards of 1.2 lb/10⁶ Btu for combustion of solid fossil fuel. If sulfide and sulfate types of sulfur are removed mechanically, all tests above 1300°F produce acceptable products.

In the tests described above, samples were heated slowly - 5° to 20°F per minute - to their terminal temperature in the thermobalance. A series of runs, with Western Kentucky No. 9 coal, employed rapid heat-up. Rapid heat-up is accomplished by heating the reaction zone to the desired temperature and then lowering the sample basket into the hot zone. Most of the total weight change occurs in the first few seconds that the sample is in the hot zone. After 15 minutes, the weight changes only slightly, regardless of the residence times. The total of sulfur removed, however, increases with residence time at rapid heat-up rate. Reduction of sulfur content by 95% has been achieved in 2 hours residence time at 1500°F; however, samples subjected to 60 minutes or more met the EPA emission limits for SO₂.

A batch reactor has been used with the Western Kentucky No. 9 and Illinois No. 6 coals to substantiate the results of the thermobalance and to extend testing to other phases. This reactor operates in a fluidized bed mode, similar to the anticipated operation of the full-scale plant. It can be subjected to controlled heat-up rates or can be heated rapidly. The batch reactor is capable of treating larger samples, and the treated product is completely characterized analytically. A total of 128 batch reactor tests (including pretreatment evaluation) have now been made.

Batch tests with conditions similar to the thermobalance experiments were made at terminal temperatures of 1400° and 1500°F. Results were excellent at these temperatures with the total of sulfur removed typically 90%, but as high as 98.6% at 1500°F; these results are in good agreement with the thermobalance tests. The treated material would produce SO₂ emissions well below the limitation.

Table 1 presents typical results from a batch reactor. For these tests, the product recovery is about 60%; the remainder of the coal has been gasified (and pretreated) into low-Btu gas that can be upgraded to pipeline quality or consumed on-site. The heating value of the treated product is about 5% less than the feedstock, primarily because of the lost heat-content of the coal-sulfur and the increased ash content of the product. The Volatile Matter content of the treated product has been reduced significantly; modified combustion equipment may be required for the consumption of the desulfurized coal. Alternatively, as in another IGT patent, the treated product can be recombined with the hydrocarbons produced during the treatment (after oil hydrodesulfurization) to improve the combustion characteristics.

Work has now progressed to larger equipment. A 10-inch fluidized-bed unit can be fed continuously with variable feed rates from 25 to 200 lb/hr. It has been used to verify pretreatment operating conditions on a continuous basis. Pretreated feedstock has been prepared on this unit for hydrodesulfurization runs which are, at the time of preparation of this paper, now planned.

This unit will be used to collect data for material and energy balances, stream characterizations, economics, and design specifications for a larger installation. We expect to have achieved positive results for oral presentation at the meeting.

Conclusions

Laboratory- and bench-scale data indicate that acceptable hydrodesulfurization of coals can be achieved with the IGT Flash Desulfurization Process. Pretreatment of the coal enhances the removal of sulfur to produce a solid fuel that can be burned in conformance with the present Federal EPA limits of 1.2 lb SO₂/10⁶ Btu. Work is progressing to prove the concept on larger, continuous, PDU-sized equipment. The complete flow sheet for the process has not yet been defined, so economic factors are at present unknown.

Acknowledgement

The work in this coal desulfurization program has been performed under contract to the U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, and its permission to publish these results is gratefully acknowledged.

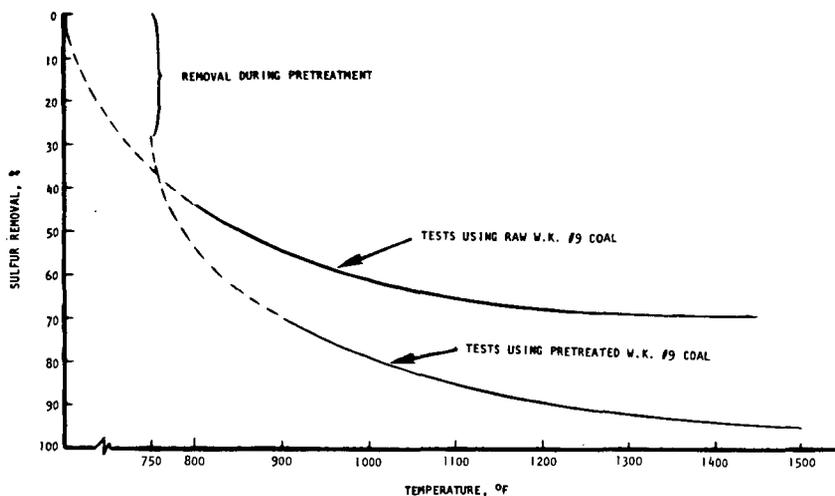


Figure 1. SULFUR REMOVAL INDICATING EFFECT OF COAL PRETREATMENT

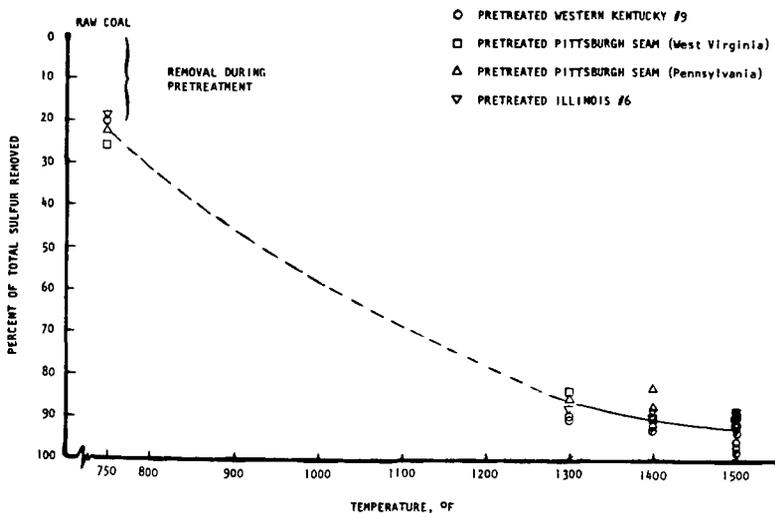


Figure 2. SULFUR REMOVAL FOR TYPICAL EASTERN COALS

Table 1. TYPICAL BATCH REACTOR RUNS

Run No.	BR-76-3		BR-76-34	
	Run-of-Mine Western Kentucky No. 9	Washed Illinois No. 6	Run-of-Mine Western Kentucky No. 9	Washed Illinois No. 6
Coal Type	Feed	Product	Feed	Product
Sample	26498	33293	33293	34428
Laboratory ID No.		1500		1500
Terminal Temperature, °F /		5		5
Heat-Up Rate, °F/min		30		30
Soaking Time, min				
Proximate Analysis, wt % (as received)				
Moisture	5.8	0.8	2.4	0.4
Volatile Matter	36.3	3.3	34.0	3.3
Ash	10.6	18.3	8.1	12.5
Fixed Carbon	<u>47.3</u>	<u>77.6</u>	<u>55.5</u>	<u>83.8</u>
Total	100.0	100.0	100.0	100.0
Ultimate Analysis, wt % (dry basis)				
Ash	11.24	18.43	8.31	12.51
Carbon	70.00	78.70	73.90	83.40
Hydrogen	4.54	0.95	4.81	1.06
Sulfur				
Sulfide	0.02	0.15	0.01	0.05
Sulfate	0.64	0.00	0.13	0.05
Pyritic	1.13	0.02	0.82	0.03
Organic	<u>1.95</u>	<u>0.46</u>	<u>1.47</u>	<u>0.49</u>
Total	3.74	0.63	2.43	0.62
Nitrogen	1.53	0.78	1.60	0.90
Oxygen	<u>8.95</u>	<u>0.51</u>	<u>8.95</u>	<u>1.51</u>
Total	100.00	100.00	100.00	100.00
Heating Value, Btu/lb	12,454	11,967	13,168	12,793
Solids Recovery, %		62.62%		62.70%
Total Sulfur Removal, %		89.45		84.00
Pyritic and Organic Sulfur Removal, %		91.96		86.58

DESULFURIZATION OF COAL IN A FLUIDIZED BED REACTOR

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INTRODUCTION

The pioneering investigation of Jacobs and Mirkus (5) showed that substantial amounts of sulfur could be removed from Illinois No. 6 coal by treatment with mixtures of air, nitrogen and steam in a fluidized bed reactor at moderately elevated temperatures. Thus by treating coal, which had been ground in a hammer mill (100% through 8 mesh screen), with a gas mixture containing 2.7% oxygen, 35% steam, and 62.3% nitrogen at 510°C for 30 min., the sulfate and pyritic sulfur content of the solids was reduced about 80% and the organic sulfur content 10%. However, at the same time the content of combustible volatile matter was reduced about 65%. Desulfurization improved with increasing residence time and decreasing particle size, but it was affected only slightly by oxygen concentrations in the range of 2 to 10% or steam concentrations in the range of 0 to 85%. The sulfur content of the char declined as the treatment temperature was raised up to 430°C but higher temperatures were not beneficial because desulfurization was accompanied by increased gasification and reduced yield of char.

Even more encouraging results were reported by Sinha and Walker (7) who were able to remove a large percentage of the pyritic sulfur from most of the samples in a series of powdered bituminous coals by treating them in a combustion boat with air at 450°C for 10 min. Moreover, the low and medium volatile bituminous coals in the series only experienced about a 5% weight loss and the high volatile bituminous coals a 10 to 17% weight loss. However, the results of a similar series of experiments by Block *et al.* (2) were less promising because less pyritic sulfur was removed and a greater weight loss was incurred.

Although the selective oxidation of pyritic sulfur appeared to play an important role in the foregoing demonstrations of desulfurization, it may not have been an exclusive role because sulfur could also have been removed through pyrolysis and reaction with hydrogen which was released by the pyrolytic decomposition of coal. Numerous studies have shown that part of the sulfur in coal is removed during carbonization and that the addition of hydrogen or carbonization in a stream of hydrogen assists the removal of sulfur, particularly at higher temperatures (2,3,6, 8). Under such conditions sulfur is removed principally as hydrogen sulfide. An investigation of coal hydrodesulfurization by a nonisothermal kinetic method revealed several peaks in the rate of evolution of hydrogen sulfide. Yergey *et al.* (9) attributed the first peak which occurred in the range of 390 to 470°C for different coals to be due to the reaction of hydrogen with two forms of organic sulfur, the second peak at 520°C to the reaction of hydrogen with pyrite, the third peak at 620°C to the reaction of hydrogen with ferrous sulfide (produced by the hydrodesulfurization of pyrite), and the fourth peak to the reaction of hydrogen with a third form of organic sulfur. Unfortunately the hydrodesulfurization of coal is inhibited by the presence of hydrogen sulfide in the gas phase which severely limits the concentration build up of hydrogen sulfide (1,4,6).

The work reported here was undertaken to determine the feasibility of desulfurizing a high sulfur bituminous coal from an Iowa mine by treatment at moderately elevated temperatures in a fluidized bed reactor with either oxidizing, neutral, or reducing gases. Nearly isothermal experiments were carried out with a small fluidized bed reactor to determine the extent of desulfurization and coal weight loss for different conditions of temperature and gas composition. Also the treatments

were applied to both run of mine coal and beneficiated coal. In addition the off-gas composition was measured during some experiments to determine the distribution of various sulfur and other compounds and to estimate the heating value of the gas. Finally consideration was given to the possibility of desulfurizing the off-gas and using it as a clean fuel to burn along with partially desulfurized coal char in the same plant in order to meet air pollution control regulations.

EXPERIMENTAL INVESTIGATION

Apparatus

Figure 1 is a schematic flow diagram of the apparatus used for this investigation. Feed gases were conducted through rotameters, combined, and heated to the reaction temperature by an electric preheater. The hot gas then passed into a fluidized bed reactor containing the coal being treated. After passing through the reactor, the gas was conducted to a glass cyclone separator which removed any fine particles of coal elutriated from the bed. The gas was cooled next to condense tar and moisture, filtered with glass wool, and bubbled through an alkaline solution of hydrogen peroxide to remove sulfurous gases. Samples of gas were analyzed periodically with a magnetic type, mass spectrometer (Model MS10, Associated Electrical Industries Ltd.).

The reactor was constructed from 2 in. I.D. stainless steel pipe and had an overall length of 18 in. It was fitted with a porous sintered stainless steel gas distributor having an effective pore size of 20μ . It was also equipped with a thermowell and a device for injecting coal at a point just above the gas distributor. The reactor was placed in an electrically-heated, fluidized sand bath for temperature control.

Procedure

The reactor was charged with a weighed amount of -40+50 mesh silica sand. The reactor was then brought up to operating temperature while air was used as the fluidizing medium. As the system approached the desired temperature, air was replaced with the appropriate treatment gas. When the temperature of the system appeared to have reached a steady state, powdered coal (-20+40 mesh) was injected into the fluidized bed of sand. This was done by first filling the injector tube with a weighed amount of coal. The tube was subsequently pressurized with nitrogen and then the quick opening ball valve between the tube and the reactor was opened allowing the coal to be discharged into the reactor. This marked the beginning of a run. During a run, the gas flow through the reactor and the temperature of the fluidized sand bath surrounding the reactor were kept constant. During some runs, samples of the off-gas were collected in glass bulbs at discrete time intervals and later analyzed with the mass spectrometer. After a run was completed, the reactor was uncoupled and doused with water to cool it to room temperature. The contents of the reactor were weighed and screened to separate the sand and coal char. The proximate analysis, heating value, and sulfur distribution of the char were subsequently determined by the ASTM method. It should be noted that this method of analysis did not distinguish between sulfur present as ferrous sulfide (FeS) and organic sulfur.

Materials

Two run of mine (R.O.M.) samples of high volatile C bituminous coal from the Jude Coal Co. strip mine in Mahaska County, Iowa, were treated. The samples were crushed and screened to provide material in the -20+40 mesh size range. After sieving, each sample was split into two fractions. One fraction was utilized as is while the other fraction was beneficiated by a float/sink technique using a liquid medium (a mixture of hexane and tetrachloroethylene) having a specific gravity of 1.30. Since this method of beneficiation greatly reduced the ash content as well

as the pyritic sulfur content of the coal, the beneficiated fraction is referred to as deashed coal. The composition and heating value of the two run of mine samples and corresponding deashed fractions are shown in Table 1.

Table 1. Composition of Jude mine coal on an as received basis.

Type of Analysis	Sample I		Sample II	
	R.O.M.	Deashed	R.O.M.	Deashed
Proximate, wt.%				
Moisture	6.35	2.24	5.37	4.04
Volatile matter	41.14	46.03	40.61	45.60
Fixed carbon	38.68	48.84	39.41	47.50
Ash	13.83	2.90	14.61	2.86
Sulfur, wt.%				
Sulfate	0.49	0.39	0.76	0.38
Pyritic	2.40	0.60	2.87	0.60
Organic	<u>3.54</u>	<u>3.97</u>	<u>4.43</u>	<u>5.37</u>
Total	6.43	4.96	8.06	6.35
Heating value,				
Btu/lb.	10,980	13,430	10,860	12,990
Specific sulfur				
content, lb. S/10 ⁶ Btu	5.86	3.69	7.42	4.89

RESULTS AND DISCUSSION

First Series of Runs

The first series of runs was carried out to determine the effects of four different treatment gas compositions and three different temperature levels (240°, 325°, and 400°C) on the desulfurization of both run of mine coal and deashed coal. The treatment gases included (1) 100% N₂, (2) 85% H₂, 15% N₂, (3) 4% O₂, 96% N₂, and (4) 10% O₂, 90% N₂. Coal identified as Sample I in Table 1 was used for this series. For each run, 50 g. of coal was injected into 400 g. of silica sand fluidized with the appropriate treatment gas at a superficial velocity of 30 to 40 cm./sec. As soon as the coal was added, the temperature of the fluidized bed in the reactor dropped 15-50°C. However, the temperature of the bed recovered to its initial temperature in 5 to 10 min. and then remained constant for the remainder of a run except for runs made at the highest temperature and oxygen levels. For these runs, the temperature of the bed continued to rise throughout a run so the final temperature was 60-70°C higher than the initial temperature. This increase in temperature seemed due to partial combustion of the coal or its decomposition products. Each run lasted 30 min. for this series of runs only the char product was recovered and analyzed; the off-gas was not sampled.

The results of runs made with Sample I, run of mine coal are presented in Table 2. Since duplicate runs were made at the lowest and highest temperature levels, each listed value represents an average for two runs at these temperature levels. On the other hand, each listed value for the intermediate temperature level represents the result of a single run. During each run the coal experienced

some loss in weight due to the escape of volatile matter. This loss increased directly with temperature but was not much different for different treatment gases except for the case when a gas containing 10% oxygen was employed at the highest temperature level and over 60% of the coal was consumed. With this one exception the weight loss seemed due primarily to pyrolysis rather than to reactions involving any of the treatment gases, although the volatile decomposition products were obviously not the same for different treatment gases. Thus some black tar was condensed from the off-gas when either nitrogen or hydrogen were employed, and only a small amount of light oil and water were condensed when either of the oxygen bearing gases were used.

The percentage of either pyritic, organic or total sulfur removed from the coal was determined as follows:

$$\text{Desulfurization (\%)} = \frac{\text{S wt. in feed} - \text{S wt. in product}}{\text{S wt. in feed}} \times 100 \quad (1)$$

Only a small percentage of the pyritic sulfur was removed at any of the temperature levels when pure nitrogen was used as the treatment gas (Table 2). However, when either hydrogen or oxygen bearing gases were used, a significant percentage of the pyritic sulfur was removed at the highest temperature level with more sulfur being extracted by oxygen than by hydrogen. The percentage of organic sulfur removed was strongly affected by temperature but it was affected very little by the treatment gas composition even though it may have appeared that more organic sulfur was removed at 400°C by either nitrogen alone or oxygen-nitrogen mixtures than by hydrogen. A qualitative chemical analysis showed that some of the "organic" sulfur present in char produced during the runs with hydrogen was actually an inorganic sulfide. A similar analysis of the char produced during the runs with oxygen in the feed gas did not reveal any sulfide. Furthermore so little pyritic sulfur was removed during the runs with pure nitrogen that not much sulfide could have been produced. Therefore only the results from the hydrogen runs are suspect and the organic sulfur removed at 400°C was probably greater than indicated because of this problem with the chemical analysis. Considering that the removal of organic sulfur depends strongly on temperature and very little on treatment gas composition, it appears that such removal is due mainly to pyrolysis and release of volatile matter.

The cumulative distribution of various forms of sulfur remaining in either run of mine or deashed coal after treatment with oxygen bearing gases is shown in Figure 2. The vertical distance separating any given pair of curves represents the percentage of the indicated species of sulfur found in the product based on the total sulfur in the feed and it was determined by employing the relation

$$\text{S species (\%)} = \frac{\text{wt. of species in product}}{\text{total wt. of S in feed}} \times 100 \quad (2)$$

The distribution at the left-hand side of each diagram corresponds to the sulfur distribution of the feed material. A comparison of the sulfur distribution at different temperatures with the initial distribution shows that for every treatment gas the total amount of sulfur remaining in the solids decreased as the temperature was raised with the greatest change generally taking place above 325°C. In the case of either run of mine or deashed coal treated with oxygen, both organic and inorganic sulfur were removed but at higher temperatures more inorganic sulfur appeared to be removed than organic relative to the amount of each species present initially.

The sulfur distribution diagrams also indicate the interconversion of one form of sulfur into another. Thus it appears that the sulfate form of sulfur gained slightly at the expense of other forms of sulfur when run of mine coal was treated

Table 2. Results of the first series of runs with run of mine coal.

Trt. Gas	Temp., °C	Wt. Loss, %	Sulfur Removed, %			lb. S ^a 10 ⁶ Btu
			Pyritic	Organic	Total	
100% N ₂	235	11.6	9.2	10.7	7.4	6.3
	320	14.0	7.8	3.2	2.5	6.6
	400	31.6	7.4	49.1	29.1	6.4
85% H ₂	235	11.8	7.1	7.0	6.6	6.1
	325	15.0	7.7	12.3	10.1	6.0
	400	33.6	29.2	35.4	39.7	5.5
4% O ₂	235	11.7	8.2	12.2	6.7	6.4
	320	16.0	12.9	25.3	19.1	5.8
	410	30.7	41.2	46.4	45.7	4.9
10% O ₂	240	10.0	7.9	18.4	11.3	6.2
	330	18.5	8.6	22.7	11.3	7.3
	440	63.0	73.3	79.8	77.9	5.6

^aSpecific sulfur content of char product.

with an oxygen bearing gas at 235°C. However, it doesn't appear that any of the treatments produced a wholesale transformation of one form of sulfur into another. There certainly was little if any evidence such as Cernic-Simic (3) had found indicating the transformation of organic sulfur into inorganic sulfur.

As a result of volatile matter loss and/or coal oxidation which accompanied desulfurization, the specific sulfur content (pounds of sulfur per million Btu) of the coal was not reduced materially by any of the treatments. In fact for a majority of the treatments, the specific sulfur content of the treated run of mine coal (Table 2) was actually slightly larger than that of the feed (5.86 lb. S/10⁶ Btu). For run of mine coal the lowest specific sulfur content (4.9 lb. S/10⁶ Btu) was obtained when it was treated at 410°C with gas containing 4% oxygen. For deashed coal the specific sulfur content of the product was slightly less than that of the feed (3.69 lb. S/10⁶ Btu) following a majority of the treatments, and at the highest temperature level the specific sulfur content of the product was almost the same regardless of treatment gas.

Second Series of Runs

The second series of runs was conducted to measure the yield and composition of the gaseous reaction product as well as the extent of sulfur removal from both run of mine coal and deashed coal. The treatment gases included pure nitrogen and two component mixtures of nitrogen and either hydrogen or oxygen. Coal identified as Sample II in Table 1 was used for this series. For each run 200 g. of coal was injected into 250 g. of silica sand fluidized with the appropriate treatment gas at a superficial velocity of 25 to 50 cm./sec. As soon as the coal was added, the temperature of the fluidized bed in the reactor dropped 115-170°C. The temperature of the bed usually recovered in 10 to 15 min. to somewhere near its initial value and then remained constant for the duration of a run except for the runs made with an oxygen bearing gas where the temperature continued to rise slowly. The runs lasted either 60 or 90 min. For this series of runs the overall yield of liquid condensate was determined, and samples of reactor off-gas were drawn periodically and analyzed with the mass spectrometer. The heating value of the fuel gas portion

of the off-gas was estimated by summing the heats of combustion of the individual components. However, for runs employing hydrogen as the treatment gas, the contribution of hydrogen to the heating value was excluded.

The results of selected runs in this series of experiments are presented in Table 3. Since these runs were made at relatively high temperatures (370-400°C) and were of long duration, appreciable amounts of volatile matter and sulfur were removed from the coal. When either nitrogen or hydrogen were employed as the treatment gas, the off-gas contained small but significant amounts of carbon monoxide and methane, lesser amounts of hydrogen sulfide, and trace amounts of ethane and propane. A significant amount of hydrogen was also found in the off-gas when pure nitrogen was fed to the reactor. For the runs made with an oxygen bearing treatment gas, the off-gas contained several percent each of oxygen, carbon dioxide, and carbon monoxide; slightly less hydrogen; a small amount of methane; and trace amounts of ethane and propane. In addition the off-gas contained small amounts of sulfur dioxide and hydrogen sulfide with the former usually exceeding the latter. Traces of carbonyl sulfide were also observed in oxidizing runs. An overall material balance made for each of the selected runs accounted for 97.5-99.9% of all the material entering and leaving the system.

Table 3. Results of selected runs in second series.

Run No.	Coal type	Trt. gas	Temp., °C	Gas vel. cm./sec.	Time, min.	Wt. loss, %	^a Total S removed, %
MSN-1	R.O.M.	100% N ₂	375	44	60	32.8	39.1
MSN-4	Deashed	100% N ₂	395	26	60	23.5	41.8
MSH-1	R.O.M.	87% H ₂	395	48	60	29.8	44.1
MSH-3	Deashed	84% H ₂	400	32	90	22.4	32.3
MSO-7	R.O.M.	10% O ₂	375	34	90	37.4	48.7
MSO-8	Deashed	10% O ₂	370	26	90	30.1	41.7

Run No.	^b Liq. yield, lb./lb. coal	^c Net fuel gas		Specific sulfur content, lb. S/10 ⁶ Btu		
		Yield, SCF/lb. coal	Heat. value, Btu/SCF	Feed	Char	Char & Gas
MSN-1	0.14	2.04	522	7.4	6.8	6.1
MSN-4	0.14	1.49	524	4.9	3.5	3.3
MSH-1	0.17	0.97	780	7.4	5.9	5.5
MSH-3	0.15	0.96	912	4.9	4.1	3.8
MSO-7	0.10	13.03	432	7.4	6.9	4.5
MSO-8	0.12	7.29	379	4.9	4.2	3.6

^aDetermined by Equation 1

^bCondensed tar and water

^cVolume of H₂, CO, CH₄, C₂H₆ and C₃H₈ in off-gas at standard conditions (0°C and 1 atm.) except Runs MSH-1 and MSH-3 where H₂ is excluded.

During each run, the total quantity of sulfur in the off-gas was also determined by absorption and oxidation of the various sulfurous gases in an alkaline solution of hydrogen peroxide, and this quantity agreed reasonably well with the

gas analysis made with the mass spectrometer. However, the quantity of sulfur appearing as noncondensable gaseous species was only 40-80% of the sulfur lost by the coal. Hence, the condensed tar and water must have contained an appreciable part of the sulfur extracted from the coal.

For the runs made with hydrogen or nitrogen, the heating value of the coal-derived combustible components in the off-gas was equivalent to 6-11% of the heating value of the char, and for the runs made with an oxygen bearing gas, the heating value of these components was equivalent to 14-36% of the heating value of the corresponding char. Consequently the combined heating value of the char and coal-derived gas was significantly larger than that of the char alone. *C*

The specific sulfur content of both the product char and the char and fuel gas combined was estimated (Table 3). For this purpose it was assumed that the off-gas could be completely desulfurized. The specific sulfur content of the char produced during each of the selected runs was significantly less than that of the feed. Furthermore by lumping the char and desulfurized off-gas together, the specific sulfur content of the combined products would be even lower. Thus for the conditions of Run MSO-7 the specific sulfur content of the char was 7% less than that of the run of mine coal and the specific sulfur content of the char and desulfurized gas together would be 39% less. The results of Run MSN-4 indicate the possibility for a 56% overall reduction in the specific sulfur content of the fuel by first beneficiating it and then applying a mild pyrolysis treatment as in this run.

Rates of Formation of H₂S and SO₂

The rates of formation of hydrogen sulfide and sulfur dioxide during the second series of runs were estimated by analyzing the time-varying composition of the reactor off-gas as determined by the mass spectrometer. The rate of formation of hydrogen sulfide as a function of the conversion of coal sulfur into hydrogen sulfide and sulfur dioxide is shown for several runs made with nitrogen in Figure 3 and for several runs made with hydrogen in Figure 4. Hydrogen sulfide was the principal noncondensable sulfur compound in the off-gas during these runs. For both treatment gases, the rate of formation of hydrogen sulfide increased first, subsequently peaked, and then decreased monotonically with increasing conversion. The initial increase in the rate was probably due to the rise in temperature of the coal after it was first placed in the reactor, and the later decrease in the rate to the diminishing concentration of sulfur in the coal. After it peaked, the rate for deashed coal appeared to be essentially a linear function of the conversion which corresponds to a first order process. Since the sulfur in deashed coal was present mainly as organic sulfur, this result indicates that the conversion of organic sulfur to hydrogen sulfide is an apparent first order reaction with respect to the sulfur species in coal which is in agreement with Yergey *et al.* (9). On the other hand, the conversion of sulfur in run of mine coal to hydrogen sulfide does not appear to be a first order process since the curves for this material in Figures 3 and 4 are nonlinear. Because the run of mine coal contained large amounts of both pyritic and organic sulfur, the nonlinear behavior could have been due to the superposition of reactions involving the two sulfur species. Although the curves representing the rate of formation of hydrogen sulfide were similar for both hydrogen and nitrogen, it is apparent that for the same temperature and type of coal, the rate was larger when hydrogen was used. This is only natural since the rate should depend on the hydrogen concentration, and when pure nitrogen was fed, any hydrogen had to come from the decomposition of the coal itself.

When an oxygen bearing gas was used for treating coal, sulfur dioxide was usually the major noncondensable sulfur compound in the off-gas but significant amounts of hydrogen sulfide were also present. The rate of formation of sulfur dioxide during several runs made with an oxidizing gas is shown in Figure 5. For each run two distinct peaks in the sulfur dioxide formation rate were observed. The first peak might have been due to devolatilization and oxidation of volatile

sulfur compounds including hydrogen sulfide. After the initial degassing of coal had subsided, oxygen could penetrate the coal more readily and react with embedded pyrites leading to the second peak. Then as the oxidation rate of pyrites became limited by the diffusion of oxygen through an increasing layer of reaction products such as iron oxide, the rate subsided. The difference in the behavior of the two types of coal further supports this theory. Thus for deashed coal with a relatively small pyrite content, the second peak was much smaller than for run of mine coal.

ANALYSIS AND CONCLUSIONS

The results of this study confirmed that it is possible to remove substantial amounts of sulfur from pulverized bituminous coal in a fluidized bed reactor operated at elevated temperatures. However, for the type of coal used in this study the removal of sulfur is accompanied by a substantial loss of volatile matter. Both the degree of desulfurization and extent of devolatilization are strongly influenced by temperature. The composition of the fluidizing gas appears to have more effect on the removal of pyritic sulfur than on the removal of organic sulfur and volatile matter in the 240-400°C range of temperature. Thus an oxygen bearing gas appears more effective for removing pyritic sulfur than a hydrogen bearing gas and nitrogen is completely ineffective. On the other hand, the removal of organic sulfur appears due mainly to pyrolysis and devolatilization and is not a strong function of the treatment gas composition. Since a significant part of the coal is volatilized, the recovery and utilization of the volatile products is important.

Although a number of industrial process alternatives based on the fluidized bed method of desulfurization are conceivable, only two will be considered here. One alternative involves treating pulverized coal in a continuous flow system with air or air diluted with recycled off-gas to remove pyritic sulfur and organic sulfur. This approach is indicated for coals containing finely disseminated pyrites which can not be removed by physical separation. It is conceivable that sufficient heat would be generated through oxidation to sustain the process. However, the off-gas would be diluted with nitrogen and have a low heating value. Also the sulfur dioxide present in low concentration would be difficult to extract. On the other hand, the light oil in the off-gas would be relatively easy to remove and there would be no tar to contend with. A second alternative involves treating coal in a flow system with recycled off-gas which has been desulfurized and heated. This approach is indicated for coals with important amounts of organic sulfur but little pyritic sulfur. The off-gas would be rich in hydrogen and methane and have a relatively high heating value. Hydrogen sulfide present in the gas would be relatively easy to remove, but the tar also present would create more of a problem than the light oil produced under oxidizing conditions. In the case of either alternative, the clean fuel gas would be utilized together with the char product.

While the methods applied in this study did not reduce the sulfur content of the selected coal to the point where the product would meet present air pollution control standards, further improvement in methodology is possible. From the published results of other workers (5,7), it is likely that either reducing the particle size or increasing the temperature would be beneficial, although increasing the temperature would remove more volatile matter as well as more sulfur. Also coals which initially contain less sulfur or are of a higher rank than the one selected could possibly benefit more from this type of treatment.

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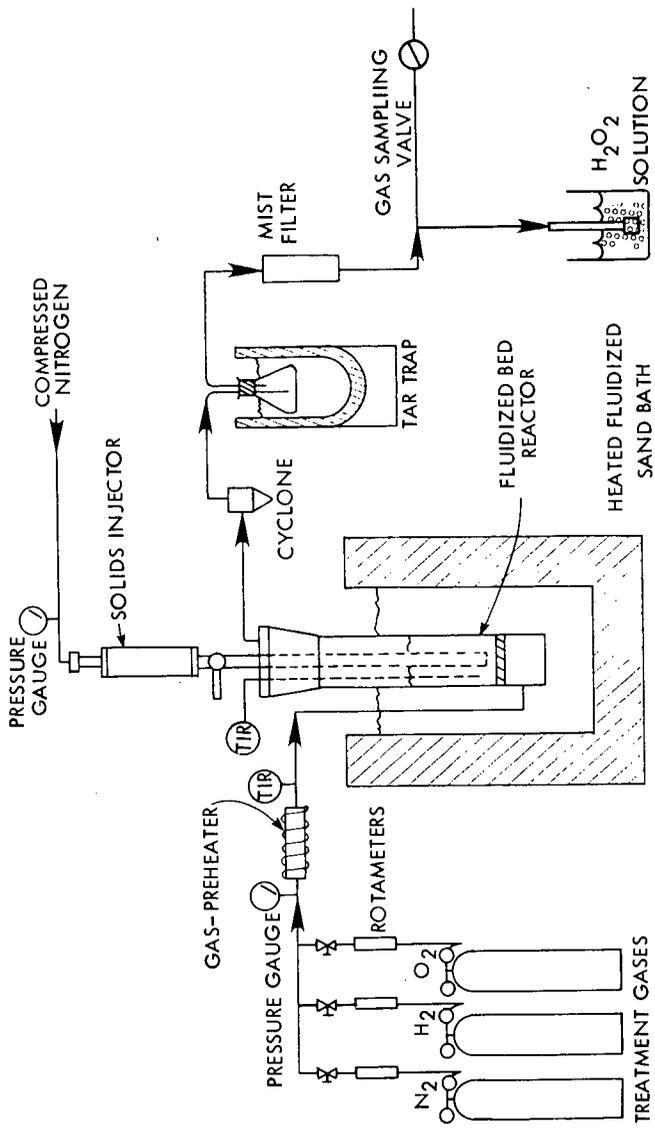


Figure 1. Experimental apparatus flowsheet.

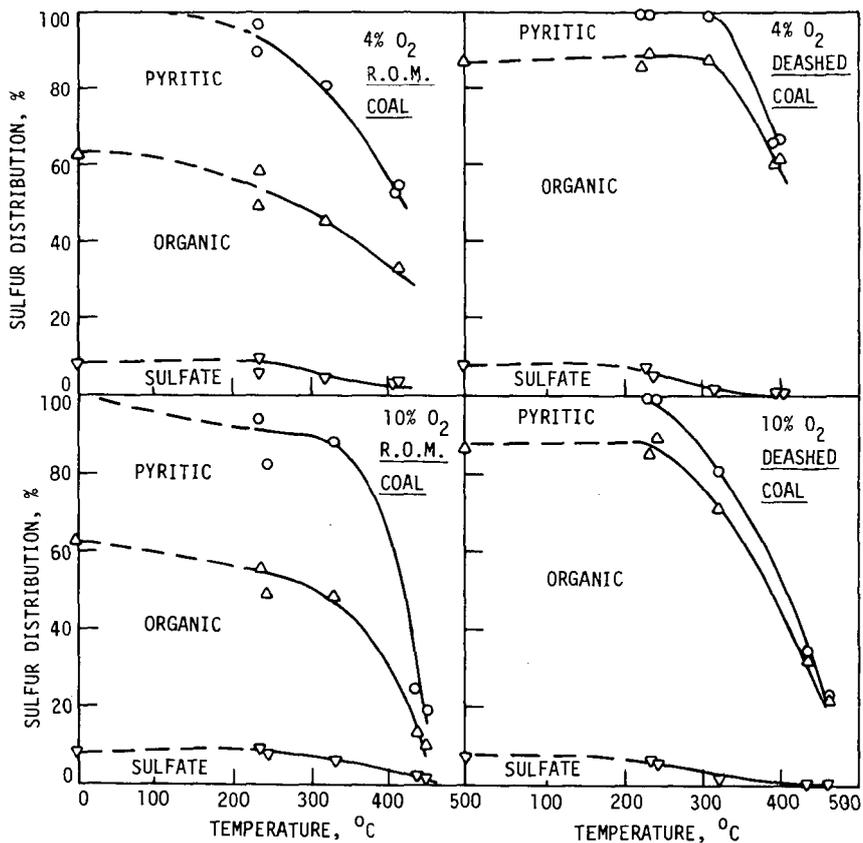


Figure 2. Sulfur distribution diagrams for coal char after oxygen treatments.

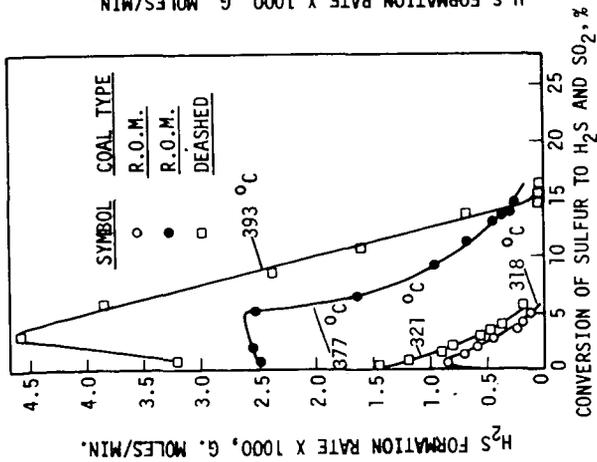


Figure 3. Rate of H₂S formation during pyrolysis in nitrogen.

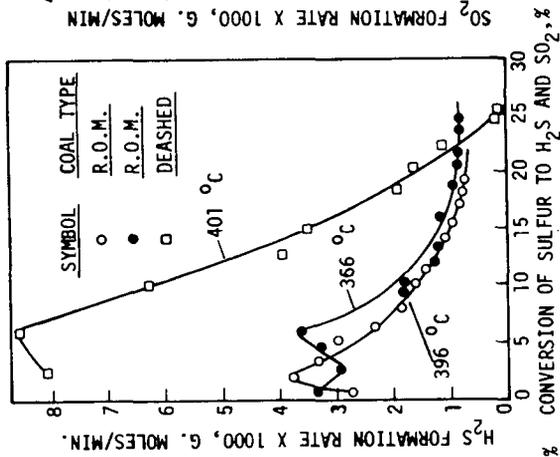


Figure 4. Rate of H₂S formation during treatment with gas containing 85% hydrogen.

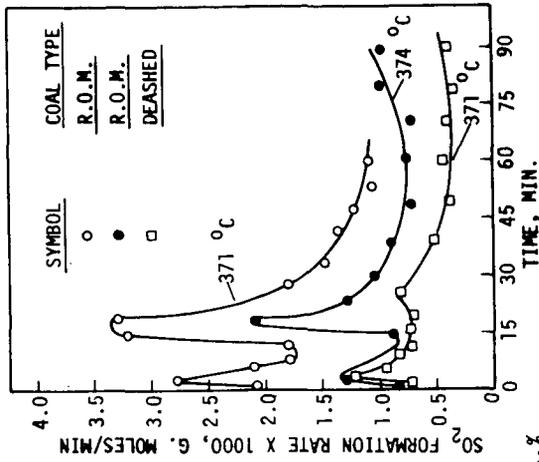


Figure 5. Rate of SO₂ formation during treatment with gas containing 10% oxygen.

7

CHEMICAL COMMINUTION: A PROCESS
FOR LIBERATING THE MINERAL MATTER
FROM COAL

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Introduction

Conventional coal preparation consists of mechanical size reduction, which results in liberation of the pyritic sulfur and other mineral matter, followed by a separation step, the cost of which is dependent upon the size consist of the crushed coal. In general, as the coal size consist decreases, the amount of liberation of mineral matter and the cost of separation increase. Physical coal cleaning processes are not able to liberate organic sulfur and, therefore, the organic sulfur concentration places an upper limit on the amount of sulfur that can be removed.

Chemical comminution provides a unique way of crushing coal for mineral matter liberation. Instead of mechanical size reduction, the coal is treated with a chemical (usually ammonia gas or a concentrated aqueous ammonia solution), resulting in selective breakage which appears to occur along the bedding planes and along the mineral matter (e.g. pyrite) and maceral boundaries. Washability comparisons of mechanically crushed and chemically comminuted coal samples have indicated that, at a given size consist, more liberation of pyritic sulfur and comparable liberation of ash is possible with chemical comminution. Figures 1, 2, and 3 provide a typical comparison of mechanical and chemical breakage and liberation. The recoveries noted in Figures 2 and 3 only apply to +100 mesh product and, therefore, the -100 mesh weight should be considered when calculating recoveries based upon feed. In terms of decreasing size consist (Figure 1), the following order is found: 1 1/2" top size ROM > chemically fractured > 3/8" top size mechanically crushed > 14 mesh top size mechanically crushed. The same order is found for the ash vs. recovery curves in Figure 2. In contrast, the total sulfur vs. recovery curves (Figure 3) demonstrate that chemical fracture (only 4.53% is <100 mesh) liberates considerably more pyritic sulfur than mechanical crushing even to -14 mesh (21.9% is <100 mesh). Similar results have been found with Redstone, Pittsburgh, and Upper Freeport seam coals (1,2) and with some Iowa coals (3).

The fact that chemical comminution can liberate more of the pyritic sulfur without grinding to small sizes has considerable economic benefits. Although, at this stage in the development, it is difficult to estimate the exact costs of a coal preparation flowsheet using chemical comminution as the size reduction method, some preliminary estimates have been developed. The total capital and operating costs for the chemical treatment alone using ammonia vapor, under conditions shown to be technically feasible in the laboratory, vary from \$1.00

to \$1.50 per ton of coal product. Using relatively inexpensive density separation techniques, feasible because of the small amount of fines produced in the chemical fragmentation step, would bring the total cost for producing clean coal to between \$2.50 - \$3.00 per ton product. This is very competitive with other processes currently being considered for producing clean coal. It is envisaged that the chemically comminuted product after cleaning will contain 80-90% less pyritic sulfur and 50-60% less ash, and, in approximately 30-40% of the Northern Appalachian seam coals, will meet EPA new source emission standards.

Because of the commercial significance of chemical comminution, the effect of different reaction conditions have been preliminarily studied to provide some insight into the mechanism of the phenomena. The available information is presented in the following sections and further information is being developed.

Mineral Liberation

Microscopic examination of chemically comminuted coal has been conducted by Greer (4) of Iowa State University using a scanning electron microscope. The results demonstrated that fragmentation due to chemical treatment was strongly controlled by maceral boundaries and other deposits within the material such as pyrite bands.

The above result demonstrates the selective breakage that occurs with chemical comminution and explains why pyrite is liberated during chemical treatment without excessive size reduction. However, the difference between sulfur and ash liberation (Figure 2 and 3) has not been determined. Further petrographic studies of this effect are anticipated.

Effective Chemicals

Although a number of chemicals have some comminution ability (5), the chemicals that appear to have the greatest effect are ammonia (gas and anhydrous and hydrous liquid) and methanol. These compounds fall in a class of chemicals containing a non-bonding pair of electrons (oxygen and nitrogen compounds) which has been shown to swell (6,7) and dissolve (7) coal at ambient temperatures. Although swelling studies have not been conducted by us, it was determined that very little coal (<0.1%) was dissolved by either methanol or liquid anhydrous ammonia. The swelling effect, which has been observed with methanol treated coal by Bangham and Maggs (6), may cause the fragmentation which occurs during chemical treatment. Other analogies between coal solvents and coal comminutants include: (1) a decrease in effect as the coal rank increases, and (2) a reduction in effect as the solvent is diluted with water. Other specific solvents mentioned as good coal solvents (7), such as *n*-propylamine and pyridine, have been briefly examined. These chemicals do cause fragmentation but are not as effectively as ammonia. Since these chemicals are larger in molecular size, it is possible that molecular size is an important parameter for chemical comminution, especially if penetration of the coal is a rate determining factor.

Effect of Reaction Conditions

The fragmentation caused by chemical treatment is affected by such parameters as moisture, pressure, water concentration in the chemical, starting size of the coal, and preconditioning of the coal before treatment. These effects, using Illinois #6 seam coal as an example, are illustrated in Figures 4-7. Illinois #6 seam coal is very susceptible to chemical comminution and, therefore, the results with this coal are not necessarily representative of other coals. Figure 4 demonstrates the importance of evacuating the reactor before chemical treatment. The contrast in the effect of evacuation between liquid and gaseous conditions is quite apparent. This effect has also been noticed with other coals, although they have not been as demonstrative. For example, all the conditions used in Figure 4 would have no effect on a Pittsburgh seam coal that was examined.

Figure 5 illustrates the effect of pressure and water content and demonstrates that methanol is not as effective a comminuting agent as even a dilute ammonia-water solution. With gas treatment, it appears that a little moisture in the coal aids fracture. Also, when using gas, a change of pressure from 90 psig to 120 psig has considerable impact on the amount of breakage. Determination of any trends with the liquid systems is difficult because the pressure was not held constant.

As might be expected, the initial size of the coal before treatment can effect the size of the treated product. This effect is illustrated in Figure 6.

As noted previously (Figure 4), evacuation before treatment appears to have a considerable effect, especially with gaseous treatment. Evacuation after treatment also appears to have an effect (Figure 7) which may be due to just a difference in reaction time, since reaction in the evacuated sample should stop rapidly while the unevacuated sample may continue to react even after the pressure is removed.

Effect of Coal Type

In general, the chemical fragmentation of coals decreases as the coal rank increases. Figure 8 depicts the size consist of sized samples of Upper Freeport (carbon 70.32%; ash 18.16%) and Illinois #6 (carbon 70.01%; ash 12.52%) seam coals which have been treated under comparable conditions. Illinois #6 coal is slightly lower in rank than Upper Freeport and considerably more breakage occurs. However, a Pittsburgh seam coal, which is lower in rank than the Upper Freeport, would not react at all in liquid anhydrous ammonia at atmospheric pressure and, therefore, the correlation does not always hold. Lignite and anthracite samples have shown some susceptibility to chemical fracture, but not as much as bituminous coals. This slight correlation between rank and comminution may be fortuitous and due instead to differences in micro or macro porosity, maceral content, cleat system, swelling ability (8), mineral matter distribution, or perhaps other factors.

Chemical Reactions

Chemical reactions between the ammonia and coal could have an adverse effect on the recovery of the ammonia and on the amount of NO_x emitted when the coal is combusted. Therefore, the nitrogen content of coal before and after ammonia treatment was determined for a variety of coal seams. The results presented in Table 1 vary slightly for different coals and the increase in nitrogen appears to be in correlation with a decrease in rank. No increase appears to take place with Upper Freeport seam coal, a slight increase (6%) with Pittsburgh seam coal, and approximately a 20% increase with Illinois #6 seam coal when the sample is air dried. However, some of the nitrogen can be removed by hot water washing. In general, the +8 mesh particles show a lower increase in nitrogen than the other sizes. The nature of the chemical reaction that may be taking place is unknown, but there are functional groups (e.g. esters) in coal that could form nitrogen compounds. With Illinois #6 seam coal, the loss of ammonia would still be small (4.4 lbs ammonia per ton of treated coal when a hot water wash is used) and it is unknown whether NO_x emissions would change.

From the above results, it can be seen that considerably more information is necessary before the mechanism of chemical comminution is understood. Studies directed at a better understanding of the phenomena and the effect it has on the chemically treated coal are presently underway.

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Table 1. Nitrogen Content of Chemical Comminuted Coal

Coal	Ammonia Treatment	Treatment to Remove Ammonia	Original Ash Sample	Air Dried at 60°C	Air Dried at 60°C and Stead 8x20% 20x100% -100%	Air Dried at 100°C for 4 hrs.	Air Dried at 200°C for 2 hrs.	Air Dried at 300°C for 1 hr.			
Pittsburgh, Green County, PA	160 min., NH ₃ gas, 120 psig, 75°F	Air dried, 2 hrs, 60°C	1.43	1.51							
		Rinsed with dilute HCl at 20°C, air dried 120 psig, 75°F		1.53							
Upper Freeport, Westmoreland County, PA	240 min., 100% NH ₃ liquid, atm. press., -30°F	Rinsed with water at 100°C, air dried		1.50							
		Air dried at 60°C	1.21	1.12	1.08	1.20	1.44	1.21	1.21	1.20	1.24
Illinois #6, Franklin County, IL	240 min., 100% NH ₃ liquid, atm. press., -30°F	Rinsed with water at 100°C for 1/2 hr.		1.21	0.97	1.15	1.37	1.22	1.24	1.37	1.38
		Rinsed with water at 100°C for 2 1/2 hrs.		1.25	0.98	1.21	1.39	1.16	1.24	1.26	1.11
Illinois #6, Franklin County, IL	240 min., 100% NH ₃ liquid, atm. press., -30°F	Air dried at 60°C	1.58	1.94	1.75	1.96	1.94	1.64	1.91	1.94	2.00
		Rinsed with water at 100°C for 1/2 hr.		1.80	1.58	1.74	1.69	1.59	1.86	1.69	1.82
		Rinsed with water at 100°C for 2 1/2 hrs.		1.72	1.62	1.74	1.71	1.43	1.70	1.69	1.96

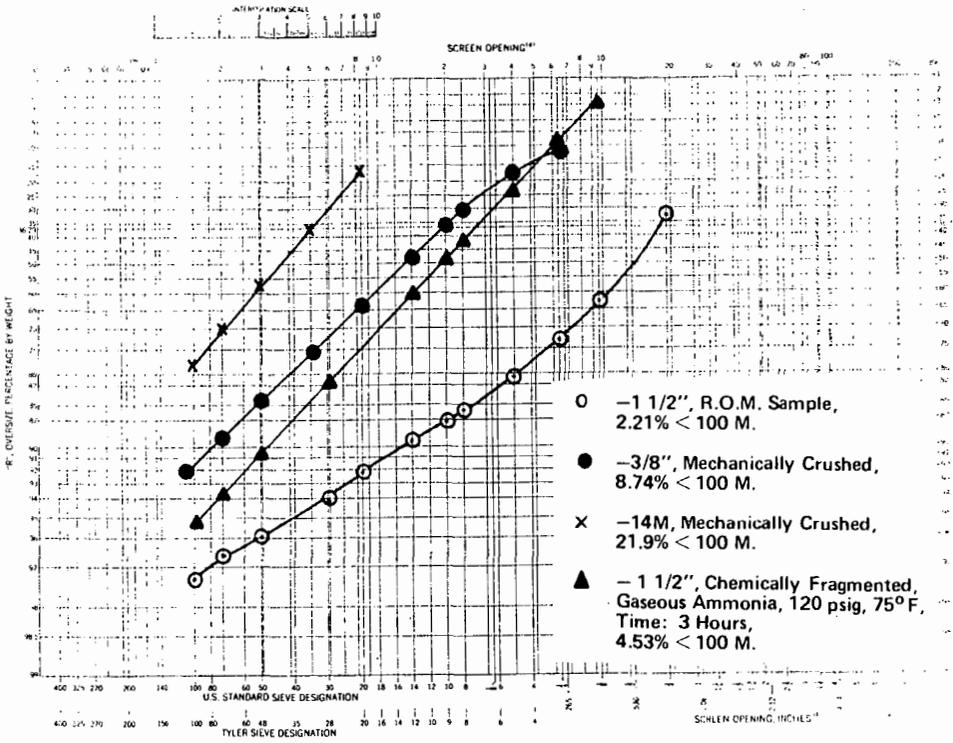


Figure 1. Size Consist of Illinois Number 6 Coal Samples (Franklin County, IL)

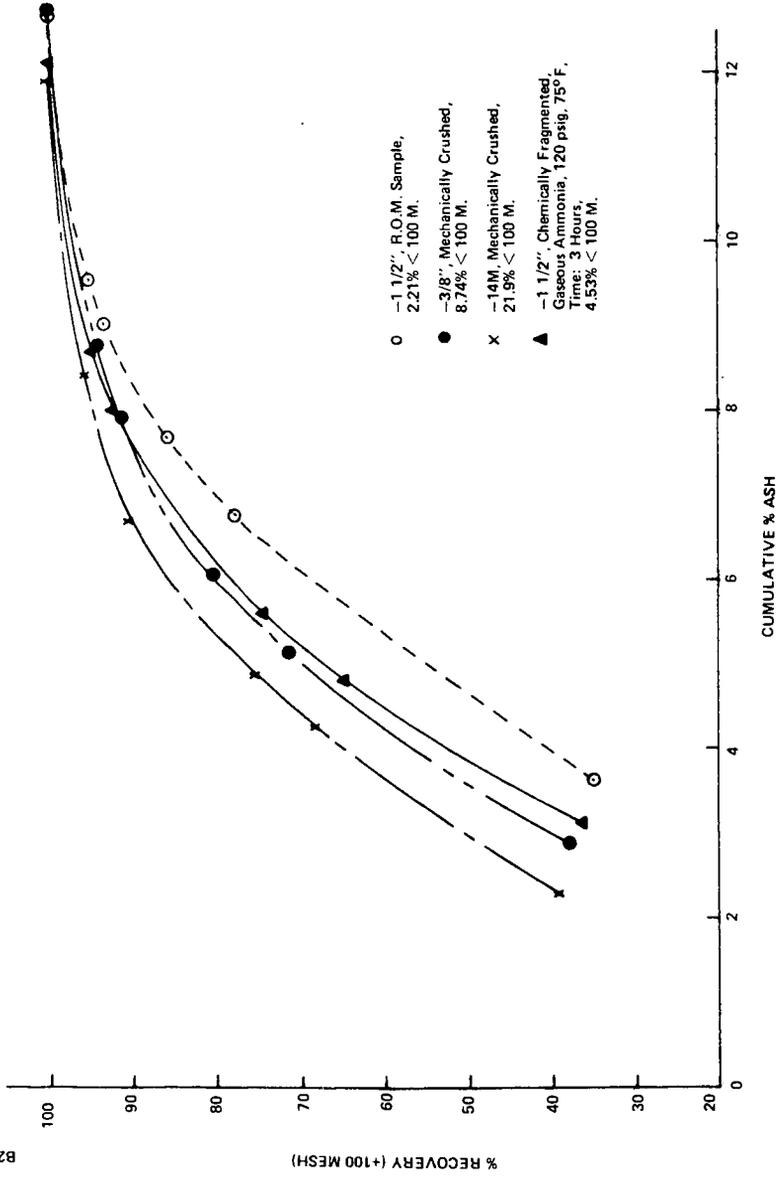


Figure 2. Ash vs. Recovery Curves Comparing the 3 Hour Chemical Comminution to the Mechanical Crushing of the Illinois Number 6 Seam Coal Sample (Franklin County, IL)

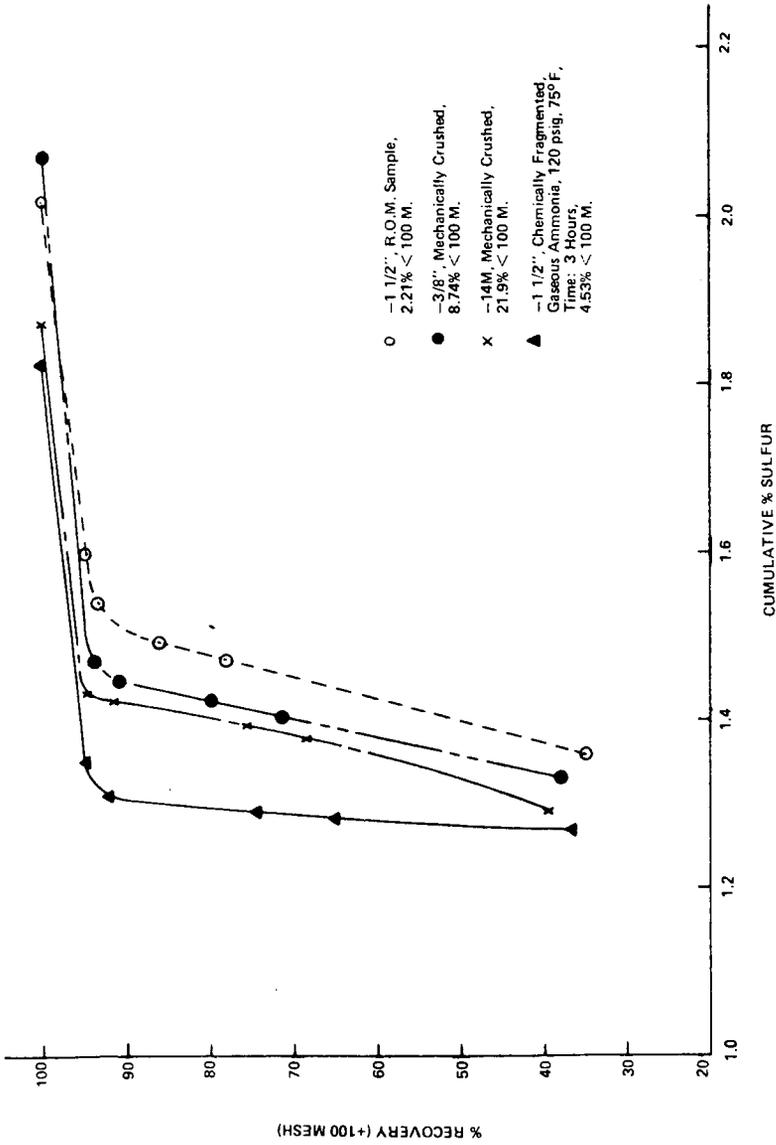


Figure 3. Sulfur vs. Recovery Curves Comparing the 3 Hour Chemical Comminution to the Mechanical Crushing of the Illinois Number 6 Coal Sample (Franklin County, IL)

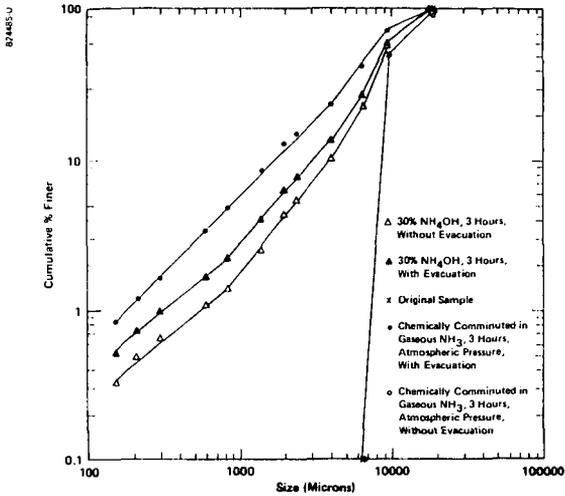


Figure 4. Effect of Preevacuation on Chemical Comminution of Illinois No. 6 Coal

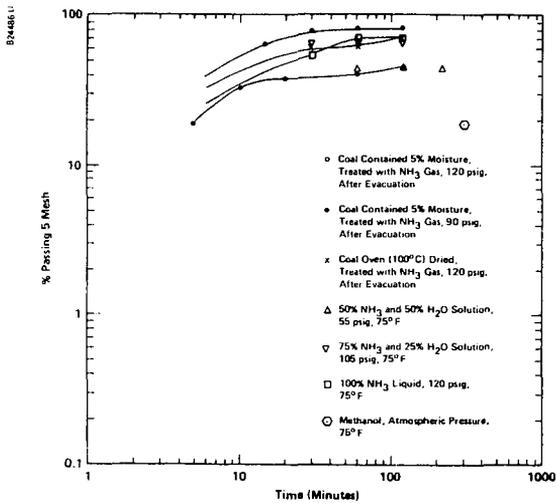


Figure 5. Effect of Reaction Pressure and Water Content in the Coal or Comminuting Agent on Fragmentation of $3/4'' \times 1/4''$ Samples of Illinois No. 6 Coal

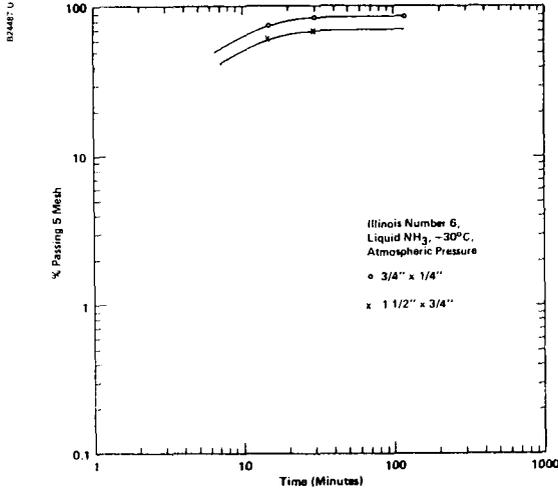


Figure 6. Effect of Starting Size on Chemical Comminution of Illinois No. 6 Seam Coal

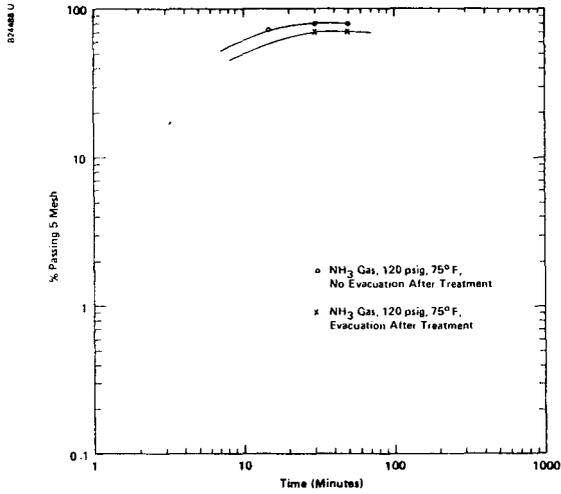


Figure 7. Effect of Evacuation After Chemical Treatment of Illinois No. 6 Seam Coal

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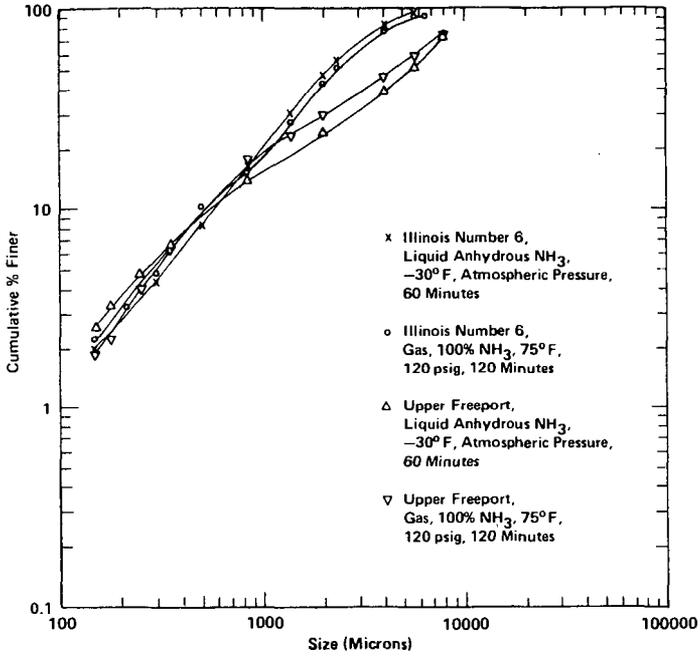


Figure 8. Size Consist of Illinois No. 6 and Upper Freeport Seam Coals (3/4" x 1/4" starting material) After Chemical Treatment

APPLICABILITY OF THE MEYERS PROCESS FOR DESULFURIZATION
OF U.S. COAL (A SURVEY OF 35 COALS)

J. W. Hamersma, M. L. Kraft and R. A. Meyers

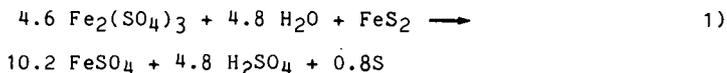
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I. INTRODUCTION

The Meyers Process (1,2) is a new chemical leaching process which will allow many coal-fired power plants and industrial sources to meet Federal and State sulfur oxide emission standards without the use of flue gas cleaning. This process utilizes a regenerable aqueous ferric sulfate leaching unit to chemically convert and remove the pyritic sulfur content of the coal as elemental sulfur and iron sulfate. Although only pyritic sulfur is removed (organic sulfur remains), the Meyers Process has wide applicability for converting U.S. coal reserves to a sulfur level consistent with present and proposed governmental sulfur oxide emission standards.

Thirty-five mines from the major coal basins were investigated in this study. Because of the relatively high pyritic sulfur and low organic sulfur contents, and high production (70 percent of current U.S. output) of Appalachian coals, the Meyers Process appears to have major impact in this area.

In the Meyers Process, aqueous ferric sulfate is used at 90-130°C to selectively oxidize the pyritic sulfur content of coal to yield iron sulfate and free elemental sulfur as shown in Equation 1. The iron sulfate dissolves in solution while the free sulfur is removed from the coal matrix either by vaporization or solvent extraction. The leaching (oxidizing) agent is then regenerated at a similar temperature using oxygen or air and recycled, while product iron sulfates are removed by liming and/or crystallization.



The detailed chemistry, leaching conditions, reaction kinetics, process engineering, and cost estimates have been published (3,7) and a reactor testing unit is being built.

This paper presents experimental results and discussion for: a) pyritic sulfur removal from coal, b) pyritic sulfur

partition by float-sink separation from the same coals, c) the effect of the Meyers Process on the trace element content of the treated coals and d) applicability of the Meyers Process for meeting air pollution control standards. This work was performed under contract to the Environmental Protection Agency (8,9).

II. SULFUR REDUCTION

A summary of the sulfur analyses of the run-of-mine coals utilized in this study is shown in Figure 1. The organic and pyritic sulfur contents are plotted along the x and y axis while the sum of these values for a given coal can be read from the diagonal lines. The average coal for this survey contained 2.02% pyritic sulfur and 3.05% total sulfur which corresponds to the U.S. Bureau of Mines average for 325 raw coals (10), indicating that the surveyed coals are reasonably representative of the sulfur distribution in U.S. coal.

The results to date for chemical removal of pyritic sulfur (100-150 micron top-size coal) and the optimal results for conventional coal washing (based on the 1.4 mm, 1.90 float fraction of a float-sink analysis) are shown in Table 1 and in graphical form in Figure 2. The table describes the results obtained on coals which contained sufficient pyritic sulfur for accurate sulfur removal determination (i.e., >0.25% w/w). Three of the mines sampled were below this limit and, therefore, do not appear in the table. Actual total sulfur values before and after chemical removal are shown in Columns 4 and 5. These may be compared with Column 6, which shows sulfur values which can be obtained with full process optimization. This latter value was calculated by adding the residual pyritic sulfur and sulfate contents of the coal to the initial organic sulfur value after correction for any concentration effects due to ash removal. In the survey program, complete removal of residual elemental sulfur and sulfate was not always obtained since conditions were standardized but not optimized for each individual coal. Thus, for example, although 96 percent pyrite conversion was obtained for the Bird No. 3 coal, the total sulfur was reduced to 0.80 percent, not the theoretical 0.45 percent due to these effects. These processing problems have now been resolved as part of other projects (3,9) and the values shown in Column 6 can be considered to represent the true potential of the process. Because of the widespread application of physical cleaning techniques for removal of non-combustible rock (which includes varying amounts of pyrite, along with some carbon) from coal, float-sink fractionation was performed in order to define the relative utility of washing and chemical desulfurization for each coal. The results are shown in Column 9 and also in Figure 2.

The sulfur reduction potential of the Meyers Process was found to be highly attractive and in particular it was found

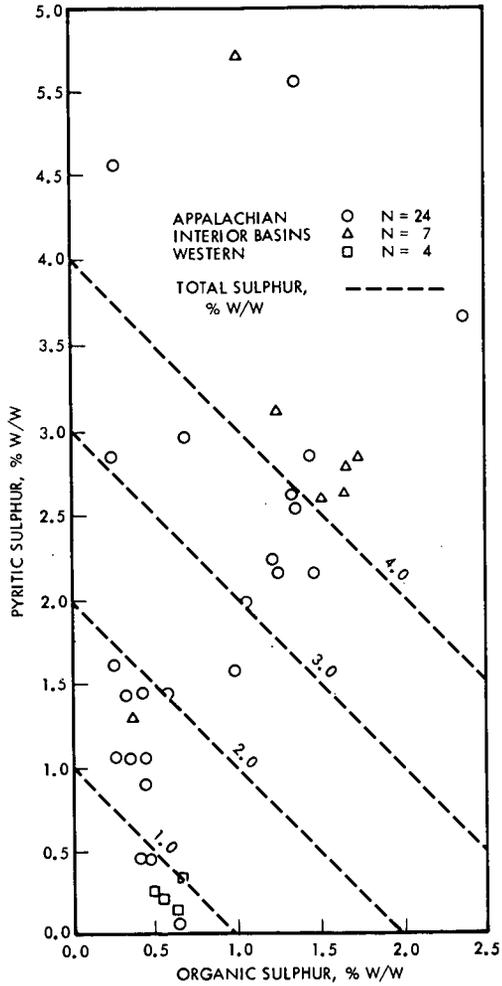


Figure 1. Sulfur Forms of Sampled U.S. Coals

Table 1. Summary of Pyritic Sulfur Removal Results (100-150 micron top-size coal)

Mine	Seam	State	% Total Sulfur w/w in Coal ^a			Meyers Process Pyrite Conversion % w/w	Meyers Process Total Sulfur Decrease % w/w	% Sulfur in Coal After Float-Sink
			Initial	After Meyers				
				Current Results	Revised Process			
Havajo	Nos. 6,7,8	M. Mexico	0.8	0.5	0.5	90	25	--
	Kopperston No. 2	W. Virginia	0.9	0.6	0.5	92	33	0.8
Harris Nos. 1&2	Eagle & No. 2 Gas	W. Virginia	1.0	0.8	0.6	94	23	0.9
	Coistrip	Montana	1.0	0.6	0.7	83	30	--
Marion	Hewick	Pennsylvania	1.4	0.6	0.4	92	54	1.0
	Upper Freeport	Pennsylvania	1.4	0.7	0.6	96	50	1.2
Mathies	Pittsburgh	Pennsylvania	1.5	0.9	0.5	95	36	1.7
	Pennsylvania	Pennsylvania	1.6	0.7	0.5	96	54	1.5
Orient No. 6	Herrin No. 6	Illinois	1.7	0.9	0.8	96	44	1.4
	Middle Kittanning	Pennsylvania	1.8	0.6	0.5	94	64	0.7
Lucas	Lower Freeport	Pennsylvania	1.8	0.7	0.6	91	63	0.8
	Lower Kittanning	W. Virginia	2.0	0.6	0.8	92	70	0.8
Hartinko	Corona	Alabama	2.1	0.9	0.8	91	55	2.2
	North River	W. Virginia	2.6	1.5	1.2	91	42	1.9
Humphrey No. 7	Pittsburgh	E. Kentucky	3.1	1.6	1.4	90	48	2.3
	Mason	Pennsylvania	3.1	0.8	0.4	96	75	1.5
Bird No. 3	Lower Kittanning	Pennsylvania	3.1	0.8	0.4	96	75	1.5
	Williams	W. Virginia	3.5	1.7	1.4	96	50	2.3
Shoemaker	Pittsburgh	W. Virginia	3.5	1.7	1.5	96	51	3.6
	Clarion 4A	Ohio	3.7	1.9	1.7	93	48	2.8
Fox	Lower Kittanning	Pennsylvania	3.8	1.6	1.2	89	57	2.0
	Dean	Tennessee	4.1	2.1	1.6	94	49	3.0
Peachatan No. 4	Pittsburgh H. 8	Ohio	4.1	1.9	1.9	85	53	3.3
	Eagle No. 2	Illinois	4.3	2.0	1.9	94	54	2.9
Star	Illinois No. 5	Illinois	4.3	2.5	1.8	91	43	3.0
	No. 9	W. Kentucky	4.3	2.5	1.8	91	43	3.0
Robinson Run	Pittsburgh	W. Virginia	4.4	2.2	1.6	97	50	3.0
	Homestead	W. Kentucky	4.5	1.7	1.6	93	47	3.2
Camp Nos. 1&2	No. 11	W. Kentucky	4.5	2.0	1.6	89	55	2.9
	No. 9 (H. Ky.)	W. Kentucky	4.5	2.0	2.1	89	55	2.9
Ken	No. 9	W. Kentucky	4.8	2.8	2.2	91	42	3.5
	Upper Freeport	Pennsylvania	4.9	0.8	0.5	96 ^d	80	2.1
Delmont	Helgs Creek	Ohio	6.1	3.2	2.7	94	47	4.4
	Muckingham	Ohio	6.4	2.2	1.7	92	65	3.9
Uedon No. 11	Des Moines No. 1	Iowa	6.4	2.2	1.7	94	65	3.9
	Egypt Valley No. 21	Ohio	6.6	2.7	2.1	89	59	4.6

^aDry, moisture-free basis
^b.90 float material, 14 mesh x 0, is defined here as the limit of conventional coal cleaning
^cCalculated using latest process improvement
^dRun at 200m x 0

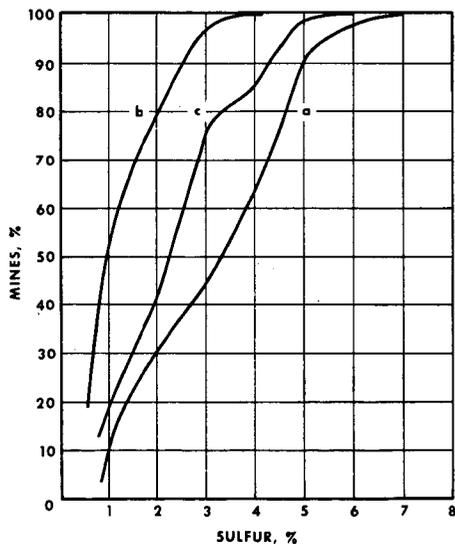


Figure 2. Sulfur Content of Survey Run-of-Mine Coals(Curve a), the Same Coals Physically Cleaned(Curve c) and Chemically Desulfurized(Curve b)

that: a) the Meyers Process, at its current state of development, removed 83 to 99 percent of the pyritic sulfur content of the 32 coals studied, resulting in total sulfur content reductions of 25 to 80 percent, b) twelve (38 percent) of the coals were reduced in sulfur content to the 0.6 to 0.8 percent sulfur levels generally consistent with the New Source Performance Standards and many state standards, c) in all cases, the Meyers Process removed significant to very large increments of sulfur over that separable by physical cleaning, and d) in two cases, the North River and Mathies mines, coal cleaning actually resulted in a sulfur content increase in the float product.

III. RATE OF PYRITIC SULFUR REMOVAL

The removal of pyritic sulfur was measured as a function of time at 100°C for 18 Appalachian and 3 Eastern Interior region coals. The results are displayed in Table 2, which shows the range of rates that were observed. It was assumed that the empirical kinetic rate expression (3) which was developed previously for this process is applicable to all coals in the survey. The kinetic equation can be simplified by holding the reagent concentration relatively constant, as was the case in this study, to yield Equation 2.

$$-d[Wp]/(dt) = k^{\circ}Wp^2 = \text{rate of pyrite removal} \quad 2)$$

where

Wp = weight percent pyrite in the coal, and

k° = function of temperature, reagent concentration, coal type, and particle size.

By integrating Equation 2, the fraction of pyrite removed as a function of time is shown in Equation 3.

$$F/(1 - F) = k^{\circ}Wp^{\circ}t_F \quad 3)$$

where

F = fraction of pyrite removed,

Wp° = initial pyrite concentration, and

t_F = time to removal at fraction F .

The initial weight percent of pyritic sulfur Sp° may be substituted for Wp° and Equation 3 rearranged to Equation 4.

Table 2. Relative Rate Constants for Pyritic Sulfur Removal

Coal Mine	Seam	Top Size, Microns	Sp ^o	t _{80%} , hrs	Relative Rate Constants	
					Sp ^o t _{80%}	Relative Rate
Kopperston No. 2	Campbell Creek	149	0.47	2.0	1.1	16
Harris Nos. 1&2	Eagle & No.2 Gas	149	0.49	2.3	0.89	13
Marion	Upper Freeport	149	0.90	3.0	0.37	5.3
Lucas	Middle Kittanning	100	1.42	3.25	0.22	3.1
Shoemaker	Pittsburgh	149	2.19	2.9	0.16	2.3
Williams	Pittsburgh	100	2.23	3.0	0.15	2.1
Ken	No. 9	149	2.85	2.5	0.14	2.0
North River	Corona	149	1.42	5.0	0.14	2.0
Star	No. 9	100	2.66	3.0	0.13	1.9
Mathies	Pittsburgh	100	1.05	9.0	0.11	1.6
Prwhattan No. 4	Pittsburgh No. 8	75	2.75	4.0	0.091	1.3
Homestead	No. 11	149	3.11	3.5	0.092	1.3
Fox	Lower Kittanning	75	3.09	4.5	0.072	1.0
Isabella	Pittsburgh	149	1.07	13.0	0.072	1.0
Martinka	Lower Kittanning	149	1.42	10.0	0.070	1.0
Meigs	Clarion 4A	149	2.19	8.5	0.054	0.77
Bird No. 3	Lower Kittanning	100	2.87	8.0	0.044	0.62
Dean	Dean	100	2.62	10.2	0.037	0.53
Muskingum	Meigs Creek No. 9	149	3.65	8.0	0.034	0.49

^a1/Sp^ot_{80%} relative to value for Martinka Mine.

$$1/(Sp^{Ot}_F) \alpha k = \text{actual rate constant} \quad 4)$$

Thus, assuming 80 percent removal as a point of comparison, the values of $1/Sp^{Ot}_{80\%}$ shown in Column 6 of Table 2 are indicative of the reactivities of the pyrite contained in the coals that were studied. A large amount of experimentation and engineering has been performed using rate data obtained for Martinka (3) coal; therefore, the Martinka coal $Sp^{Ot}_{80\%}$ has been set equal to 1 for a basis of comparison (as shown in Column 7).

It can be easily seen from Table 2 that there is a wide band of rate constants rather evenly spread over a factor of approximately 30. The Kopperston No. 2 and Harris Nos. 1 and 2 coals react more rapidly than the slowest coals (Dean and Muskingum) by a factor of about 30. Thus, it is apparent that real and significant rate differences do exist between pyrite in various coals. Characteristics of coal such as pore structure, size and shape distribution of pyrite, etc., may be the primary factors affecting the rate constant as reflected in the observed band of values found for the rates given in Table 2.

IV. TRACE ELEMENT REMOVALS

Because both chemical leaching and physical cleaning processes have the ability to remove potentially harmful trace elements from coal either by leaching or physical partitioning, 50 coal samples have been analyzed in duplicate or triplicate to determine the extent of the removal, if any, for 18 elements of interest to the Environmental Protection Agency. The samples included 20 as received, 20 chemically leached and 10 float-sink treated coal samples. The results are shown for 12 elements in Figure 3 in cumulative fashion. Six elements, B, Be, Hg, Sb, Se, and Sn yielded negative or inconclusive results due to low levels or analysis difficulties and thus are not plotted. Although the results varied greatly from coal to coal in respect to the elements extracted and the degree of extraction, some general conclusions can be reached.

- As, Cd, Mn, Ni, Pb, and Zn are removed to a significantly greater extent by the Meyers Process,
- F and Li are partitioned to a greater extent by physical separation procedures,
- Ag and Cu are removed with a slight preference for float-sink separation, and
- Cr and V are removed for both processes with equal success.

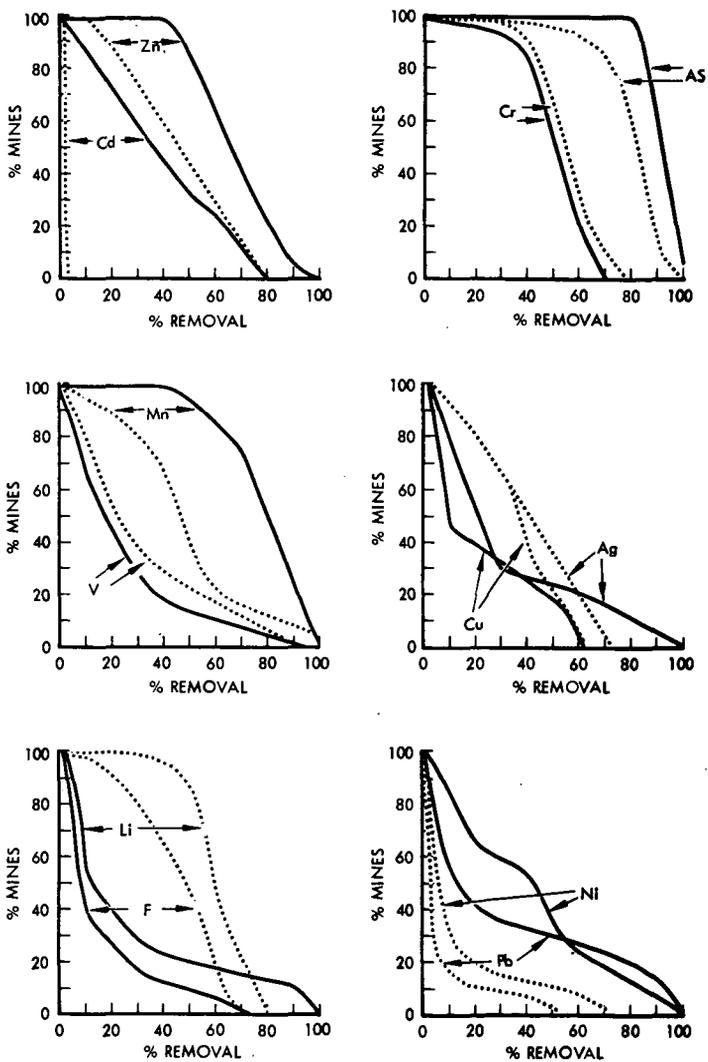


Figure 3. Trace Element Removal Data
 (— Meyers Process, Physical Cleaning)

The effective removal of As, Cd, Cr, Ni, Pb, and Zn from the coal by the Meyers Process is especially noteworthy as these compounds are concentrated (along with Se) in the fine particulates emitted from coal-fired power plants. This fine particulate matter has been demonstrated to pass through conventional fly-ash control devices.

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A PROCESS DEVELOPMENT PLANT FOR TESTING OF THE MEYERS PROCESS

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I. INTRODUCTION

Low organic sulfur coal can be desulfurized prior to combustion using the Meyers Process(1,2) to meet governmental requirements for sulfur oxide emissions.

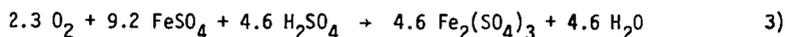
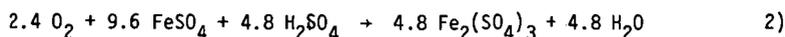
The process removes up to 80 percent of the total sulfur content of coal through chemical leaching of 90 to 95 percent of the pyritic sulfur contained in the coal matrix with aqueous ferric sulfate solution at temperatures of 90° to 130°C. The ferric sulfate content of the leach solution is regenerated at similar temperatures using air or oxygen, and elemental sulfur and iron sulfates are recovered as reaction products or alternatively gypsum can replace a portion of the iron sulfates as a product. The physical form of the coal remains unchanged; only pyrite and some inorganic materials are removed.

The Environmental Protection Agency estimates that 90×10^9 tons (82×10^9 metric tons) of coal reserves in the U.S. Appalachian Coal Basin can be reduced in sulfur content by the Meyers Process to levels which will meet New Source Performance Standards. Successful bench-scale testing(3,4) and promising engineering analyses(3,5-7) together with applicability testing(8,9), have led the Environmental Protection Agency to sponsor the construction and operation of a test plant.

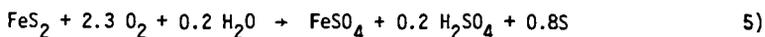
Process chemistry, and test plant design and operation will be described below.

II. PROCESS CHEMISTRY, KINETICS AND SCHEME

The process is based on the oxidation of coal pyrite with ferric sulfate solution (Equation 1). The leaching reaction is highly selective to pyrite with 60 percent of the pyritic sulfur converted to sulfate sulfur and 40 percent to elemental sulfur. The reduced ferric ion is regenerated by oxygen or air according to Equations 2 or 3.



Regeneration can be performed either concurrently with coal pyrite leaching in a single operation or separately. The net effect of the process is the oxidation of pyrite with oxygen to yield recoverable iron, sulfate sulfur, and elemental sulfur. The form of process products varies to some extent with the degree of regeneration performed. Thus, Equations 1 and 2 lead to the overall process chemistry indicated by Equation 4 with the products being a mixture of iron sulfates and elemental sulfur. Equations 1 and 3 yield ferrous sulfate, sulfuric acid, and elemental sulfur as indicated by Equation 5.



Several options exist in product recovery. Iron sulfates may be recovered as pure solids by stepwise evaporation of a spent reagent slipstream with ferrous sulfate being recovered first because of its lower solubility. Alternately, ferrous sulfate may be recovered by crystallization and ferric sulfate or sulfuric acid removed by liming spent reagent or spent wash water slipstreams. Iron sulfates may be stored as such for sale or may easily be converted to highly insoluble basic iron sulfates (by air oxidation) or calcium sulfate (by low-temperature solid phase reaction) for disposal. Elemental sulfur may be recovered from coal by vaporization with steam or by vacuum or it can be leached out with organic solvents such as toluene. Product marketability and product recovery economics will dictate the choice. Recovery economics may be influenced by quantity and concentration of product in the process effluent streams which in turn are influenced by the pyrite concentration in the coal and the desired extent of desulfurization.

The process has been extensively studied at bench-scale. Parameters investigated included coal top-size, reagent composition, slurry concentration, reaction temperature and pressure, and reaction time. Additional investigations completed or underway include concurrent coal leaching-reagent regeneration, product recovery, product stability, and the effect of coal physical cleaning on process performance and economics. The process scheme depicted in Figure 1 is based on the bench-scale testing. Coal is a) crushed to the desired size for processing, b) contacted with hot recycled reagent in the Mixer (90-100°C), c) leached of pyrite in the Reactor(s) with simultaneous or separate reagent regeneration, d) washed with hot water, and e) stripped of elemental sulfur, dried and finally cooled. The iron and sulfate sulfur are recovered from spent reagent slipstreams prior to reagent recycle. Figure 2 shows typical data on pyrite removal rates from Appalachian coal as a function of temperature. Removal of 10-20 percent of the pyrite is obtained during slurry mixing and heat-up.

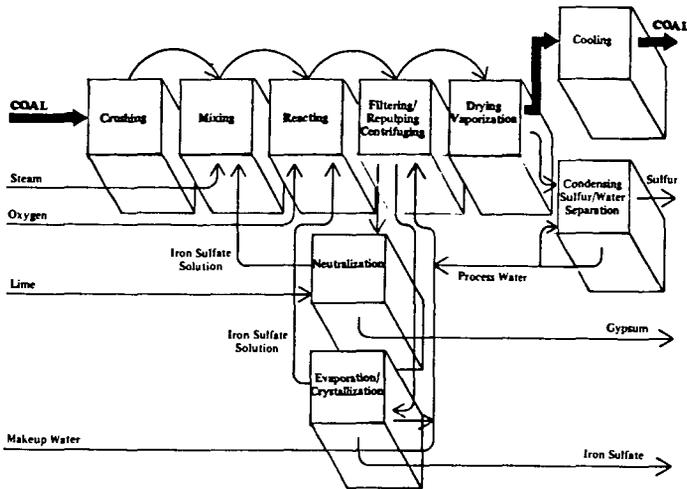


Figure 1. Process Flow Schematic

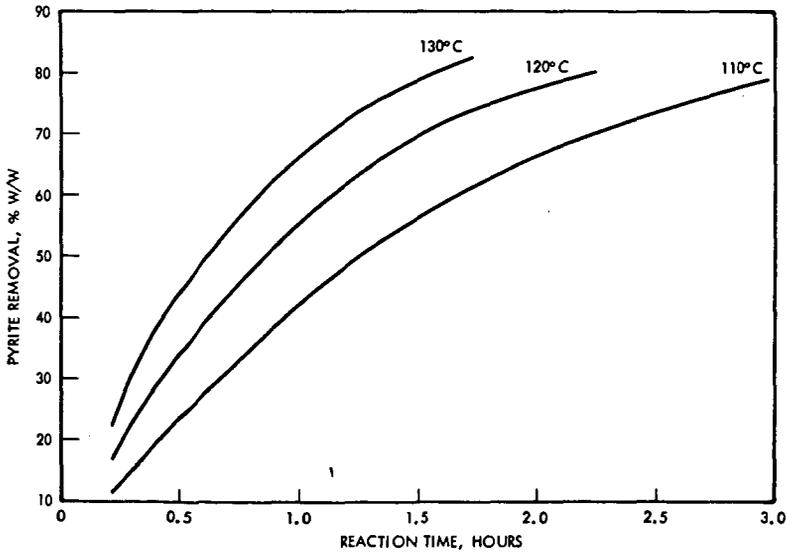


Figure 2. Temperature Effect on Processing of 14 Mesh Top-Size Lower Kittanning Coal (33% w/w Slurries)

Bench-scale data indicated that the pyrite leaching rate from coal can be adequately represented by the empirical rate expression (Equation 6).

$$r_L = - \frac{dW_p}{dt} = K_L W_p^2 Y^2 \quad 6)$$

where

$$K_L = A_L \exp(-E_L/RT),$$

$$W_p = \text{wt percent pyrite in coal,}$$

$$Y = \text{ferric ion-to-total iron ratio in the reactor reagent, and}$$

$$A_L \text{ and } E_L \text{ are constants for each coal and particle size at least over most of the reaction range.}$$

The leach rate is a function of coal type. Pyrite extraction rates vary considerably as detailed in a study of the Meyers Process as applied to U.S. coals(9) - e.g., there was more than one order of magnitude difference between the fastest and slowest reacting coal in attaining 75 percent pyrite removal at 100°C. The reagent regeneration rate is governed by the rate expression (Equation 7).

$$r_R = - \frac{dFe^{+2}}{dt} = K_R P_{O_2} (Fe^{+2})^2 \quad 7)$$

where

$$K_R = A_R \exp(-E_R/RT),$$

$$P_{O_2} = \text{oxygen partial pressure,}$$

$$Fe^{+2} = \text{ferrous ion concentration in the reagent solution, and}$$

$$A_R \text{ and } E_R \text{ are constants.}$$

Engineering evaluation of available data shows that it is preferable to process fine coal (< 2mm top-size) under simultaneous leaching-regeneration conditions in the temperature range of 110-130°C until the majority of the pyrite is leached out. Ambient pressure processing (approximately 100°C) is indicated for the removal of the last few tenths percent of pyrite since the low W_p value substantially reduces the rate of ferric ion consumption and, therefore, the need for simultaneous reagent regeneration. Ambient pressure processing appears to be indicated also for coarse coal (e.g., 10 millimeter top-size) for several reasons. It is difficult to continuously feed a non-slurryable coal into and remove it from a pressure vessel. It is much easier and less costly to drain leach solution from the coal and pump it into a small pressure vessel for regeneration. Also the

slower reaction rate with coarse coal would require much longer residence times and unreasonably large total volume for the pressure vessels. These engineering evaluations were part of the data used to design the test plant.

III. TEST PLANT DESIGN AND OPERATION

A test plant sized to process up to 8 metric tons per day of coal is being built, under the sponsorship of Environmental Protection Agency at TRW's Capistrano Test Site. A plant flow diagram is shown in Figure 3. The facility will be capable of on-line evaluation of the following critical process operations:

- Pressure leaching of pyritic sulfur from 150 micron to 2 mm top-size coal at pressures up to 100 psig,
- Regeneration of ferric sulfate both separately, for processing larger top-size coal or low pyrite coal, and in a single vessel with the leaching step for processing of suspendable coal,
- Filtration of leach solution from reacted coal,
- Washing of residual iron sulfate from the coal.

Iron sulfate crystallization, elemental sulfur recovery and coal-drying unit operations will be evaluated in an off-line mode in equipment vendor pilot units. Leaching of 10 mm top-size coal can be evaluated in an off-line mode in an atmospheric pressure vessel installed in the test plant. Coarse coal processing (5-10 mm top-size) has been very promising in laboratory tests⁽³⁾. If this approach proves out in bench-scale evaluations, more extensive and on-line coal leaching units can be readily added to the present test plant. Processing fine coal allows the highest rate of pyritic sulfur removal, while processing coarse coal, although slower, allows lower cost coal dewatering units and the direct shipping of desulfurized coal product without need for pelletizing.

The test plant under construction at the Capistrano Test Site is a highly flexible facility capable of testing the numerous alternate processing modes of potential interest in the Meyers Process. The flow diagram shown in Figure 3 presents an equipment train for continuous process testing of slurried coal. Fine coal ground to the desired size is stored under nitrogen gas in 1.8 metric ton sealed bins. As required, bins are emptied into the feed tank (T-1). Dry coal is continuously fed by a live bottom feeder to a weigh belt which discharges through a rotary valve to the three stage mixer (Stream 1). The aqueous iron sulfate leach solution (Stream 2) enters the mixer after first passing through a foam breaker (T-2). Steam is added (Stream 3) to raise the slurry to its boiling point. Foaming will occur in the early stages of mixing, but will cease when particle wetting is complete. It is believed that the mixing time and conditions necessary to complete the wetting and defoaming of the slurry will depend on the coal type and size and on the residual moisture in the feed coal. To allow study of the mixing parameters, the mixer stages have variable volume, with variable speed agitators and the feed flow rates for coal, leach solution and steam can be varied over wide ranges.

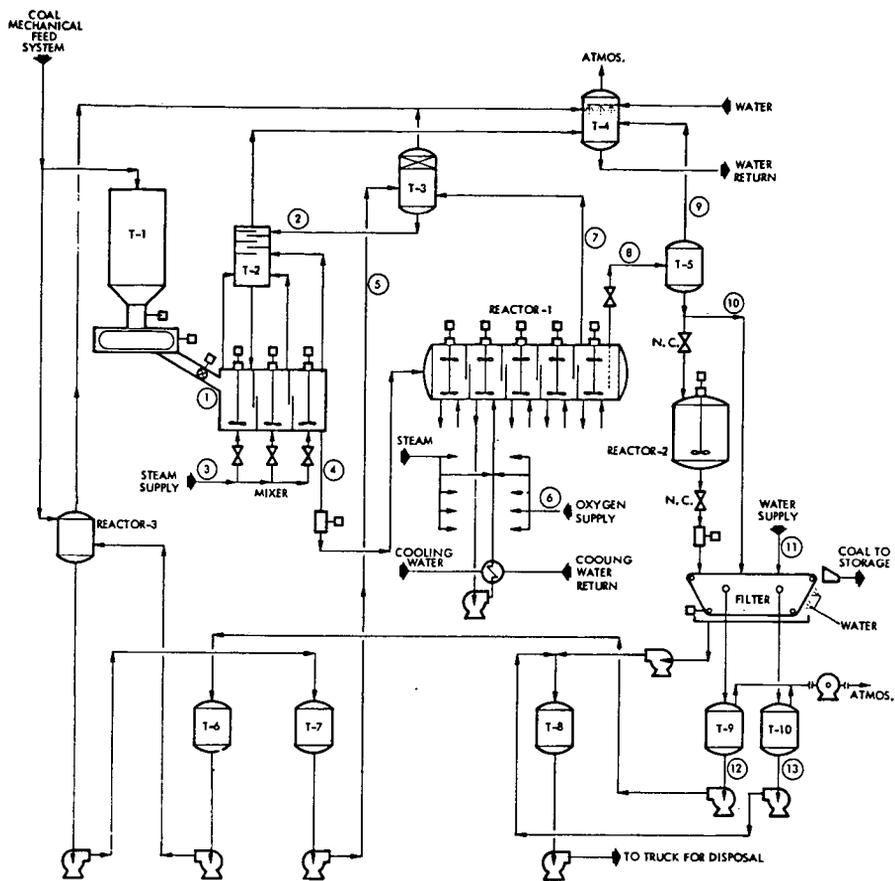


Figure 3. Test Plant Flow Diagram

The defoamed slurry (Stream 4) is pumped to a five stage pressure vessel (Reactor 1) in which most of the pyrite removal reaction occurs. Some of the pyrite reaction occurs during mixing, but in the mixer the reaction rate slows rapidly because the remaining pyrite (W_p) decreases and because the ferric iron is rapidly being converted to ferrous iron (Y decreases). The pressure reactor overcomes the decreased rate in two ways. First, it increases the temperature (and pressure) to increase the reaction rate constant. Second, oxygen is introduced under pressure to regenerate ferric iron and maintain a high solution Y . The flow diagram shows that steam and oxygen can be added to any or all of the five stages and that cooling can be provided for any stage if necessary to remove the excess heat of reaction. The unused oxygen saturated with steam (Stream 7) is contacted in a small pressure vessel (T-3) with the feed leach solution (Stream 5) to provide heated leach solution for the mixer (Stream 2) and cooled vent gas. The vent gas from both T-2 and T-3 are scrubbed in T-4 to remove any traces of acid mist. The reaction parameters of importance have already been well studied at laboratory and bench-scale in batch mode. The test plant reactor will accommodate the necessary studies of key parameters in a continuous reactor at coal throughputs between 2 and 8 metric tons per day. Parameters which will be studied include: temperature, pressure, oxygen purity, slurry concentration, iron sulfate concentration, acid concentration, residence time per stage, number of stages, mixing energy, type of mixing, coal size and type. The reactor can also be used to study leach solution regeneration in the absence of coal.

Reacted coal slurry (Stream 8) at elevated temperature and pressure is flashed into a gas-liquid separator vessel (T-5). The steam generated (Stream 9) is condensed in T-4 and the condensate plus any entrained acid mist is removed with the water. The residual slurry (Stream 10) is fed to a belt filter. The filtrate, which is regenerated leach solution, is removed from the coal slurry through a vacuum receiver (T-9) and pumped (Stream 12) to a large leach solution storage tank (T-6). The coal on the filter belt is washed with water (Stream 11) and discharged from the filter belt. The wash water is removed through a vacuum receiver (T-10) and sent to a large liquid-waste holding tank (T-8) for subsequent disposal. The filter is a highly versatile unit which should provide the data necessary for scale-up. It has variable belt speed, variable belt areas assigned to washing, variable cake washing rates, belt sprays if needed to control blinding of the pores in the belt, and steam nozzles to provide for partial cake drying.

As an alternate process step, the slurry from the flash tank (T-5) can be passed into a secondary reaction vessel (Reactor 2). At typical coal feed rates, this vessel can be filled in about two hours and then closed off, stirred and heated for any desired period of time before being pumped to the filter. Residence times up to about 10 hours are available in the primary reactor, Reactor 1. This secondary reactor can be used to extend residence times to much longer times for examining the removal of final traces of pyrite or examining any other long term behavior. The stirred vessel also can serve to repulp the filter cake for additional coal washing studies.

The final item of major equipment in the test plant is the coarse coal contact vessel (Reactor 3). This insulated and heated tank will hold a full bin (about 1.8 metric tons) of coarse coal (5 to 10 millimeter top-size). The principle use for this vessel is to convert the regenerated leach solution in storage tank T-6 to a more depleted solution in the process feed tank, T-7. In general, the iron sulfate leach solution in the filtrate going to tank T-6 will have a high Y because no secondary reactor was in use. For some test conditions, the feed to the process must be at a lower Y to simulate recycle leach solution from a secondary reactor. Passing all or some portion of the solution through coal will lower the Y of the solution to the desired value. This vessel is basically a coarse coal reactor and if appropriate sampling ports and possibly some flow distribution internals were added, it could be used to obtain design data for coarse coal processing.

Solution tanks are sized at about 50,000 liters to provide for about a week of continuous operation on the same feed without recycle or change. It also provides for uniform leach solution and coal samples of a large enough size for product recovery studies performed by equipment vendors. Operation at the scale of the test plant will provide experience and data expected to be adequate for the design of a demonstration-size commercial plant.

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SULFUR REMOVAL FROM COALS: AMMONIA/OXYGEN SYSTEM

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INTRODUCTION

The emergence of chemical desulfurization of coal as a viable alternative to stack gas scrubbing(1) has prompted researchers in this field to consider a variety of chemical systems which remove pyritic sulfur or both the pyritic and part of the organic sulfur (2,3,4,5,6). A review of the more prominent chemical desulfurization schemes is presented in a recent article(6). Because chemical desulfurization is cost competitive with stack gas scrubbing(1), utilities are beginning to show an interest in the development of this technology which could provide them with a source of clean fuel to meet the rigorous EPA standards for sulfur emissions.

This paper discusses the sulfur removal from coals using an ammonia/oxygen system which removes almost all of the pyritic sulfur and up to 25% of the organic sulfur in about 2 hours. Because organic sulfur removal necessarily implies coal carbon losses, a balance must be struck between the amount of organic sulfur removed and the thermal losses than can be economically tolerated from the coals being cleaned.

Although no effort has been made to optimize the system reported here, the results of BTU loss, oxygen consumption, retention time, etc. are fairly consistent with the oxygen/water system for pyrite removal from coals(2). The carbon losses, as might be expected, are somewhat higher. Furthermore, the data presented here can be used to construct an optimization scheme for future development work.

PROCESS DESCRIPTION

In this desulfurization scheme, run-of-mine coal is treated in a conventional preparation plant, where the coal is crushed and washed to remove rock and clay material. The coarsely crushed coal is then fed into close-circuited wet ball mills where it is further ground to -100 mesh. The ground slurry is pumped into oxygen sparged leach reactors which operate at about 130°C and 300 psi oxygen pressure. All of the pyritic sulfur and up to 25% of the organic sulfur is removed in about two hours. The desulfurized slurry now goes through a solid/liquid separation operation where the coal and liquid are separated. Because of the formation of sulfates and the absorption of some of the CO₂ (from coal oxidation) into the ammonia solution, this mixed sulfate/ carbonate stream must be regenerated to recycle the ammonia back into the process. The ammonia regeneration may be accomplished by calcining and/or steam stripping.

A discussion of the sulfur removal from coals as a function of ammonia concentration and retention time is presented below.

EXPERIMENTAL CONDITIONS

All of the experiments reported here were carried out in a batch mode in high pressure autoclaves. The autoclaves were equipped with baffles, and the speed of agitation controlled with the help of a tachometer and verified at frequent intervals with a stroboscope. The system was heated with a jacketed electric heater exterior to the chamber and the temperature controlled to within a couple of degrees with the aid of a temperature controller. The reaction was cooled rapidly at the end of the experiment with the help of a cooling system fitted inside the high pressure reactors. The mode of operation was as follows: 120 gms (dry basis) of Illinois #6 coal was slurried in ammoniacal solutions to give a solids pulp density of 20 w/o. The autoclaves were sealed and the air purged with inert gas. This insured no reaction with the coal sulfur during the heatup period. The heater and stirrers were turned on and the temperature allowed to stabilize at 130°C. The system was then pressurized with oxygen to 300 psi, and the reaction permitted to proceed. The vapor space of the reactor was connected to a gas chromatograph for measurement of the gas phase for products of reaction.

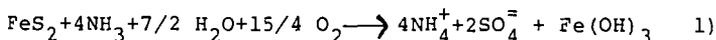
Minus 100 mesh coal was used, and the degree of agitation fixed to maintain the system in a kinetically controlled regime(2). Ammonia concentrations between 0.5 molar and 5 molar were studied. An analysis of the starting Illinois #6 coal is listed in Table I.

TABLE I -- Starting Coal Analysis

Total Sulfur 4.99%	Ash 19.27%
Pyritic Sulfur 2.06%	Vol. Matter 35.6%
Sulfate Sulfur 0.65%	Fixed Carbon 45.13%
Organic Sulfur 2.28%	BTU(maf) 13477

EXPERIMENTAL RESULTS

The chemical reaction for the oxidation of pyrite in an ammoniacal system is given by Equation 1).



where all of the sulfide sulfur is oxidized to soluble sulfates. Care was taken to insure that the NH_3/FeS_2 molar ratio for the experimental study was always in excess of the 4 required stoichiometrically: a range between 6.5 and 65 was considered.

The effect of retention time and ammonia concentration on sulfur removal from Illinois #6 coals is graphically displayed in Figure 1. Approximately 90% of the pyritic sulfur can be removed, and there appears to be no apparent effect of NH_3 concentration on pyrite removal. There appears to be a definite trend, however, in the organic sulfur removal as a function of NH_3 concentration. Measurements of total change in sulfur content of the coal, expressed as $\text{lbs. SO}_2/\text{MMBTU}$, shows a 50% change between the starting coal and the desulfurized coal. This compares against a 25% change after desulfurization of Illinois #6 coals when using the $\text{O}_2/\text{H}_2\text{O}$ system(2) where only pyritic sulfur is removed. The desulfurized coals, after an NH_3/O_2 treatment, also show no residual sulfate sulfur.

An important consideration in any chemical desulfurization process, in which the coal sulfur is oxidized, is the oxidant consumption. For this process the oxygen consumption to oxidize the coal sulfur species, and the coal itself, may be listed as follows:

- a) reaction with pyrite
- b) oxidation of organic sulfur
- c) oxygen uptake by the coal
- d) oxidation of coal to form CO and CO₂ in the gaseous phase
- e) formation of carbonates in solution.

The stoichiometric oxygen consumption for the pyrite reaction, given by Equation 1), calculates to be 1.0 lb.O₂/lb.FeS₂.

In the oxidation of pyrite with oxygen it is inescapable that oxygen will also react with the coal carbon. This oxidation of the coal usually results in the formation of CO and CO₂, together with soluble coal acids. There is a greater propensity for the formation of coal acids in basic systems than in acid systems. Furthermore, there is some pickup of oxygen by the coal to form an intermediate oxygen-coal complex.

The gases, as analyzed in the vapor space of the autoclaves, using a gas chromatograph, show that CO formation is negligible and that CO₂ is the major product of reaction. Some of the CO₂ formed due to carbon oxidation tends to dissolve in the ammoniacal liquor and report as carbonates in solution. To accurately determine the exact oxygen consumption for coal oxidation, solution analyses were conducted to measure this amount of carbonate formed. These analyses showed that the amount of carbonate measured in solution increased with increasing ammonia concentration. The total oxygen consumption for coal oxidation, both as CO₂ in the vapor space and carbonate in solution, as a function of retention time and ammonia concentration is shown in Figure 2. These results show that the coal oxidation is fairly insensitive to the ammonia concentration.

Due to the formation of an oxygen-coal complex, there is some oxygen tied up with the coal. This consumption is graphically displayed in Figure 3, which again shows no dependence on ammonia concentration. A minimum oxygen consumption for this process is tabulated in Table II.

TABLE II -- Minimum Oxygen Consumption

	<u>lbs.O₂/lb.coal</u>
O ₂ for pyrite reaction	0.0375*
O ₂ uptake by coal	0.034**
O ₂ for CO ₂ + CO	0.035**
	<u>0.1065</u>

* Based on 2% pyritic sulfur coal

** After 2 hours of sulfur removal

This table does not take into account any oxygen consumption for organic sulfur oxidation, which is difficult to measure. For a plant processing 8000 TPD of 2% pyritic sulfur coal (with a pyritic sulfur/organic sulfur ratio of 1), the oxygen demand, based on Table II, calculates to by 850 TPD. With a 25% contingency factor

to allow for organic sulfur oxidation, a 1000 TPD oxygen plant would be needed. This total oxygen duty is the same as that required for coal desulfurization using the O_2/H_2O system(2).

An important consideration for the viability of any desulfurization process is the overall thermal efficiency of the system. The BTU loss, on a moisture-ash-free basis, as a function of reaction time and ammonia concentration is presented in Figure 4. This graph shows that between 8% and 13% loss may be expected after two hours of sulfur removal. The pairing of the BTU loss as a function of ammonia concentration shown in Figure 4 is not immediately obvious. The loss of carbon during the desulfurization process is graphically displayed in Figure 5. In all cases the carbon loss is much greater than can be accounted for by CO_2 and carbonate formation.

This suggests that the difference reports in solution as coal acids. The formation of these acids is not surprising since the reaction of alkalis with coal to form humic acids is well known.

SUMMARY AND CONCLUSIONS

1. Increasing reaction time and ammonia concentration improved the extent of organic sulfur removal. For example, after 2 hours when using a 5 M NH_3 solution, 25% of the organic sulfur can be removed.
2. Changing the NH_3 concentration had no apparent affect on pyritic sulfur removal.
3. The oxygen consumption to oxidize the coal carbon (reporting as CO_2 in the gas phase and carbonae in solution) is fairly insensitive of the NH_3 concentration.
4. Ammonia concentration has no apparent affect on oxygen uptake by the coal.
5. Both the ammonia concentration and reaction time have an affect on the BTU and carbon values of coal. Increasing either one decreases the BTU and carbon value. As much as a 13% BTU and 10% carbon loss may be realized with using a 3 M NH_3 solution and reacting the coal for 2 hours. The large carbon losses are due to the formation of coal acids.

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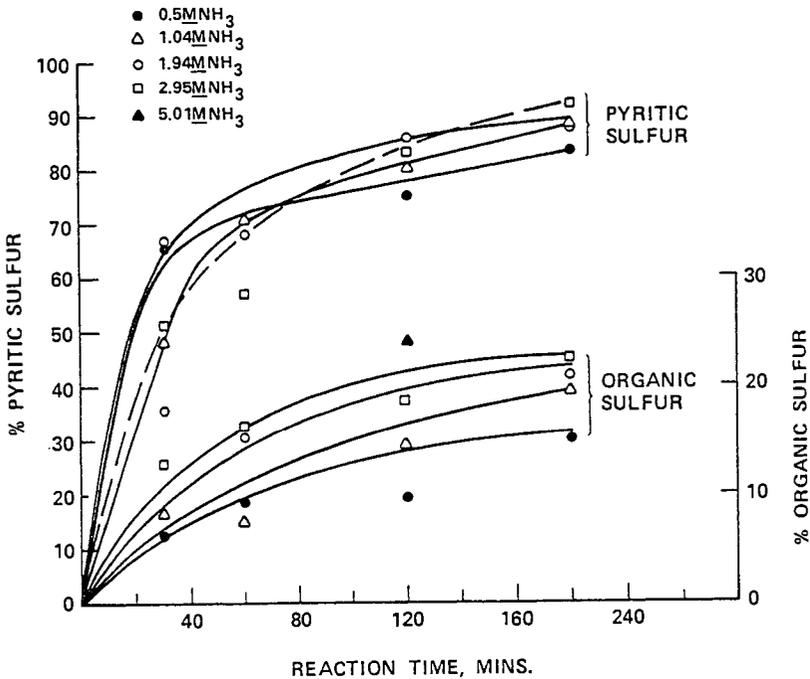


Figure 1. Sulfur Removal as a Function of Ammonia Concentration and Time.

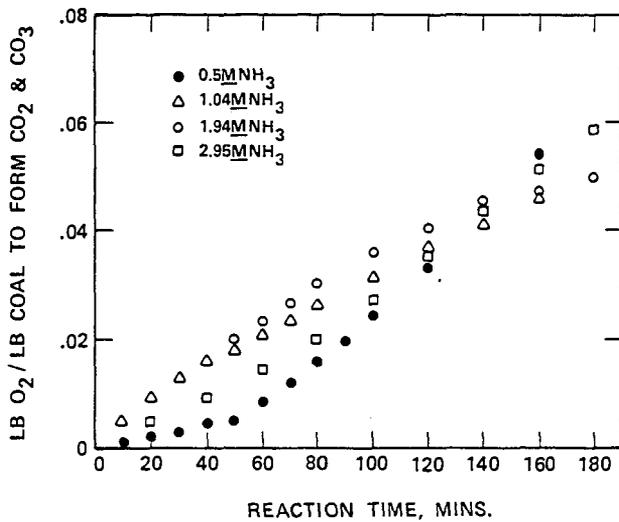


Figure 2. Oxygen Consumption for Coal Oxidation

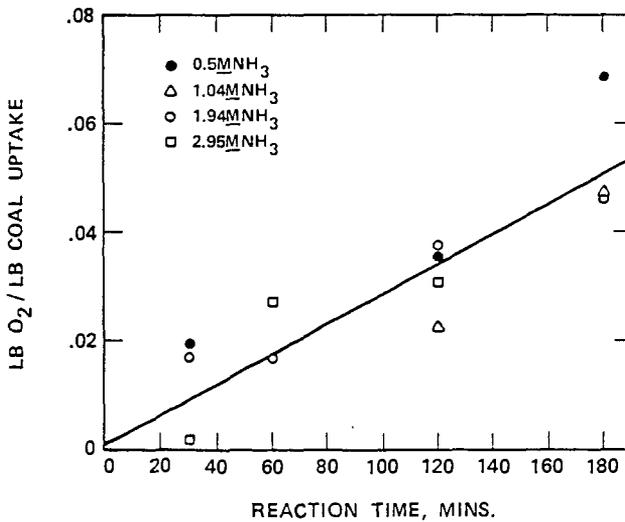


Figure 3. Oxygen Uptake by Coal

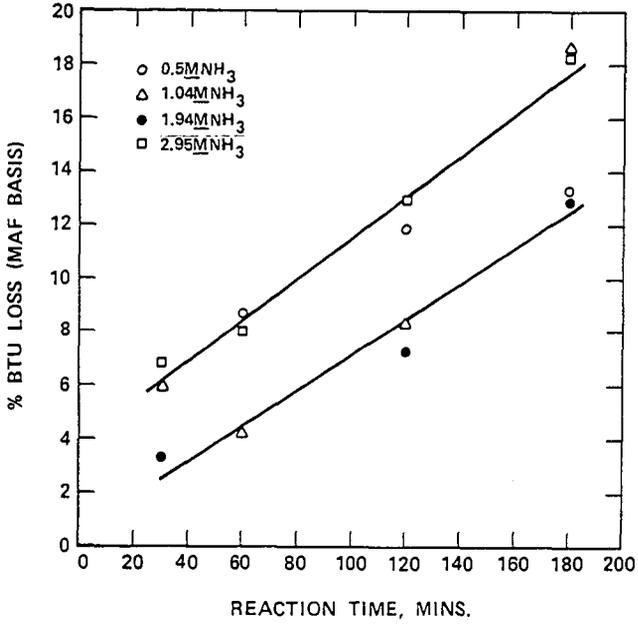


Figure 4. BTU Loss from Coals

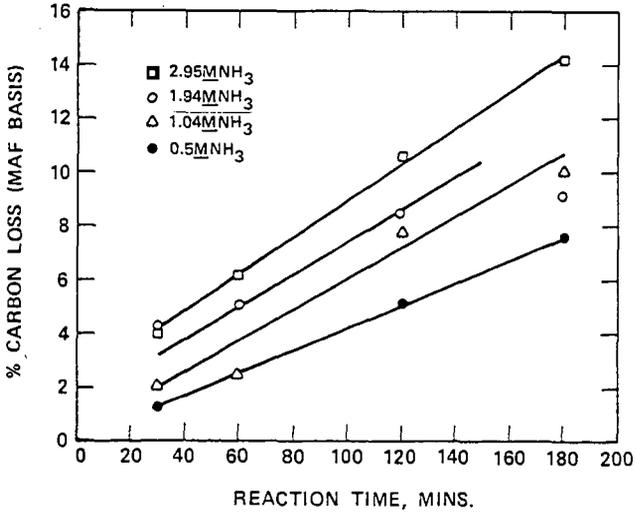


Figure 5. Carbon Loss from Coals

OXIDATIVE DESULFURIZATION OF COAL

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INTRODUCTION

It is becoming increasingly apparent that the solution to our national energy problems will require a variety of approaches, and that these must be compatible with environmental restrictions. Coal, only recently considered destined for obscurity, has been rescued by a combination of international political events and increasing difficulties in developing a nuclear power industry. Although coal as an energy source presents problems, at least it is available and can be utilized.

The Federal Government, as part of the program administered by the Energy Research and Development Administration, is carrying out research on many phases of coal utilization to overcome the environmental problems involved in the combustion of coal. One such project, which has been in progress at the Pittsburgh Energy Research Center since 1970, is concerned with chemical beneficiation of coal, and most specifically, with removal of sulfur from coal prior to combustion.

EXPERIMENTAL

Batch Experiments. Thirty-five grams of -200 mesh coal and 100 ml of water were placed in a liner (glass or teflon) in a 1-liter, magnetically stirred, stainless steel autoclave. The autoclave was pressurized with air (from a cylinder) to the required gauge pressure, and then heated with stirring until the specified temperature was reached (approximately 1 hour heat-up time). After a specified time at reaction temperature, the autoclave was cooled by means of an internal cooling coil. The contents were removed at room temperature, filtered, washed until the pH of the filtrate was neutral, and then extracted in a Soxhlet thimble with water until sulfate (present as CaSO_4) was no longer present in the fresh extract. The coal was then thoroughly dried in a vacuum oven at 100°C and analyzed by the Coal Analysis Section, U. S. Bureau of Mines.

Semicontinuous Experiments. Using a similar autoclave fitted with pressure regulating valves, the autoclave containing the coal and water was heated to the specified temperature under one atmosphere (initial pressure) of N_2 . At temperature, or shortly before reaching it, air was admitted to the desired pressure. Temperature was kept at the required value by using heating and cooling (cooling coil) while air (approximately $2 \text{ ft}^3/\text{hr}$) flowed through the autoclave. After the required time at temperature, the autoclave was cooled, and the products worked up as in the previous example.

RESULTS AND DISCUSSION

Although the project was initially divided into removal of organic and of inorganic sulfur (1), it was soon evident that, though one could remove pyritic sulfur without removing organic sulfur, the reverse was not true. Any process which removed organic sulfur would also remove pyritic sulfur. So the approach to the problem became one of finding chemistry suitable for removing organic sulfur from coal.

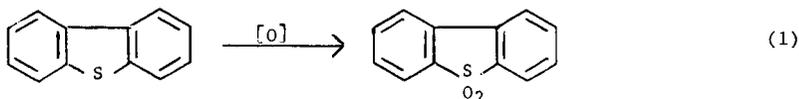
The chemistry which we chose to explore was based on two premises:

1. The major portion of the organic sulfur in coal was of the dibenzothiophene (DBT) type, and,
2. The reagents had to be inexpensive.

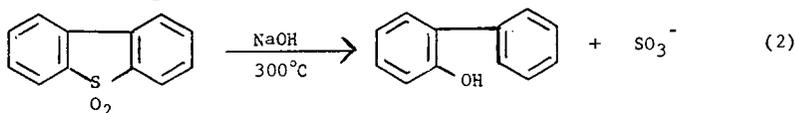
While we now believe that at least a sizable fraction of the organic sulfur in coal is not dibenzothiophenic, we have no reason to doubt that over 50% of it may be.

These premises led us to the following hypothetical two-step removal of organic sulfur from coal.

1. Oxidation of organic (or dibenzothiophenic) sulfur to sulfone.



2. Elimination of the SO_2 from sulfone by base.



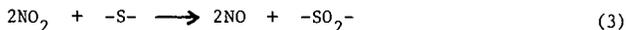
Both of these reactions are in the literature, and so our task became one of modifying and improving them so that they could be applied to desulfurization of coal.

The second step -- the removal of SO_2 from DBT sulfone by base -- was found to be essentially quantitative when the sulfone was heated to 300°C in the presence of aqueous NaOH and nearly as efficient with Na_2CO_3 . This was an improvement on the nonaqueous treatment (2).

The first step in the reaction -- oxidation to sulfone -- though extensively documented in the literature, presented more of a challenge. There are numerous oxidants reported which can effect the conversion of organosulfur compounds to sulfones, including KMnO_4 , HNO_3 , CrO_3 , $\text{H}_2\text{O}_2/\text{HOAc}$, and hydroperoxides (3). These obviously do not fit the second premise -- the reagents must be inexpensive. It was agreed that the only reagent which could be used as an oxidant was the oxygen in air. But DBT, and presumably the organic sulfur in coal, is inert to air at relatively high pressure and temperature. Transfer of oxygen to a carrier to form a hydroperoxide, followed by reaction of the hydroperoxide with DBT, did give sulfone. We found that with a large variety of hydrocarbons, such as tetralin, decalin, and cyclohexane, merely heating DBT with air under pressure in the presence of the hydrocarbon resulted in formation of sulfone (4), presumably as a result of in situ formation of hydroperoxides. Benzene, which does not form a hydroperoxide, affords no sulfone formation under comparable conditions.

Applying our two-step reaction -- air oxidation followed by treatment with aqueous base -- to coal, we were able to achieve up to 50% removal of organic sulfur, as well as almost complete elimination of pyritic sulfur as a bonus. Though this scheme appeared promising, it did require a suitable organic liquid and also NaOH .

We also explored another oxidation system which utilizes air as the ultimate source of oxygen. Nitrogen dioxide -- NO_2 -- is a good reagent for converting sulfides to sulfones, and it can be utilized in an easily regenerable system.



We found that we could, indeed, oxidize DBT to its sulfone in this manner, using NO_2 and air. When the reaction was extended to coal, however, a significant amount of concurrent reaction took place, including nitration of the coal, which consumed the nitrogen oxides and thus would have necessitated a continuous addition of NO_2 rather than the recycling shown in Equations 3 and 4.

In the meantime, our experiments on air oxidations of organosulfur using hydroperoxide precursors led us to the ultimate experiment, the one in which H_2O was used in place of an organic liquid phase. This reaction of coal with steam and compressed air almost quantitatively converted the pyritic sulfur in coal to H_2SO_4 . In addition, we found that we had also removed 25% of the organic sulfur as well. Here was evidence that there was some organosulfur in coal which was not DBT-like, since DBT failed to react with air and water under these conditions.

Initial experiments on the air-steam oxydesulfurization of coal were carried out using a batch, stirred autoclave system. In this apparatus in order to replace oxygen as it was used, it was necessary to cool the autoclave to near room temperature, vent the spent air, repressure, and reheat. Though this gave satisfactory desulfurization, it was an impractical approach for studying reaction parameters. The results cited in Tables 1-3 are from batch studies without repressurization and thus represent less than maximum desulfurization in some cases.

The apparatus was modified to allow air to flow through the stirred reactor while the coal-water slurry remained as a batch reactant. This is our current system. In this way, we can study many of the variables as they will affect the reaction in a continuous system.

Our newest apparatus, now beginning operation, is a fully continuous unit, feeding both air and coal-water slurry into a reactor tube. This system is designed to obtain data on reaction rates, develop information for economic evaluation, and answer those questions which arise concerning engineering aspects of the process.

Heating high-pyrite coals in aqueous slurry with compressed air at total pressure of 1,000 psi and at 150-160°C results in decrease of pyritic sulfur to near the lower limit of detection by standard analytical procedure. Some results of 1-hour batch experiments are shown in Table 1. The sulfur which is removed is converted completely to aqueous sulfuric acid. Experiments in a semicontinuous experiment show as much as 80% of the reaction occurs within the first 5 minutes. At a pressure of 200 psi, the reaction is much slower, requiring several hours to achieve even 60% pyritic sulfur removal. For some coals, at least, the desulfurization is almost as rapid at 500 psi as at 1,000 psi. The oxidation of pyritic sulfur is temperature dependent, but at the conditions of our experiments, reaction is sufficiently fast that above 150°C little improvement is noted. In a few cases, where a coal appears to have some residual pyrite which is not oxidized readily at 150°C, it may be removed at 180°C.

As the temperature at which the oxidation is conducted is increased above 150°C, an increasing amount of organic sulfur is removed from the coal. Although the percentage of organic sulfur removed parallels the temperature rise, so does the amount of coal which is oxidized. To prevent excessive loss of coal a practical limit of 200°C has been chosen for carrying out the reaction on most coals. Removal of organic sulfur from a series of coals, shown in Table 2, varies from 20 to over 40%. Further reduction of organic sulfur content is probably possible with some of these coals without sacrifice of coal recoverability.

An upper limit on organic sulfur removal appears to be between 40 and 50%, and varies from coal to coal. We believe this is due to the functionality of the organic sulfur, and gives some rough measure of oxidation resistant, or DBT type, of sulfur. Obviously, that sulfur which is removed by oxydesulfurization must be in some other structure which is readily oxidized, such as thiol, sulfide, and/or disulfide. These values coincide with removal of sulfur from coal observed when it is heated with aqueous alkali at 300°C, a reagent which does not attack DBT (5,6).

Even at 150-160°C many coals, including some with rather high sulfur contents, can be dramatically desulfurized, as shown in Table 3.

TABLE 1. Pyrite Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp, °C	Pyritic sulfur, wt pct	
			Untreated	Treated
Illinois No. 5	Illinois	150	0.9	0.1
Minshall	Indiana	150	4.2	0.2
Lovilia No. 4	Iowa	150	4.0	0.3
Pittsburgh	Ohio	160	2.8	0.2
Lower Freeport	Pennsylvania	160	2.4	0.1
Brookville	Pennsylvania	180	3.1	0.1

TABLE 2. Organic Sulfur Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp °C	Organic sulfur, wt pct	
			Untreated	Treated
Bevier	Kansas	150	2.0	1.6
Mammoth ^a	Montana	150	0.5	0.4
Wyoming No. 9 ^a	Wyoming	150	1.1	0.8
Pittsburgh	Ohio	180	1.5	0.8
Lower Freeport	Pennsylvania	180	1.0	0.8
Illinois No. 6	Illinois	200	2.3	1.3
Minshall	Indiana	200	1.5	1.2

^a Subbituminous

TABLE 3. Oxydesulfurization of Representative Coals

Seam	State	Temp, °C	Total sulfur, wt pct		Sulfur, lb/10 ⁶ Btu	
			Untreated	Treated	Untreated	Treated
Minshall	Indiana	150	5.7	2.0	4.99	1.81
Illinois No. 5	Illinois	150	3.3	2.0	2.64	1.75
Lovilia No. 4	Iowa	150	5.9	1.4	5.38	1.42
Mammoth ^a	Montana	150	1.1	0.6	0.91	0.52
Pittsburgh	Pennsylvania	150	1.3	0.8	0.92	0.60
Wyoming No. 9 ^a	Wyoming	150	1.8	0.9	1.41	0.78
Pittsburgh	Ohio	160	3.0	1.4	2.34	1.15
Upper Freeport	Pennsylvania	160	2.1	0.9	1.89	0.80

^a Subbituminous

The reaction conditions which we have found to be suitable for oxydesulfurization are:

- Temperature - between 150° and 220° C.
- Pressure - between 220 and 1,500 psi operating pressure.
- Residence time - 1 hour or less.

Most of our experiments have been carried out below 220°C and at approximately 1,000 psi. Recoveries of fuel values are excellent, being generally 90% or better. The only byproduct of the reaction is dilute H_2SO_4 . This can be recycled with no observable effect on desulfurization for at least 5 cycles. When the H_2SO_4 becomes too concentrated for further use, it can be converted to a commercial grade of sulfuric acid if a suitable, economic market exists, or it can be disposed of by limestone neutralization as a readily filterable $CaSO_4$.

The process, outlined in Figure 1, needs no novel technology to produce coal having over 95% of its pyritic sulfur and as much as 40% of its organic sulfur removed. Other than the coal, air, and water, the only other material needed for the process is the limestone used to neutralize the H_2SO_4 . No sludge is formed, much of the water can be recycled, and the only waste product is solid $CaSO_4$ (7).

A preliminary cost estimate for this process indicates a cost of \$3.50 to \$5.00 per ton. Even at twice this cost, the process would still be considerably less expensive than coal conversion to gas or liquid fuel. Assuming removal of 95% pyritic sulfur and 40% organic sulfur, an estimated 40% of the coal mined in the eastern United States could be made environmentally acceptable as boiler fuel, according to EPA standards for new installations. And the sulfur content of the remainder of the eastern coal could be drastically reduced, making it environmentally acceptable for existing boilers.

CONCLUSIONS

Treatment of coal with compressed air and steam at 150°-200°C represents a practical method to desulfurize to acceptable levels a sizable percentage of the available coal in the eastern United States at a cost in money and fuel value less than coal conversion and to an extent greater than can be achieved by physical depyriting methods.

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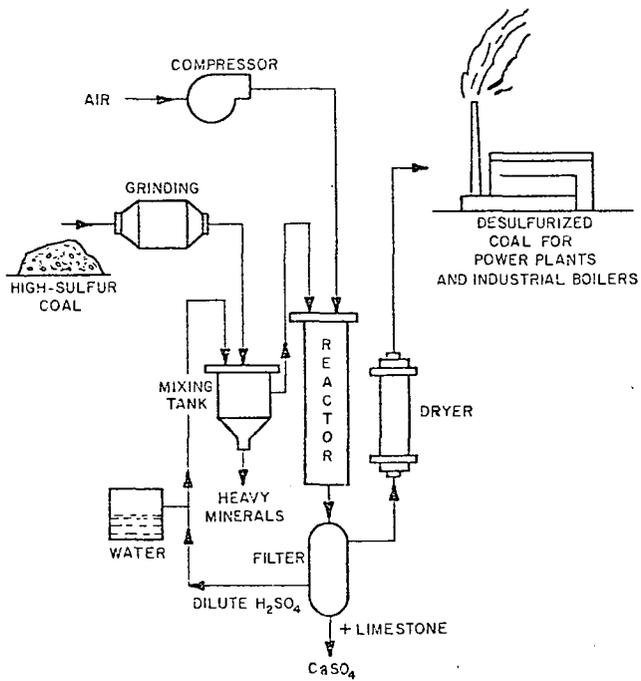


Figure 1 - Air-steam coal desulfurization process.

MAGNETIC DESULFURIZATION OF SOME ILLINOIS BASIN COALS*

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INTRODUCTION

High extraction magnetic filtration (HEMF) is used successfully to process kaolin (1). This is the first successful commercial application of a new level of magnetic separation equipment and processing technology which resulted from the joining of four major concepts (2).

1. Discovery of the importance of retention time in mineral separation.
2. Development of very high gradient matrix collectors.
3. High intensity fields in wet magnetic separators (up to 20 kilogauss).
4. Modern design of large high field magnets.

Use of longer retention time permits finely divided particles to migrate and be captured by a magnetized collection surface. The canister in the magnet is filled with a matrix of steel wool, screens made of sharp thin ribbons, or other filamentary material which provides very high gradients. Modern electronic and magnet technology led to the design of a magnet with a high field throughout a large cavity. A diagrammatic sketch of a large high intensity magnet is shown on Figure 1. The diameter of the canister can be up to 84 inches with a height of 20 inches. Up to 100 tons of kaolin per hour can be processed through the 84 inch unit. Fabrication of equipment larger than 84 inches is feasible but the problems involved in shipping and for on site fabrication are such that it is probably more efficient to consider multiple installations of 84 inch machines.

High extraction magnetic filtration is very successful in removing iron and titanium impurities from kaolin. Potential applications for its use for beneficiation of other industrial minerals and coal have been demonstrated by Murray (3,4,5). Present HEMF equipment utilizes electromagnets to generate fields of 20 kilogauss. Power consumption of this equipment is in the range of 400-500 KW.

The present HEMF equipment is optimized for separation of slurry containing fines below 200 mesh and preferably below 20 microns. Other matrix types can be substituted for stainless steel wool to accommodate coarser feed materials (up to 20 mesh) including Frantz screens, loosely packed coarse steel wool, steel shot, steel filings, and other filamentary material. New developments are underway in matrix design and composition which can greatly enhance HEMF technology.

MAGNETIC DESULFURIZATION OF COAL

The earliest work concerning the reduction of sulfur in coal by magnetic separation was described in a German Patent by Siddiqui in 1957 (6). Yurovsky and Remesnikov (7) published a paper in 1958 reporting that coal pulverized finer than 16 mesh size subjected to a thermal steam-air treatment reportedly made the pyrite more magnetic, which enhanced beneficiation when processed in a specially built magnetic separator. Sulfur reduction of 85, 74.9, and 70 percent were reported. Perry (8) reported that fine pyrite (65 to 100 mesh) treated in steam-air atmosphere at temperatures of 570° to 750°F for varying times, up to 10 minutes, resulted in increased quantity of pyrite becoming amenable to magnetic separation with increasing intensity of treatment. Kester (9, 10,) demonstrated that sulfur could be reduced to a greater extent by making a high intensity magnetic separation directly on raw untreated coal without employing the

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thermal pretreatment step. Thus, by pulverizing the coal to a typical power plant size and by magnetically separating the coarse 48 by 200 mesh size fraction significant sulfur reduction was achieved.

Kester reported that pyritic sulfur accounts for 40 percent to as much as 80 percent of the sulfur content of most coals (9). Gluskoter and Simon (11) reported that the mean total sulfur content in 474 analyses was 3.57 percent in coals from Illinois and the mean value of pyritic sulfur in these same coals was 2.06 percent. They found that there is on an average approximately one and one-half times as much pyritic sulfur in a sample as there is organic sulfur.

Macroscopic pyrite occurs in coal in, 1)veins, usually thick and filmlike along vertical joints, 2)lenses that are extremely variable in shape and size, 3)nodules or balls, 4)disseminated crystals and irregular aggregates. Microscopic pyrite occurs as small globules and blebs, fine veinlets, dendrites, small euhedral crystals, cell fillings, and replacement plant material.

Kester, Leonard, and Wilson (12) reported that the mass susceptibility of powdered pyrite was 4.53×10^6 cgs units. Another value commonly used for the magnetic susceptibility of pyrite is 25×10^{-6} electromagnetic units per cubic centimeter. The strength of magnetism, which can be induced into a mineral is dependent upon the permeability of the mineral according to the equation.

$$B = uH$$

B - magnetic induction in gauss in the mineral

u - Permeability of the mineral

H - magnetic field intensity in gauss

Therefore the susceptibility is:

$$B/H = 1 + 4\pi K$$

K - magnetic susceptibility expressed in electromagnetic units cm/gm/sec

If the value of K is positive, the mineral is termed paramagnetic and experiences a force which tends to attract it in the direction of increasing magnetic gradient. If K is negative, the mineral is diamagnetic and experiences a repulsive force. Ferromagnetic minerals, such as iron, experience strong magnetic forces in the direction of increasing magnetic gradient and thus have very large positive values of K. Coal is diamagnetic (13) and pyrite is paramagnetic. Thus, if the coal is crushed and pulverized fine enough to liberate the pyrite a good magnetic separation is possible.

A recent study by Kindig and Turner (14) reported on a new process for removing pyritic sulfur and ash from coal. The pulverized coal is treated with iron carbonyl vapor which puts a thin skin of magnetic material on the pyrite and ash but does not affect the coal. Thus magnetic separators yield a non-magnetic coal low in sulfur and ash and a magnetic fraction high in sulfur and ash.

The coal samples utilized for this report were pulverized so that 90 percent passed through a 200 mesh sieve. The samples were slurried at 30 percent solids for the wet magnetic tests. Frantz screens made from thin sharp ribbons of 430 magnetic stainless steel were used as the matrix in the canister. For the wet magnetic tests retention times of 30, 60, and 120 seconds were used for one series and multiple passes with a retention time of 30 seconds each were used for a second series. For the dry tests the series were run using gravity feed with multiple passes.

The coals used for this report were commercially mined coals in the Illinois Basin. These are Coals V and VI from Illinois and Indiana. The Indiana samples were from Warrick County in southern Indiana and the Illinois samples were from

Wabash and Williamson Counties.

Table I shows the sulfur content of the various samples.

TABLE I - Sulfur Content (Percent)

Coal	Total Sulfur	Inorganic Sulfur	Organic Sulfur
Indiana V	4.63	2.44	2.19
Indiana VI	4.17	2.20	1.97
Illinois V	3.59	2.39	1.20
Illinois VI	1.98	1.02	0.96

Figures 2 and 3 indicate the sulfur reduction obtained with increasing retention time and up to three passes through the magnet using wet separation methods. Figure 4 shows the sulfur reduction obtained using a dry separation technique. The data shows that the best results as far as sulfur reduction is concerned was attained using a slurry and three passes through the magnet each with a retention time of 30 seconds. Table II is a summary of the sulfur reduction obtained using both wet and dry separation methods.

TABLE II - Sulfur Reduction (Percent)

Coal	Total S	Total S in Product	Inorganic S in Product	%Inorganic S in Product
Indiana V	4.63	3.00 ¹	0.81	67
Indiana V	4.63	3.30 ²	1.11	55
Indiana V	4.63	3.78 ³	1.59	25
Indiana VI	4.17	2.30 ¹	0.10	85
Indiana VI	4.17	2.45 ²	0.25	78
Indiana VI	4.17	3.31 ³	1.01	39
Illinois V	3.59	1.96 ¹	0.83	65
Illinois V	3.59	2.18 ²	0.99	59
Illinois V	3.59	2.87 ³	1.67	30
Illinois VI	1.98	1.15 ¹	0.21	79
Illinois VI	1.98	1.29 ²	0.32	69
Illinois VI	1.98	1.57 ³	0.61	40

1. Wet-three passes 2. 120 second retention 3. Dry-three passes

One sample of Coal V from Indiana was pulverized so that 90 percent of its particles passed 325 mesh and using 3 passes with 30 seconds retention each, 93 percent of the pyritic sulfur was removed. Further tests on fine grinding and optimization of the test conditions are now being carried out in the authors laboratories. In addition to the sulfur reduction, ash reduction is being measured. The loss of coal in the magnetic fractions varied from six to fourteen percent and is related to the size and distribution of the pyrite in the coal.

ECONOMICS

Quinlan and Venkatesan (15) recently discussed the economics of coal preparation coal cleaning processes comparing jig versus heavy media plant circuits. The operating cost of the jig plant was \$0.85 per clean ton and for the heavy media circuit \$1.25 per clean ton. The capacity of each was 500 TPH and the capital cost of the jig circuit was \$6,000,000 and for the heavy media circuit \$8,500,000.

To design a cleaning circuit to produce 500 TPH of coal would require five 84 inch magnets. The capital cost (installed) would be approximately \$8,000,000.

	Cost per hour	Cost per ton 500 TPH
Amortization of installed separators over 10 years 80,000 hrs.	100.00	0.20
Magnet power (2000 KW @2¢ KWH)	40.00	0.08
Pumping and Flushing Power (1000 @2¢ KWH)	20.00	0.04
Labor	15.00	0.03
Maintenance	10.00	0.02
TOTAL	185.00	0.37

The cost per ton of magnetic cleaning is relatively low compared with the other two methods cited. In addition to the potential removal of 70 to 90 percent of the inorganic sulfur, the ash content of the coal would be substantially reduced. A high percentage of the following impurities, if present, in addition to pyrite, would be removed magnetically because all of these minerals and rocks have a mass susceptibility higher than pyrite except for limestone: siderite, limonite, ferrous and ferric sulfate, limestone, clay and shale, and sand.

Much additional research and development work must be done to substantiate the preliminary results reported in this paper. Several studies are underway in the author's laboratories at Indiana University. With the advent of coal becoming the major energy source in the United States in the foreseeable future, magnetic cleaning of coal looks as if it will be a viable method of processing which can provide a low sulfur, low ash coal.

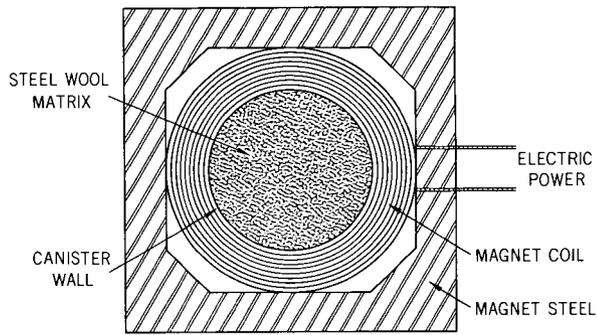
CONCLUSIONS

1. High Energy Magnetic Filtration (HEMF) is proven commercial process.
2. Fine pulverization to liberate the pyrite is necessary before magnetic filtration.
3. Sixty-five to ninety percent of the inorganic sulfur can be removed from the coal by HEMF processing a coal slurry.
4. The estimated cost per ton is lower than using a jig circuit or heavy media circuit.
5. The coal product from the HEMF process will be relatively clean both from sulfur and ash content.

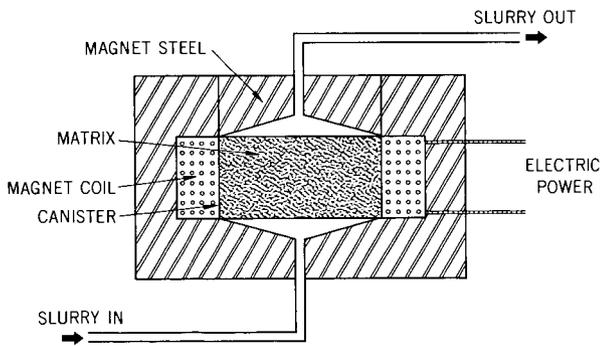
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TOP VIEW



SIDE VIEW
SECTION THRU MAGNET

FIG. 1-Diagrammatic Side and Top View of HMF Unit

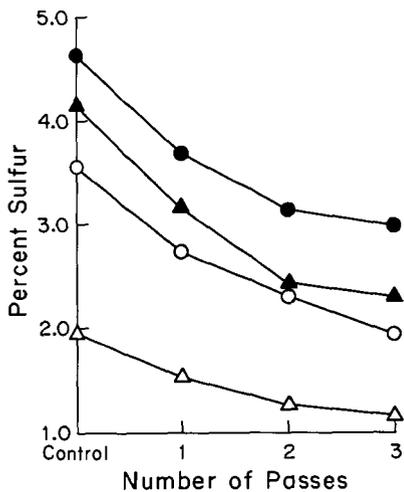


Fig. 2 Sulfur content after 1, 2 and 3 passes at 30 seconds retention each (wet).

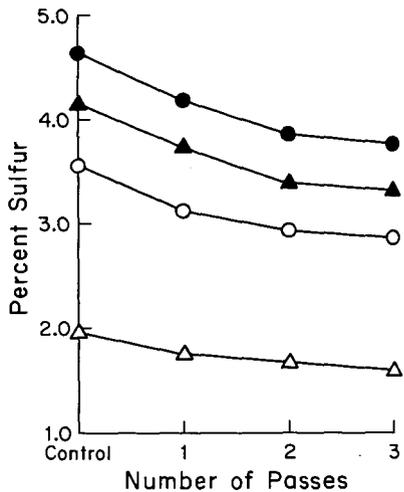


Fig. 4 Sulfur content after 1, 2 and 3 passes (dry).

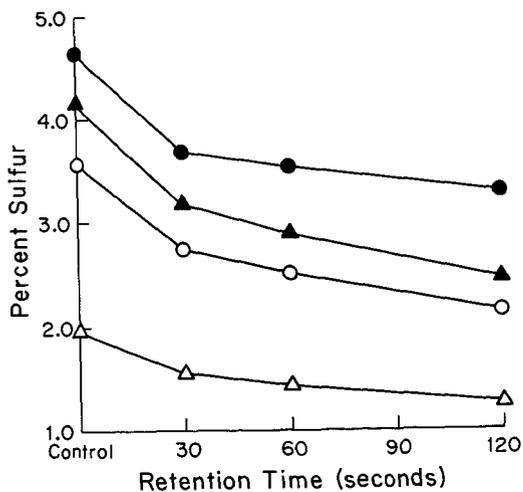


Fig. 3 Sulfur content with increasing retention time (wet).

EXPLANATION

- Coal V, Warrick Co., Ind.
- ▲ Coal VI, Warrick Co., Ind.
- Coal V, Wabash Co., Ill.
- △ Coal VI, Williamson Co., Ill.

DESULFURIZATION OF COALS BY HIGH-INTENSITY HIGH-GRADIENT
MAGNETIC SEPARATION: CONCEPTUAL PROCESS DESIGN AND COST ESTIMATION

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BACKGROUND

It is well-known that the main difficulty in increasing the utilization of coal in the United States lies in the pollution problem, as the emission level of sulfur oxides and ash particles from coal burning facilities are being regulated by stringent environmental standards. Although the particulate emission standard can generally be met by using electrostatic precipitators, there apparently exists no accepted technology for controlling the sulfur oxide emissions from the flue gases (28). Thus, there has been a growing effort recently in developing effective and economical alternatives to flue gas desulfurization, and one of the most attractive alternatives is the pre-combustion cleaning of coal. Several new physical and chemical methods for removing sulfur and ash from coal prior to its combustion have already been proposed and are currently under intensive further developments (4). An important physical method for cleaning coal that appears to hold much promise is the well-established magnetic separation technique. Previous experimental investigations have clearly indicated that most of the mineral impurities in coal which contribute to the pyritic sulfur, the sulfate sulfur and the ash content are all paramagnetic. These sulfur-bearing and ash-forming minerals, if sufficiently liberated as discrete particles, can normally be separated from the pulverized diamagnetic coal by magnetic means (14, 16, 17, 31). Indeed, the technical feasibility of the magnetic cleaning of coal has been demonstrated in a number of previous studies, with substantial amounts of sulfur and ash removal reported (18, 19).

During the past few years, the magnetic cleaning of coal has been given new impetus with the introduction of a new level of magnetic separation technology, the high-intensity high-gradient magnetic separation (HGMS). The HGMS technology was developed around 1969 for the wet cleaning of feebly magnetic contaminants from kaolin clay (9,10,22,23 25). A typical HGMS unit in this wet application is shown schematically as Figure 1(a). The electromagnet structure consists of the energizing coils and the surrounding iron enclosure. The coils in turn enclose a cylindrical, highly magnetized working volume packed with fine strands of strongly ferromagnetic packing materials such as ferritic stainless steel wools. With this design, an intense field intensity up to 20 kilo-gauss can be generated and uniformly distributed throughout the working volume. Furthermore, because of the placement in the uniform field the ferromagnetic packing materials which increase and distort the field in their vicinity, large field gradients of the order of kilo-gauss/micron can be produced. In the wet beneficiation of kaolin clay, the HGMS unit is employed in a batch or cyclically operated process like a filter. The kaolin feed containing the low-concentration feebly magnetic contaminants is pumped through the stainless steel wool packing or matrix of the separator from the bottom while the magnet is on. The magnetic materials (mags) are captured and retained inside the separator matrix; and the nonmagnetic components (tails) pass through the separator matrix and are collected as the beneficiated products from the top of the magnet. After some time period of operation, the separator matrix is filled to its loading capacity. The feed is then stopped and the separator matrix is rinsed with water. Finally, the magnet is turned off, and the mags retained inside the separator matrix are backwashed with water and collected. The whole procedure is repeated in a cyclic

fashion. In general, if this batch process is employed in other wet applications where the magnetic materials occupy a large fraction of the feed stream, the down time for backwashing will be considerable, possibly necessitating the use of one or more back-up separators. To overcome this problem which is inherent to batch operations, a continuous process employing a moving matrix HGMS unit, called the Carousel separator, has been proposed (10, 22, 23, 25) as shown schematically in Figure 1(b). A number of pilot-scale studies of the wet beneficiation of kaolin clay and iron ores using the Carousel separator have been reported (23).

Because of the very low costs and the outstanding technical performance of the HGMS demonstrated in the kaolin application, the HGMS was recently adapted to the removal of sulfur and ash from a finely pulverized Brazilian Coal suspended in water in a bench-scale exploratory study (31). Other investigators later utilized pilot-scale HGMS units for the desulfurization and deashing of water slurries of some Eastern U.S. Coals. For instance, results from pilot-scale studies that demonstrated the technical feasibility of the magnetic separation of sulfur and ash from water slurries of pulverized Illinois No. 6, Indiana No. 5 and No. 6, and Kentucky No. 9/14 coals have been published (16, 17, 21). In particular, the quantitative effects of residence time, field intensity, packing material and density, slurry concentration and recycle on the grade and recovery of the magnetic separation of sulfur and ash from water slurry of pulverized Illinois No. 6 coal have been established experimentally and can be predicted reasonably by an available magnetic filtration model (16, 17). Depending upon the types of coals used and the separation conditions employed, the existing bench-scale and pilot scale results have already shown that the use of single-pass HGMS was effective in reducing the total sulfur by 40-55%, the ash by 35-45%, and the pyritic sulfur by 80-90%; while achieving a maximum recovery of about 95% (19). These available results have also indicated that both the grade and recovery of the separation can be generally enhanced with the use of larger separator matrix or by the recycle of the tail products. Further detailed review of the reported results on the magnetic cleaning of pulverized coals in water slurries can be found in the literature (18,19). An important point to be made here is that these published data and other recent analyses (3,4,7,19,24,29,30) have indicated that a significant portion of the United States coal reserve, low enough in organic sulfur, can be magnetically cleaned for use as an environmentally acceptable, low sulfur fuel. It has been estimated that a total of 100 million short tons of U.S. coals per year may be magnetically cleaned. This amounts to over 17% of the total U.S. production per year (19). Although the existing data have not yet established the total deashing by magnetic means, there are some indications that by optimizing the separation conditions, and enhancing the magnetism of ash-forming minerals, etc., further improvement in the effectiveness of magnetic separation of ash from coal can be made (19).

Recent studies (8,16-19, 26) have also suggested that coal cleaning by the HGMS technique could serve as a significant adjunct to coal liquefaction processes. In particular, the technical feasibility of adapting the HGMS as an alternative, effective mineral residue separation method as compared to the conventional precoat filtration in the solvent refined coal (SRC) process has already been demonstrated in the bench-scale, exploratory study done at Hydrocarbon Research, Inc. (HRI). The HGMS was effective in removing up to 90% of the inorganic sulfur from the liquefied SRC filterfeed slurry of Illinois No. 6 coal, and about half of the experimental runs conducted by HRI indicated over 87% inorganic sulfur removal (8,19,26). In general, the work done by HRI showed that the HGMS was less effective in ash removal, but did remove 25 to 35% of the ash. Quite recently, a pilot-scale HGMS system for the removal of mineral residue from the liquefied coal has been designed and constructed by the authors (17). Typical results from experiments conducted with the liquefied SRC filter feed slurry of Kentucky No. 9/14 coal have been quite encouraging.

indicating that the HGMS could reduce the total sulfur, ash and pyritic sulfur contents by as high as 70, 76 and 95%, respectively. Available data from the above bench scale and pilot-scale investigations have also showed that an even greater deashing of the liquefied SRC filter feed can be achieved by improved separation conditions. A detailed discussion of these results along with their technical implications can be found in the literature (19,26). Furthermore, a close examination of the inherent physical and chemical characteristics of the hydrogenated product prior to the filtration step in the SRC and other related liquefaction processes will indicate that the HGMS may be developed as a practically applicable mineral residue separation method. It is known that the hydrogenation reaction will generally reduce a major portion of the pyritic sulfur to the highly magnetic pyrrhotite; and the sulfur-bearing and ash-forming minerals tend to be more easily liberated from the dissolved organic components in the filter feed slurry when compared to the case of pulverized coal suspended in water. Furthermore, the typical mean particle size of the SRC filter feed sample is often less than 5 microns, which dictates the use of methods capable of handling micron-size materials like the HGMS. All of these factors seem to suggest that the significant potential of utilizing the HGMS for removing the mineral residues from liquefied coal. For certain types of coals, it has been pointed out that even without further enhancement of the magnetic removal of ash, the magnetically cleaned SRC would be acceptable for use as a feed to boilers which already have electrostatic precipitators (34). This follows because the cost of solid-liquid separation in coal liquefaction is generally substantial, and the moderately low-ash SRC should be less expensive (2,26, 34). Indeed, a preliminary cost estimation of the magnetic desulfurization of liquefied coal based on the laboratory data obtained by HRI seems to support this observation (26).

The preceding discussion has indicated that the scientific and technical feasibility of the magnetic desulfurization of both wet and liquefied coals has been well established. Recently, there have been several estimates of the costs of magnetic desulfurization reported in the literature (9,20,21,24,26,31). Because of the simplifying assumptions involved as well as the technical performance specified and the estimation methods used in these analyses, however, most of them seem to be somewhat approximate in nature. In this paper, the latest data from pilot-scale studies of sulfur and ash removal from both wet and liquefied coals by the HGMS are used to design conceptual processes for magnetic desulfurization of coals. Estimates of magnetic desulfurization characteristics and conceptual process requirements, as well as installation and processing costs are determined. In particular, the extents to which the processing conditions can affect the magnetic desulfurization costs are to be examined. The latter will provide some indications on the possible impact of future process improvements. Finally, the results are compared with other approaches to the desulfurization of coals (2,4,15,27,33).

MAGNETIC DESULFURIZATION OF COAL/WATER SLURRY: PROCESS AND COSTS

A conceptual process for the magnetic desulfurization of pulverized coal suspended in water by the HGMS is shown schematically in Figure 2. A coal slurry of a fixed concentration is prepared first by mixing known amounts of pulverized coal, water and a dispersant (wetting agent) like Alconox. The HGMS unit employed here is the largest commercial unit now in use for producing high quality paper coating clays. It is operated at a fixed field intensity of 20 kilo-gauss generated in an open volume of 7-foot in diameter and 20-inch in length. A stainless steel wool separator matrix of 94% void is placed in the open volume. The coal slurry is pumped through the energized separator matrix at a fixed residence time (flow velocity) until the matrix reaches its loading capacity. After rinse with water, the maqs are sent to a settling pond or a classifier for recovering water for re-use. The tails are collected, dewatered and dried.

By removing 80 to 90% of the pyritic sulfur magnetically and achieving a recovery of 85 to 90% as was demonstrated from the results of reported studies of magnetic desulfurization of pulverized coals in water slurries (16-19,21,31), the process can be used for the cleaning of about one-fifth of the recoverable U.S. coals with a low organic sulfur content of 0.7 to 0.9 Wt% as an environmentally acceptable fuel. A detailed documentation of the reserve and production of U.S. coals which may be magnetically cleanable to 1 Wt% total sulfur according to the Seam, district and county in each state, along with the total and organic sulfur contents can be found in the literature (7). Here, a reasonable range of add-on costs (excluding those for grinding, dewatering and drying) can be estimated for the wet magnetic cleaning of coal slurries designed to achieve the similar desulfurization characteristics as reported in the recent studies (16-19,21,31). The method used for estimating the costs of magnetic desulfurization was based on the technique employed by the Federal Power Commission Synthetic Gas-Coal Task Force in their report on synthetic gas (2,5). The investor capitalization method used in this approach was the discount cash flow (DCF) financing method with assumed DCF rates of return such as 15% after tax. This method essentially determines the annual revenue during the plant life which will generate a DCF equal to the total capital investment for the plant. Several major assumptions were included in the method (2,5): (a) The plant life was assumed to be 20 years with no cash value at the end of life. (b) A straight-line method was used to calculate the annual depreciation. (c) Operating costs and working capital requirements were assumed to be constant during the plant life. (d) The current value of the investment included the cost of capital during the construction period and 100% equity capital was assumed. (e) Total plant investment, return on investment during the plant life and working capital were treated as capital costs in year zero (the year ending with the completion of start-up operations). (f) Start-up costs were treated as an expense in year zero. (g) 48% federal income tax was assumed. Based on these assumptions, equations for calculating the unit costs (\$ per ton coal processed annually) can be suggested from the referenced documents (2,5). They are summarized in Table 1, in which some further cost information used in the present estimation is given. Note that the costs of major installed equipments and the unit costs listed in Table 1 were based on the values of June 1976. For instance, the costs of pump and tank used were estimated first according to reference 6 and then brought them up to date by multiplying a CE plant cost index ratio of (205/113.6); while the cost of the installed HGMS unit with a separator matrix of 7-foot diameter and 20-inch length was estimated to be 1.936 million (11).

The estimated capital investments and unit costs for four typical cases, designed as A-D, are summarized in Table 2. Slurry velocities of 2.61 and 4.0 cm/sec, slurry concentrations of 15,25 and 35Wt%, as well as separation duty cycles from 59.0 to 77.9% have been considered. These separation conditions are similar to those used in the latest pilot-scale investigations reported (16-19,21,31). The results shown in this table clearly illustrate the effects of slurry velocity and concentration, as well as separation duty cycle. For instance, the comparison of cases A-C shows that at the same slurry velocity and similar magnetic desulfurization characteristics, the higher the slurry concentration, the cheaper will be the investment and unit costs. While this observation is to be expected, it is worthwhile to mention that there have been pilot-scale testing data which indicate the fact that increasing the slurry concentration of pulverized Illinois No. 6 coal from 2.57 to 28.4 Wt% did not appreciably change the grade and recovery of the separation. Further effects of processing conditions, as well as operating and cost factors, etc. on the unit costs are illustrated in Table 3. It is seen from the table that by doubling the amount of coal processed per cycle relative to a fixed amount of stainless steel wools packed in the separator matrix, a reduction of the unit cost by about 15% can be achieved. This result shows the importance of the separator matrix loading characteristics on the costs of magnetic desulfurization. Another factor which affects the unit costs considerably is the washing time required in a complete separation cycle. This can be illustrated by comparing items 4 and 6 in Table 3. In particular, the computed results indicate

that doubling the amount of washing water required only leads to a negligible increase (0.27 to 0.60 %) in unit costs. However, if both the amounts of washing water and the washing time are doubled, the unit costs are increased by about 15%. The above observations clearly suggest the important economic incentive for further pilot-scale investigations of the separator matrix loading and washing characteristics in the magnetic desulfurization of coal/water slurry. Finally, item 7 of Table 3 shows that labor cost seems to be a significant fraction of the unit cost. Fortunately, it is not expected that the labor requirement is to be doubled in actual commercial practice from the nominal case in Table 2. This follows because the existing experience in the commercial cleaning of kaolin clays by the HGMS indicate that the labor requirements in both operation and maintenance are minimum (9,23).

In Table 4, the estimated costs of magnetic desulfurization are expressed in terms of the capital and unit costs per ton coal processed annually, and compared with the results of this study. The costs given by Murray (21) were based on the existing cost estimates for kaolin beneficiation by the HGMS given in reference 9. At a residence time of 0.5 minute, the coal feed rate to a commercial HGMS unit of a separator matrix of 7-foot diameter and 20-inch length was set at 100 tons per hour by Murray. This rate appears to be higher than that expected in the commercial practice. In addition, the costs of labor and maintenance per HGMS unit were estimated by Murray to be 1 and 2 \$ per hour, respectively. These costs also appear to be lower than those reported in reference 9. Consequently, the costs estimated by Murray shown in Table 4, especially the unit cost U_0 (0.37\$ per ton processed annually), are believed to be lower than the actual costs. Next, while the costs estimated by Oder (24) seem to be relatively comparable to those obtained in this study, it appears to be difficult to identify clearly the differences in both estimates. This follows because the specific details regarding the costs of major installed equipments, cycle time, and washing time, etc. were not reported in reference 24. Finally, the costs estimated by Trindade (31) are also believed to be lower than the actual costs. Note that in the cost estimation by Trindade, the Carousel separator was taken as the desired HGMS unit, although there have not yet been any testing data reported on the magnetic desulfurization of coal/water slurry using the Carousel separator. Only the separator cost was included as the capital cost in the analysis by Trindade, and it was about one-half of the cost of installing an equivalent cyclic HGMS unit. This led to the relatively low capital investment per ton coal processed, 0.82 to 1.64 \$, estimated by Trindade as shown in Table 4. It may also be noted that the cost estimation method used by Trindade will generally lead to lower unit costs. For instance, by using Trindade's method, the unit cost U_0 obtained in this work at a slurry velocity of 2.61 cm/sec shown in Table 4 will be decreased from 1.06 to 0.85 \$ per ton coal processed annually.

An approximate comparison of estimated capital and unit costs of different pyritic sulfur removal processes currently under active developments (1,4,15,33) is given in Table 5. With the exception of the MAGNEX process (15), all the approaches listed in Table 2 are wet processes, thus requiring relatively comparable dewatering and drying costs. This table indicates that the costs of wet magnetic desulfurization by the HGMS apparently appear to be attractive when compared to those of other approaches, even after adding the necessary costs of grinding, dewatering and drying. However, it should be emphasized that the above comparison is only an approximate one, because of the difference in the methods used in estimating the costs and in the desulfurization characteristics reported, etc. Based on the available cost information on these pyritic sulfur removal processes (1,4,15,33), it is not yet possible to carry out a rigorous comparison.

MAGNETIC DESULFURIZATION OF LIQUEFIED COAL: PROCESS AND COSTS

A flow diagram for the conceptual process for removing the mineral residue from the liquefied SRC by the HGMS is shown in Figure 3. The HGMS unit used here is the same commercial separator employed in the desulfurization of coal/water slurry. The magnetic desulfurization of the liquefied SRC is to be conducted at elevated temperature to reduce the viscosity of the coal slurry. Furthermore, the packed stainless steel

wool matrix is also to be heated up to the desired separation temperature during operation. The elevated temperature in the matrix will prevent the coal slurry from congealing and plugging the matrix. It is also necessary to insulate the heated portion of the matrix from the magnet windings. The insulated matrix is further surrounded by a water jacket. These provisions for heating, insulating and cooling the separator matrix slightly reduce the actual working volume of separator matrix from 7-foot to 6'10" in diameter. In actual separation runs, the unfiltered liquefied SRC is pumped through the energized separator at a constant flow rate until the separator matrix reaches its loading limit. After rinse with a process generated solvent, the matrix is backwashed with the same solvent with the magnet de-energized. The mags are sent to a hydroclone separator. The overflow from the hydroclone is recycled back to the wash solvent tank for re-use; while the underflow is sent to an evaporator to recover the solvent, and the residual solids are packed for other uses. The tails from the separator are sent to a vacuum column to recover the solvent for process recycle and the vacuum bottom is sent to a product cooler to produce the solidified SRC.

The conceptual process is designed to achieve the same extents of inorganic sulfur and matrix loading observed by HRI for slurry velocities varied from 0.25 to 14.0 cm/sec (8). The specific magnetic desulfurization characteristics corresponding to those slurry velocities are summarized as the first three rows of Table 6. Note that according to the survey of the sulfur reduction potential of 455 U.S. coal samples conducted by the Bureau of Mines, the average total and inorganic sulfur contents are 3.02 and 1.91 Wt%, respectively (3). Thus, if the hydrogenation step in the SRC and other related liquefaction processes can remove 70% of the organic sulfur, a reduction of the inorganic sulfur content by about 67% after the hydrogenation will be sufficient for producing a SRC with an emission level smaller than 1.20 lb SO₂/million Btu, assuming that the SRC has a heating value of 16,000 Btu/lb. By using the same method for cost estimation summarized in Table 1 with the exception of replacing the dispersant by steam with a nominal cost of 2\$/1000 lb, the estimated capital investments and unit costs for the conceptual process are presented in Table 6. Here, the costs of majored installed equipments have included those of the HGMS unit, wash solvent tank, feed surge tank, feed pump, flush pump and evaporator, etc. In Table 7, the effect of steam price on the unit cost U₀ of magnetic desulfurization of liquefied coal is illustrated. It is seen that doubling the steam price will increase the unit cost U₀ by 3 to 32% in the range of slurry velocities considered. As steam is mainly used in the process in conjunction with the evaporator for recovering the wash solvent, this comparison also implies that the higher the process throughput, the more expensive will be the operating cost for solvent recovery. Finally, an approximate comparison of the capital investments and unit costs of several solid-liquid separation methods, including precoat filtration, centrifugation, solvent precipitation and HGMS, is given in Table 8 (2). This table shows that although the precoat filtration and the solvent precipitation can generally meet the stringent environmental standards for both sulfur and ash, the costs of these methods are more expensive than those for the HGMS. Thus, there seems to be some economic incentive for using the magnetically cleaned SRC as a feed to boilers which already have electrostatic precipitators. Obviously, additional development work is needed to firmly support this observation.

CONCLUSIONS

In this paper, the latest data from pilot-scale studies of sulfur and ash removal from both pulverized coals suspended in water slurries and liquefied SRC coal by the HGMS have been used to design conceptual processes for the desulfurization. Estimates of magnetic desulfurization characteristics and conceptual process requirements, as well as installation and processing costs have been determined. The results indicate that the magnetic desulfurization appears to be attractive when compared to other approaches for the desulfurization, in terms of costs and performance.

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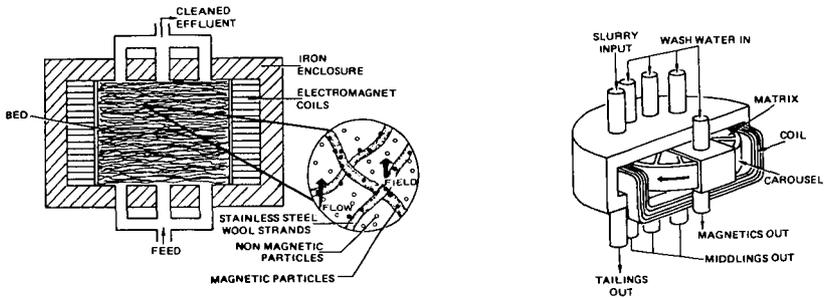


Figure 1 (a) Cyclic High Gradient Magnetic Separator (Left)
 (b) Carousel High Gradient Magnetic Separator (Right)
 (Taken from Reference 25)

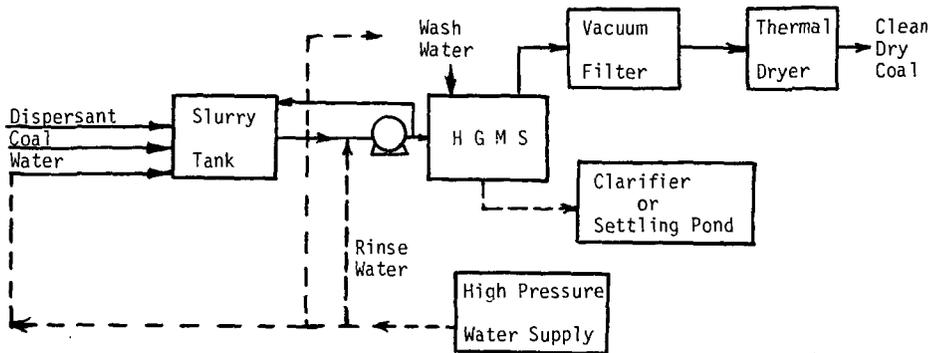


Figure 2. Desulfurization of Coal/Water Slurry by H G M S.

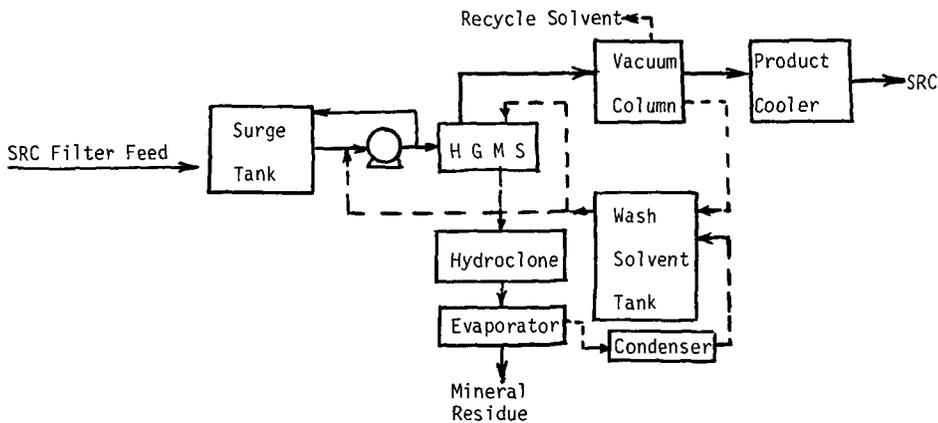


Figure 3. Desulfurization of Liquefied Coal by H G M S.

Table 1
 Basis for Estimating the Unit Costs of
Magnetic Desulfurization of Coal/Water Slurry (2,5,6,11)

A. Investment Costs:

1. Costs of Major Installed Equipments:
 HGMS unit, pump, tank, etc.

2. Add 20% Contingency
 Total Investment, I \$

B. Operating Costs:

1. Dispersant (57¢/lb)
 2. Electric Power (2¢/KWH)
 3. Water (3¢/1000gal)
 4. Operating Labor (men/shift x 8304 man-hours/year x 6.5\$/man-hour)
 5. Maintenance Labor (1.5% of investment cost)
 6. Supervision (15% of operating and maintenance labor costs)
 7. Operating Supplies (30% of operating labor cost)
 8. Maintenance Supplies (1.5% of investment cost)
 9. Local Taxes and Insurance (2.7% of investment cost)
- Annual Net Operating Cost, N \$
 Coal Processed Annually, G tons

C. Unit Costs (\$/ton coal processed annually):

1. Based on 0% DCF Rate of Return, $U_0 = (N+0.05I)/G$
2. Based on 15% DCF Rate of Return, $U_{15} = (N+0.34749I)/G$
3. Based on Capital Amortization over
 20 Years at 10% Interest Rate, $U = (N+0.11746I)/G$

Table 2

Cost of Desulfurization of Coal/Water Slurry by HGMS
Using Separator Matrix of 7-Foot Diameter and 20-Inch Length

	<u>Case A</u>	<u>Case B</u>	<u>Case C</u>	<u>Case D</u>
1. Slurry Velocity, cm/sec	2.61	2.61	2.61	4.0
2. Slurry Concentration, Wt%	15	25	35	25
3. Coal Feed Rate, ton/hr	44.77	66.13	83.07	89.61
4. Cycle Time, minute	9.00	6.10	4.85	4.50
5. Duty Cycle, %	77.9	67.4	59.0	59.6
6. Tons of Coal Processed Per Cycle	403	403	403	403
7. Unit Costs, \$ Per Ton Coal Processed Annually				
U	2.083	1.401	1.109	1.067
U ₀	1.802	1.063	0.858	0.829
U ₁₅	3.676	2.479	1.967	1.880
8. Capital Investment Per Ton Coal Processed Annually, \$	6.93	4.69	3.73	3.53

Basis:

- (1) Amount of coal processed per cycle=7 times weight of stainless steel wool
- (2) Amount of rinse water required per cycle=1.5 times volume of separator matrix
- (3) Amount of wash water required per cycle=7 times volume of separator matrix
- (4) Velocity of rinse water=velocity of coal slurry
- (5) Washing time=1 minute
- (6) Time for energizing the magnet=0.5 minute
- (7) Labor required=2 men per shift
- (8) Amount of dispersant required=10 ppm

Table 3

Sensitivity Analysis of Unit Costs (\$ Per Ton Coal Processed Annually)
of Desulfurization of Coal/Water Slurry by HGMS

	U_0		U_{15}	
	\$	%Change	\$	% Change
1. Basis: 2.61 cm/sec, 25 Wt% slurry, and other conditions in Tables 1-2.	1.0628	0.00	2.4117	0.00
2. Amount of Coal Processed Per Cycle Doubled	0.9004	-15.28	2.0341	-15.66
3. 25% Reduction in Capital Investment	0.9389	-11.66	1.9506	-19.12
4. Amount of Washing Water Required Doubled (Washing Time Unchanged)	1.0691	+0.60	2.4181	+0.27
5. Cost of Water Increased 5/3 Times (5¢/1000gal)	1.0835	+1.95	2.4324	+0.86
6. Both Amounts of Washing Water and Washing Time Doubled	1.2256	+15.32	2.7883	+15.62
7. Labor Requirement Doubled	1.3587	+27.82	2.7077	+19.12

Table 4

Comparison of Estimated Costs of Desulfurization
of Coal/Water Slurry by HGMS*

	<u>Murry (21)</u>	<u>Oder (24)</u>	<u>Trindade (31)</u>	<u>This Work</u>
1. Slurry Velocity, cm/sec	1.7-3.4	2	4	2.61 4.0
2. Slurry Concentration, wt%	30			25
3. Unit Costs, \$ Per Ton Coal Processed Annually				
U_0	0.37	0.70-0.25	0.39-0.84	0.22-0.45
U_{15}		2.47-0.93		1.06
4. Capital Investment Per Ton Coal Processed Annually, \$	2.02	5.95-2.28	1.64	0.82
				2.48
				4.69
				3.53

*Note: See text of the paper for further discussion.

Table 5

Approximate Comparison of Estimated Capital and
Unit Costs (\$ Per Ton Coal Processed Annually)
of Different Pyritic Sulfur Removal Processes

<u>Process</u>	(\$ Per Ton Coal Processed Annually)		
	<u>U₀</u>	<u>U₁₅</u>	<u>Capital Investment</u>
1. MAGNEX-Hazen Reserach, Inc. (15)	5.83	7.05	4.17
2. Froth Flotation- Bureau of Mines (15)	2.77	4.47	5.71
3. Meyers- TRW Systems and Energy (33)	6.00-14.00		13.80 (leaching only)
4. Ledgemont Oxygen Leaching- Kennecott Copper Corporation (1)	Comparable to Meyers		11.30 (leaching only)
5. HGMS-This Work, See Table 2	0.83-1.06	1.88-2.48	3.53-4.69

Table 6

Costs of Desulfurization of Liquefied Coal by HGMS
Using Separator Matrix of 6'10"-Diameter and 20"-Length

1. Slurry Velocity, cm/sec	0.25	1.60	2.71	2.71	5.42	14.0
2. Apparent % Pyritic Sulfur Removal	90	87	78	74	67.7	66.4
3. Cycle Time, Minute	45.86	9.15	5.84	11.33	4.32	2.39
4. Duty Cycle, %	85.8	74.9	66.3	82.6	59.8	33.5
5. Tons of Liquefied Coal Processed Per Cycle	22.52	24.71	23.63	57.21	31.48	25.25
6. Filtration Rate Based on Actual Filtering Time, GPM/ft ²	3.74	23.56	39.91	39.91	79.82	206.2
7. Unit Costs, \$ Per Ton Coal Processed Annually						
U ₀	6.58	1.45	1.10	0.76	0.67	0.61
U ₁₅	15.65	3.31	2.53	1.80	1.54	1.37
U	8.64	1.87	1.42	1.00	0.87	0.79
8. Capital Investment Per Ton Coal Processed Annually, \$	30.5	6.26	4.79	3.49	2.89	2.53

Table 7

Effect of Steam Price on the Unit Cost for Desulfurization of Liquefied Coal by HGMS

<u>Slurry Velocity, cm/sec</u>	<u>Unit Cost U₀, \$ Per Ton Liquefied Coal Processed Annually</u>		<u>% Increase from Case A to Case B</u>
	<u>Case A</u>	<u>Case B</u>	
0.254	6.580	6.600	3.0
2.71*	1.100	1.311	30.0
2.71**	0.763	0.850	11.0
5.42	0.670	0.836	25.0
14.00	0.614	0.811	32.0

Case A: Steam Price = 2 \$/1000 lb.

Case B: Steam Price = 4 \$/1000 lb.

* Amount of Liquefied Coal Processed Per Cycle = 23.63 Tons
=25.83 Times of Stainless Steel Wool Weight.

** Amount of Liquefied Coal Processed Per Cycle=57.21 Tons
=62.53 Times of Stainless Steel Wool Weight.

Table 8

Approximate Comparison of Capital and Unit Costs
(\$ Per Ton Liquefied Coal Processed Annually) of
Different Solid-Liquid Separation Methods (2)

<u>Method</u>	(\$ Per Ton Liquefied Coal Processed Annually)		
	<u>U₀</u>	<u>U₁₅</u>	<u>Capital Investment</u>
1. Rotary Drum Filtration (SRC)	2.77	8.10	17.89
2. Pressure Leaf Filtration (SRC)	7.03	9.87	9.52
3. Two-Stage Centrifugation* (H-Coal)	2.57	7.57	15.38
4. Solvent Precipitation (H-Coal)	1.82	3.98	6.70
5. HGMS*			
5.4 cm/sec	0.68	1.54	2.89
2.7 cm/sec	1.10	2.53	4.79

* The ash content of separated product may not satisfy EPA specification, and the use of electrostatic precipitators may be needed.

DRY TABLE - PYRITE REMOVAL FROM COAL

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INTRODUCTION

An awareness for particle segregations in material handling equipment is usually the result of negative experiences. Preventing demixing of a granular composite which is moving through bins, feeders, stockpiles, etc., generally leads to frustration. Three factors determine the extent of particle segregation in these situations,

- the physical configuration of the material handling equipment,
- the forces which convey the particles through that equipment,
- and the differences between the particles in one or more of their physical properties (size, shape, bulk density, resiliency and surface roughness).

The following described equipment, specifically designed as a separator for dry particulates combines the above factors to exploit this inherent segregation within moving particle beds.

EQUIPMENT DESCRIPTION

Figure 1 contains a perspective drawing of the Dry Table and a cross-section through the unit illustrating the particle bed. The drive unit for the table is an electro-mechanical exciter of the type used for vibrating feeders. In fact, this recently developed coal cleaning unit is a feeder, but with the following design differences.

- The deck surface is short but very wide.
- The coal is inserted at one side of the feeder's deck.
- The conveying force is reversed, it feeds the material into its backwall.
- The particle bed's net flow is from one side of the feeder to the other side.
- The deck is non-symmetrical about the vertical plane passing through its center of gravity and the exciter's line of drive.

Coal is fed onto the longest side of the unit and the conveying force from the drive moves the particles towards the backwall. A large pile of particles forms against the backwall, filling the entire trough. Gravity moves the particles on the pile's surface down the open slope as the conveying force continues to drive the underlying material against the backwall. The result is the continuous overturning of the bed. The pressure of the incoming feed forces the overturning bed to flow across the deck away from the feed side in a helical motion. And because the deck's length diminishes (tapers) in this direction, the toe of pile is being continuously discharged. Simultaneously, size and bulk density separations are occurring in the overturning bed. The large or low density particles move into a spiralling path that migrates towards the toe of the pile, Section A-A of Figure 1, whereas the small or high density particles move into a smaller spiral and concentrate towards the backwall. Those particles that are both large and of low density, coal, advance past the large and high density particles, rock and pyrite, and prevail in obtaining positions at the toe of the pile. Also small particles of pyrite will concentrate at the backwall in preference to small particles of coal.

The overall resulting discharge from the horizontal deck portion of the unit is a series of staggered particle size gradations of different densities. To avoid this overlapping of the size gradations of the rock and pyrite with the coal, the feed to the unit is presized to definite size ranges. For the coal, rock and pyrite separation, the usual top size to bottom size of the feed particles in any one pass is a 4 to 1 ratio (8" x 2", 2" x 1/2", etc.), the rock-coal size gradations are usually controlling this ratio.

The particles discharge from the nearly horizontal deck onto an attached downward sloping surface referred to as the "discharge lip". This "lip" can make further separations based on particle shape, resiliency and surface roughness if desired. The shape separation is based on the cubical coal particles being unstable on the "discharge lip" and the near tabular rock and pyrite particles being stable when

the unit is vibrating. The unstable coal will thus be discharged by rolling off the "lip" while the tabular rock and pyrite are conveyed back up the lip into the pile. The surface roughness of the highly mineralized particles is greater than that for the clean coal particles. This additional roughness aids in conveying the rock and pyrite back into the deep particle bed; whereas, the slick coal tends to slip off the "lip". Generally, the resiliency of the coal is greater than that of the rock particles. The conveying vibrations causes the more resilient coal particles to bounce and assure their unstability on the "discharge lip".

The Dry Table has a discharge similar in character to that of a wet concentration table in that it is a gradation from a clean coal product through mineralized particles to pyrite along the discharge edge. This dry method of separation is functional over a broad span of particle sizes. The limiting factor for the minimum size particles is the formation of particle agglomerations due to electrostatic charges or surface moisture. No limiting factor has been encountered for the maximum size particles. The present practical range in coal preparation is 1/8" to 8".

The majority of the Dry Table experience is in the reduction of the ash content of coals. However, there has been a recent increase of inquiries into the use of the Dry Table as a method for sulfur reduction.

EXPERIMENTAL SECTION

Runs were made with the following described samples by passing them through the 12" lab unit or the 8' pilot plant unit Dry Table in one pass and collecting the discharge as multiple products. In Figure 1, an eleven product discharge is shown, "A" through "K", where the discharges are of equal increments spaced along the "discharge lip". Each discharge product was analyzed for ash, pyritic sulfur and BTU content, following the accepted ASTM methods D-271 and D-2492. The analytical results were used to construct the distribution curves shown in the graph. The coal samples used are a cleaned New Mexico Bituminous Coal and a raw Arizona Subbituminous Coal. Both samples were screened to a 4:1 size range prior to running on the Dry Tables.

RESULTS

The data for the Bituminous and Subbituminous examples are shown in Graph I, "Dry Table Discharge Distribution". The horizontal axis for both the upper and lower portions of the graph represents the discharge from the Dry Table as the eleven discharge products. In the upper portion, the vertical axis gives the recovery as a percentage of the original feed for heating content (BTU), ash and pyrite. The clean coal product is the accumulation of discharge products starting at the far left (percentage on left vertical axis) and the reject starts on the far right (right vertical axis). The data points plotted on the graph are for a run which had an eight product discharge. In the lower portion of the graph, separate curves are plotted for Product and Reject which shows the distribution for the pyritic sulfur as pounds per million BTUs. The composition of the feeds are:

	Bituminous	Subbituminous
BTU/lb	13,460	8,060
Ash, %	10.1	25.8
Pyritic Sulfur, %	0.44	0.19

DISCUSSION

As with all coal cleaning equipment, the performance is a function of the coal being cleaned. The Dry Table is no exception to this and can even be considered more sensitive because it uses as many as five of the particles' physical properties for separation rather than just the density alone. Also affecting the separation is the degree to which the major constituents of the raw coal (clean coal, rock and pyrite) are liberated, one from the other. The performance of the Dry Table is based on the probability of particle movements. Therefore, the proportion of mineralized particles removed is constant for any specific coal feed over a wide range of compositions.

The pyrite in the two examples selected for this discussion is unliberated and of relatively low concentration. The lettered discharge products "A" through "K", are divisions of the Dry Table's discharge arbitrarily selected for analytical and discussion purposes. The large number of product divisions, or their specific boundaries need not be used in actual coal cleaning applications.

Subbituminous coal. The only preparation this coal received prior to being fed to the Dry Table was the presizing into 4:1 size ranges. The sequence of the distribution curves, upper Graph 1, show that in this three component system, clean coal (BTU) - rock (ash) - pyrite, the major separation is between the clean coal and the rock. The pyrite-ash separation is reversed to what would be expected for the more dense pyrite, which further demonstrates that the pyrite is not liberated. There are three zonal types of discharge from the Dry Table with this coal. In the first zone, product discharges "A" and "B", the coal contains low ash and has the pyrite mainly associated with the coal. In the second zone, product discharges "C" through "G", the coal contains low pyrite and ash but the pyrite is associated with the ash. In the third zone, product discharges "H" through "K", the discharge contains a coal and rock mixture where the pyrite is associated with both coal and rock at higher concentrations.

Selecting discharges "A" through "I" as a clean coal product, "J" and "K" as reject, gives a 90% recovery of the coal's potential heating content, and removals of 74% of the ash and 50% of the pyrite. The compositions of the Product and Reject are:

	Product	Reject
Yield, %	72	28
BTU/lb	10,360	2,160
Ash, %	10.8	64.1
Pyritic Sulfur, %	0.13	0.32

With the discharge split into just a clean coal product and a reject, the well known compromise must be made between recovering as much clean coal as possible while rejecting most of the rock and pyrite. With the Dry Table, however, it is possible to have as many products as found to be reasonable. Therefore, one could select the zone of low ash content "A" through "G" as the clean coal product and "H" through "J" for retreatment where there is a mixture of both rock and coal and "K" as the reject which essentially contains no usable heat.

	Product	Retreatment	Reject
Yield, %	47	37	16
BTU/lb	11,260	7,390	0
Ash, %	4.7	30.0	78
Pyritic sulfur, %	0.08	0.27	0.29

Both the clean coal "product" and the "reject" are desirable in this arrangement and its success depends upon the character of the "retreatment" discharge. In this particular case the "retreatment" is a mixture of clean coal and liberated rock with a small amount of middlings. The "retreatment" can be recycled through the same unit or sent to another unit for a second pass.

Bituminous. This coal is the product from a preparation plant, and therefore, there is essentially no liberated pyrite or rock present. The sequence of the curves shows that the unliberated pyrite is unevenly distributed among the coal particles and that the major separation is between the clean coal and pyrite. The ash and BTU curves are very similar, except for a slight difference in slopes, showing that there is a near constant inherent ash in the coal for the discharge products "A" through "H". The pyrite curve is quite different in shape and shows small amounts of pyrite in discharge products "A" through "D", increasing amounts in "E" to "J", and substantial quantities in "K". There are four zonal types of discharge for this particular separation. In the first zone, discharge products "A" through "D", the coal has a minimum ash and pyrite content. In the second zone, discharge products "D" to "H", the coal contains a minimum of ash, but has an increasing

pyrite content. In the third zone, discharge products "I" through "J", the ash and pyrite content progressively increase in the coal. In the fourth zone, discharge product "K", the coal is highest in both ash and pyrite, and contains all the misplaced "sink" material from the wet washing process.

The specific gravity difference between the first and second zones is quite small, so the separation is most likely caused by the other physical properties of the particles. Since the ash difference is also small, it is assumed that the presence of the pyrite is related to the physical property differences which the Dry Table can distinguish for separation purposes. The suggested method of processing is to collect the discharge from discharge products "A" to "H" as a clean coal product and "I" to "K" for retreatment.

	Product	Retreatment
Yield, %	75	25
BTU/lb	13,750	12,600
Ash, %	7.5	17.5
Pyritic sulfur, %	0.22	1.08

For this coal sample the "retreatment" discharge should not be processed as a second pass on the Dry Table because little benefit would be realized in ash and pyrite reduction. The best approach would be the recycling of this material to the wet preparation plant after crushing.

CONCLUSION

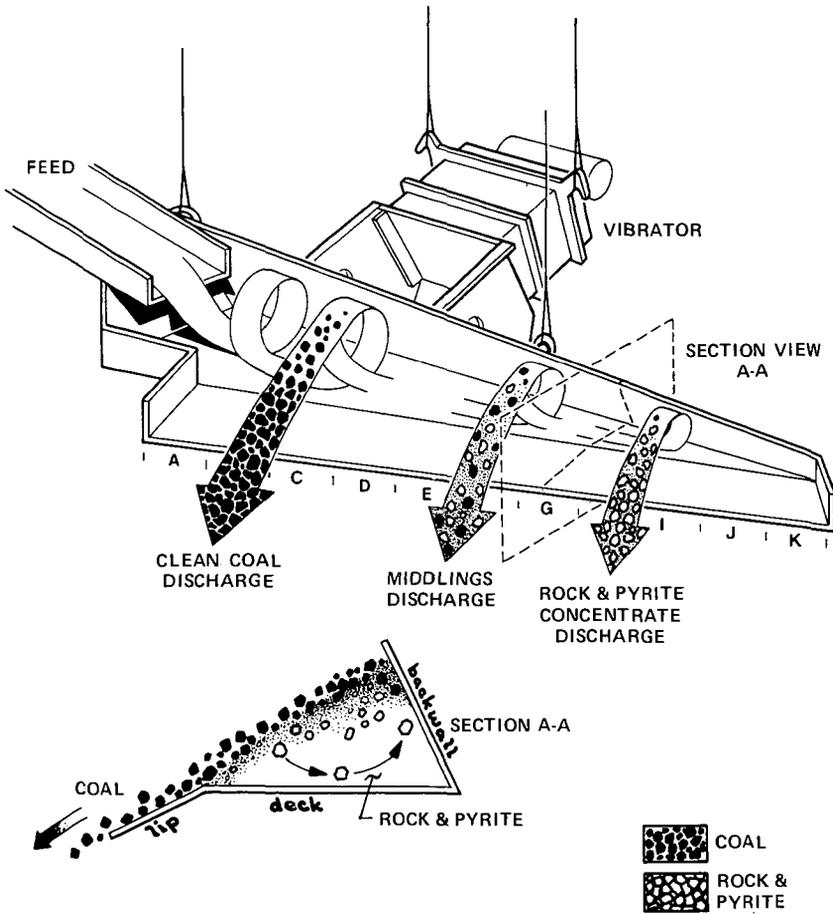
The Dry Table can reduce the sulfur content in a coal through pyrite removal. The extent of the coal-pyrite separation will be a function of pyrite liberation and the physical property differences between the free flowing coal and pyrite particles. However, there are cases where even coal containing unliberated pyrite can be separated into coal products of low and high pyritic sulfur contents.

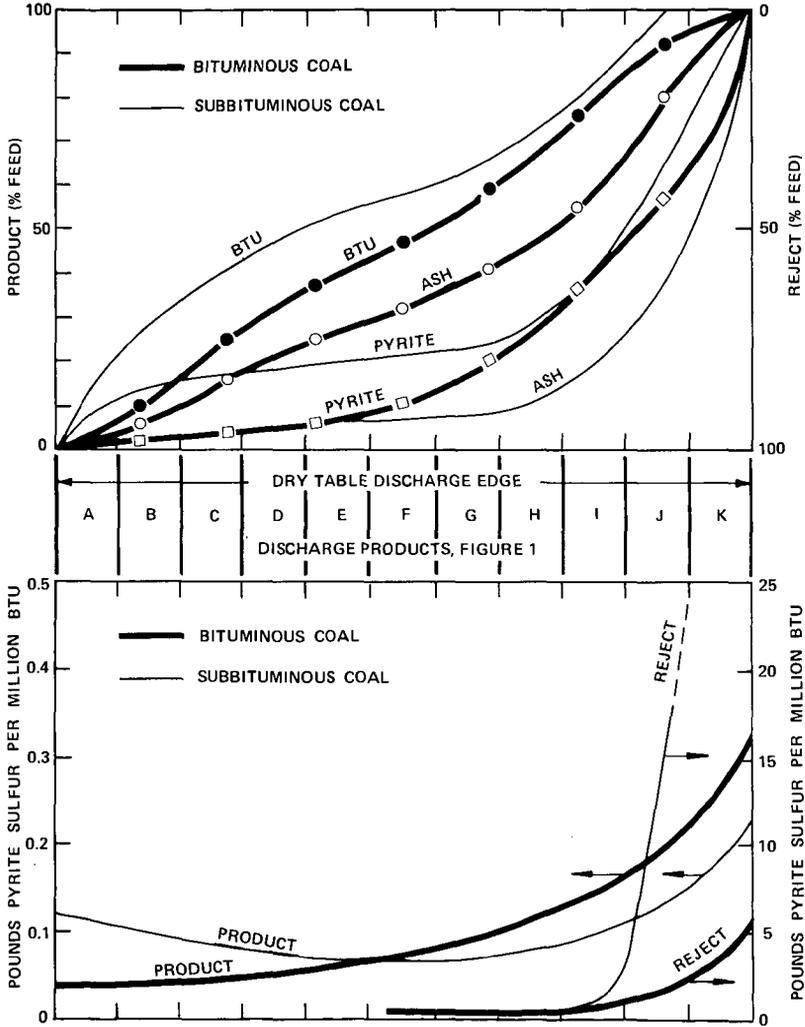
The Dry Table is best employed as a rougher, it has a separation performance similar to that of a Baum Jig. It can be used alone or in conjunction with existing coal cleaning equipment. And it is especially applicable where the use of water is restricted due to limited supply, freezing, or costly treatment prior to discharge or reuse.



FIGURE 1

DRY TABLE PRINCIPLE; SCHEMATIC VIEW





GRAPH I - DRY TABLE DISCHARGE DISTRIBUTION

"The Synthesis of Light Hydrocarbons from CO and H₂ Mixtures over Selected Metal Catalysts"

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INTRODUCTION

The synthesis of hydrocarbons and oxygen containing organic chemicals by reaction of CO and H₂ over catalysts has been investigated extensively in the past. This work is summarized in a number of review papers (1-4). More recently a number of workers have been active in investigation of these reactions (5-9). In this extensive previous literature no particular emphasis was given to the preferential production of lower molecular weight hydrocarbons. Mostly the previous work has been concerned with the formation of methane and C₅ hydrocarbons and oxygenated derivatives. There is an exception to this in the extensive work done in Germany on isobutylene production in the Isosynthesis Process (10).

It, therefore, was thought to be worthwhile to reinvestigate the possibilities for the specific production of C₂-C₄ materials with de-emphasis on the production of CH₄ and C₅ substances or their elimination as products, if possible. This route might open up new sources of C₂-C₄ hydrocarbons for use in the important petrochemical industry which in recent years has been moving in the direction of heavier feed stocks to meet the demands for ethylene, propylene and C₄ hydrocarbons (11).

This paper is a first of a series of publications from this laboratory on the production of C₂-C₄ hydrocarbons from CO/H₂ mixtures and deals with exploratory research on a variety of known Fischer-Tropsch catalysts. Using the literature as a guide a number of catalysts were prepared and tested. Reaction conditions, temperature, pressure, gas flow rate and H₂/CO ratio of the feed gas were preliminarily investigated to select the most promising regime for study of the chosen catalysts. The catalysts chosen for testing were Fe, Co, Ni, Cu, and ThO₂. The catalysts preparation, testing procedures and the results obtained are presented in this paper.

EXPERIMENTAL

I. Catalyst

The catalysts tested in these studies were prepared by coprecipitation and impregnation methods. Compositions of the catalysts are based on the quantities of metal salts used in the preparation assuming complete precipitation or in the case of impregnation, complete adsorption of the aqueous solutions used. More complete compositional analysis of the catalysts are now being done by analytical methods. Table (I) contains information on the catalysts tested.

II. Description of Catalyst Testing Equipment

The reactor flow diagram is shown in Figure 1. Carbon monoxide-H₂ mixtures prepared by Linde Speciality Gas Division of Union Carbide Co., were used. The H₂/CO ratios were 1/1, 3/2, 2/1, 7/3, and 3/1.

The reactor was made of 314 stainless steel tubing, one foot long having an outside diameter of 1 inch and an inside diameter of 0.5 inch. A 1-inch thick aluminum shield was placed around the reactor tube to insure even temperature distribution in the reactor. Catalysts were loaded in the middle section of the reactor tube and ceramic spacers were used before and after the catalysts bed. One thermocouple was used to measure the catalyst bed temperature and another thermocouple was used to measure the temperature of the aluminum shield. The thermocouple in the aluminum shield was connected to a temperature controller. There was less than an 0.5°C difference between the two measured temperatures when the reaction conditions

reached equilibrium.

The catalysts were oven dried at 110° C, ground to pass through a 200-mesh sieve and then tabletted into pellets. These pellets were later crushed to -14, +25 mesh size before loading in the reactor. The reaction variables were adjusted to the desired temperature, pressure, and input flow rate prior to sampling of products. Gas samples were taken at appropriate times and injected directly into chromatograph columns for analysis.

III. Analysis and Calculation of Results

A molecular sieve 5A column was used to analyze H₂, N₂, CO and CH₄. Silica gel was used to analyze H₂, CO₂ and C₂H₆. An activated alumina column with F.I.D. was used to analyze light hydrocarbons (12). A carbowax 1500-teflon column was used to analyze water and alcohols. An OV-17 column was used to analyze liquid hydrocarbons. Liquid condensate was captured in a cyclone separator and a room temperature collector. Reaction conditions were adjusted to minimize production of liquid hydrocarbons. At times small amounts were produced; these were recovered and analyzed. The C₅ fraction was analyzed using an activated alumina column as the G.C. oven was heated up to 370° C. These products came out in sequence of carbon atom number, the amounts decreasing with molecular weight.

Calculation of an accurate material balance was not possible since we did not have integrator equipment on the input flow. Consequently, all calculations are on an output basis. This will lead to small errors only since considerable care was taken to obtain complete recovery and accurate analysis on the product. Calculations of conversion and selectivities were done by computer on the basis of carbon atom balance. Water was collected as a liquid product but was not included in the conversion or selectivity calculations. At a later date water will be included in the analysis when material balances are possible.

CO conversions were calculated in the following manner:

$$X = \text{CO} + \text{CO}_2 + \sum_{i=1}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=2}^{10} i\text{C}_i\text{H}_{2i} + \sum \text{alcohols}$$

(all in the product gas)

$$Y = \text{CO}_2 + \sum_{i=1}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=2}^{10} i\text{C}_i\text{H}_{2i} + \sum \text{alcohols}$$

(all in product gas)

$$C_5^+ = \sum_{i=5}^{10} i\text{C}_i\text{H}_{2i+2} + \sum_{i=5}^{10} i\text{C}_i\text{H}_{2i}$$

$$\text{CO conversion \%} = \frac{Y}{X} \times 100$$

Selectivities for different product fractions are calculated as:

$$\text{CO}_2\% = \frac{\text{CO}_2 \text{ in product gas}}{Y} \times 100$$

$$\text{CH}_4\% = \frac{\text{CH}_4 \text{ in product gas}}{Y} \times 100$$

$$C_2-C_4 = \frac{C_2-C_4 \text{ in product gas}}{Y} \times 100$$

$$C_5^+ \% = \frac{C_5^+ \text{ in product gas}}{Y} \times 100$$

$$O/P = \frac{C_2H_4\% \times 2 + C_3H_6\% \times 3 + (1C_4H_8\% + 2C_4H_8\% + i C_4H_8\%) \times 4}{C_2H_6\% \times 2 + C_3H_8\% \times 3 + (nC_4H_{10}\% + i C_4H_{10}\%) \times 4} \times 100$$

$$R-OH\% = \frac{\Sigma \text{ alcohols in product gas}}{Y} \times 100$$

The composition analyses carried out and calculated as described are thought to be quite reliable. At the present state of development the reproducibility and accuracy of the results are estimated to be within $\pm 3-5$ units on the percentages given.

RESULTS AND DISCUSSION

While the literature dealing with carbon monoxide hydrogenolysis is quite voluminous on the metals we have chosen for study, it is difficult if not impossible to determine their relative effectiveness for the particular products of interest in our research. Also catalysts of interest for our purposes are all not commercially available so it was necessary to synthesize our own as well as use commercially available catalysts. Likewise, the literature of Fischer-Tropsch is a rough guide only in choice of reaction conditions for our studies. It was necessary to carry out a number of preliminary studies to orient our program to suitable temperatures, pressures, H_2/CO ratios and flow rates. The synthesis is highly exothermic, consequently conversion rate must be adjusted so that temperature rise is not excessive in small catalyst bed. Temperature proved to be the most important variable influencing conversion and once the temperature range was set the ranges of the other variables were chosen not only for processing reasons but also for convenience in experimentation, handling of materials and minimizing the use of feed gases.

Iron Catalyst

Referring to Table II a number of conclusions are apparent. Iron catalysts after proper reduction and nitriding are very active for reduction of CO at the conditions chosen. Catalyst 26 was so active that the temperature of the catalyst rose to $260^\circ C$ instead of $225^\circ C$ which was intended at the beginning of the run. These catalysts give low methane production relative to C_2-C_4 and give the lowest CH_4/C_2-C_4 ratio of all the catalysts tested. The amount of CO disappearing to C_5^+ is also modest as is the production of R-OH. Notably outstanding for the iron catalysts is the high olefin/paraffin ratio of the C_2-C_4 hydrocarbon. The iron catalysts generally give high CO_2 yields. This was expected since iron is known to be a good catalyst for the water gas shift reaction. Iron catalyst 22 prepared by precipitation of the nitrate and containing copper as a promoter was not active at $225^\circ C$. However, it became quite active at $265^\circ C$ (Table III).

Catalysts 22 and 26 contain copper as a promoter, however, the activities and product distributions of these catalysts are comparable with iron alone on Kieselguhr (23) and sintered iron synthetic ammonium catalyst (ICI). The latter was very active and altogether gave the most favorable product distribution of all catalysts tested. The effect of copper on iron catalyst is not known at this time and is a subject for further work.

Table III gives further data on iron catalysts. Catalyst (ICI) was given two different reduction treatments. Pretreatment by reduction in H_2 at $550^\circ C$ followed by nitriding with NH_3 at $325^\circ C$ gives a catalyst which is more active than pretreatment with H_2 at $450^\circ C$ (temperature required for similar conversion was $25^\circ C$ higher than that for the same catalysts with pretreatment b). The important difference here is the step of nitriding in the pretreatment step. Such a step is known to make iron catalysts more active for Fischer-Tropsch synthesis (13,14).

Data in Table III for catalyst 22 shows the effect of temperature on catalyst activity. Whereas this particular iron catalyst was inactive at 225° C it becomes quite active above 265° C. Table IV shows the effect of on-stream time on catalyst 26. Activity appears to drop quite rapidly with time and after 10 hours was almost nil; however, raising the temperature to 250° C restored the catalyst to moderate activity. Treating the catalyst with H₂ at 450° C restores the catalyst to near its previous activity. The cause of activity loss while on stream and its restoration are not understood at present but this may have to do with blocking of the catalyst surface by high molecular substances which are produced in small amounts but which do not leave the catalyst surface at the temperature of reaction. This is the subject of further investigation.

Cobalt Catalyst

Catalyst 33 is a cobalt on γ -alumina catalyst prepared by coprecipitation of cobalt and aluminum nitrates with sodium carbonate. This catalyst had low activity compared with iron but could be brought up to appreciable activity by raising the temperature to 250° C. At this condition, this catalyst showed high methane and C₂ production with no alcohol formation. Still the activity for C₂-C₄ production was considerable and these products were better than 40% unsaturated. These results make cobalt an interesting metal for additional study.

Copper Catalyst

Catalyst 34 is copper supported on γ -alumina prepared in the same manner as the cobalt catalyst. Copper has low activity and the principle product is R-OH, mostly methanol. This was as expected and it was also expected that copper would show CO₂ formation since it is an important component of low temperature water gas shift catalysts (15). Even though water was there as a product, copper showed no CO₂ formation. This is an interesting finding and should be studied further.

Nickel Catalyst

Catalyst K6 is a γ -alumina supported nickel catalyst prepared by precipitation as with previous copper and cobalt catalysts. This particular catalyst formulation contained copper as well. It is well known that nickel is an excellent methanation catalyst. Consequently, we have not yet examined nickel by itself in our treating program. Copper was found to alter the catalytic properties of cobalt in a favorable way for our purposes so a corresponding catalyst of nickel-copper was investigated. The data in Table II show this catalyst to have low activity requiring 275° C to show 18% conversion of the CO. Carbon dioxide formation indicates strong water gas shift tendency. Copper does not appear to be present as copper metal since no alcohol was formed.

Cobalt-Thoria

This catalyst K1 was prepared by a method given in the literature (16). Cobalt and thorium as nitrates were coprecipitated with ammonium carbonate solution and to the resulting slurry Kieselguhr was added. This mixture was then dried and pelleted. It was found to be highly active and produced high yields of paraffins particularly CH₄ and C₅-C₃₀ long chain hydrocarbons. The C₂-C₄ hydrocarbons were mostly saturated. This was expected based on data in the literature (16).

Ruthenium Catalyst

A catalyst based on this metal has not yet been tested. Literature data indicate that such a catalyst is likely to yield CH₄ and C₅ high molecular weight paraffins. It will, however, be tested under our conditions and reported later.

CONCLUSIONS

Catalysts based on iron and cobalt appear to have the most potential for synthesizing C₂-C₄ hydrocarbons. Future work will be concentrated on improving the selectivity and stability of iron catalysts. Additional effort is also indicated for cobalt and possibly nickel to improve selectivity. Some work is also planned on the mechanism of CO₂ production.

The water gas shift appears to be an important reaction between CO feed and water produced in the reaction. Additional effort is indicated to determine the activity of our catalysts for this reaction, and the role this reaction plays in our synthesis. Other types of catalytic metals and different supports will also be investigated in future work.

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TABLE I
Composition and Treatment of Catalysts Studied

Wt-pct (f)	ICI	22	23	26	33	34	K6	K1
Fe ₃ O ₄	1/ 94.0	2/ --	2/ --	2/ --	3/--	3/ --	4/ --	4/ --
Fe	--	79.3	52.2	59.4	--	--	--	--
Cu	--	19.7	--	29.3	--	18.4	12.8	--
Co	--	--	3.9	--	14.7	--	--	49.2
Ni	--	--	--	--	--	--	13.7	--
CaO	2.0	--	--	5.9	--	--	--	--
MgO	0.3	--	--	0.9	--	--	--	--
Al ₂ O ₃	2.5	--	--	3.7	85.3	81.6	73.5	--
SiO ₂	0.4	--	--	--	--	--	--	--
K ₂ O	0.8	1.0	1.0	0.8	--	--	--	--
Kieselguhr	--	--	42.9	--	--	--	--	43.1
ThO ₂	--	--	--	--	--	--	--	7.7

1/ Pretreatment a, e, b

2/ Pretreatment a, e

3/ Pretreatment c

4/ Pretreatment d

a Reduced in H₂ at 550^o C for 20 hr; then nitrided in NH₃ for 6 hr

b Reduced in H₂ at 450^o C for 20 hr

c Reduced in H₂ at 500^o C for 4 h4.

d Calcined in air at 520^o C for 4 hr, then reduced in H₂ at 275^o C for 4 hr

e Regenerated in H₂ at 500^o C for 20 hr

f Compositions of catalysts are based on the calculated quantities of each metal salt taken for preparation.

TABLE II

Operating data on catalysts tested

Catalyst	Fe 23	Fe 22	Fe 26	Fe IC1	Co 33	Cu 34	Co ₂ O ₃ K1	CuNT K6
Pretreatment*	a	a	a	a	b	b	c	c
Temp, C	225	225	260	225	250	275	225	275
Pressure, psig	750	750	750	750	750	750	120	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	1.54	0.77	0.77	0.6	0.77
H ₂ /CO	1/1	1/1	1/1	2/1	2/1	2/1	7/3	7/3
CO conversion, %	57.6	0.9	94.7	89.4	16.96	11.57	84.0	18.3
Product selectivity, %								
CO ₂	51.6	0.0	64.7	39.4	5.3	0.0	7.0	63.1
CH ₄	15.8	25.9	8.3	11.7	34.0	11.6	32.0	24.4
C ₂ -C ₄	18.7	51.6	17.5	24.8	27.4	5.3	12.0	9.7
C ₅ ⁺	10.3	22.5	8.7	22.0	33.3	1.2	49.0	2.8
R-OH	3.6	0.0	0.8	2.1	0.0	81.9	--	0.0
O/P	2.0	2.2	1.3	2.9	0.77	0.44	0.14	0.06
Pretreatment*								
a Reduced in H ₂ at 550° C for 20 hr nitrided in NH ₃ , 325° C for 6 hr								
b Reduced in H ₂ at 520° C for 4 hr								
c Calcined in air-520° C for 2 hr reduced in H ₂ at 275° C for 4 hr.								

TABLE III
Effect of pretreatment and temperature of reaction for commercial
iron catalyst

	ICI-35-4		22		
	a	b	a	a	a
Pretreatment					
Temp, ° C	225	250	225	265	250
Pressure, psig	750	750	750	750	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	0.77	0.77
H ₂ /CO	2/1	1/1	1/1	1/1	1/1
CO conversion, %	89.4	75.9	0.9	47.7	20.7
Product selectivity, %					
CO ₂	39.4	57.9	0.0	54.3	50.0
CH ₄	11.7	2.5	25.9	8.5	8.1
C ₂ C ₄	24.8	21.5	51.6	22.2	23.1
C ₅ ⁺	22.0	18.1	22.5	12.1	17.3
R-OH	2.1	0.0	0	2.9	1.5
O/P	2.90	4.65	2.2	1.62	1.5

a Reduced in H₂ 550⁰ C, for 20 hr, nitrided in NH₃, 325⁰ C for 6 hr

b Reduced in H₂ at 450⁰ C for 20 hr

TABLE IV
Effect of On-Stream Time and Regenerability of Iron Catalyst

Catalyst	Fresh 26*			Regenerated with H ₂ at at 450° C. for 20 ² hr		
Hr on stream	0.5	5.0	6.0	21**	0.5	4.0
Temp, ° C	260	220	220	250	225	225
Pressure, psig	750	750	750	750	750	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	1.54	1.54	0.77
H ₂ /CO	1/1	1/1	1/1	1/1	1/1	1/1
CO conversion, %	94.7	54.9	35.6	38.3	57.0	46.4
Product selectivity, %						
CO ₂	64.7	46.0	45.3	39.3	52.8	44.8
CH ₄	8.3	11.5	9.1	4.9	10.9	5.0
C ₂ C ₄	17.5	19.0	18.4	15.7	17.7	20.7
C ₅ ⁺	8.7	22.3	25.9	31.8	18.6	29.3
R-OH	0.8	1.2	1.3	8.3	0.0	0.2
O/P	1.24	3.33	3.81	3.63	2.8	3.8

* Reduced in H₂ at 550° C 20 hr, nitrified in NH₃ for 6 hr (#26).

** Catalyst run discontinued at 10 hr left standing at 220° C in helium overnight; at hr 21 in the cycle the temperature was increased to 250° C

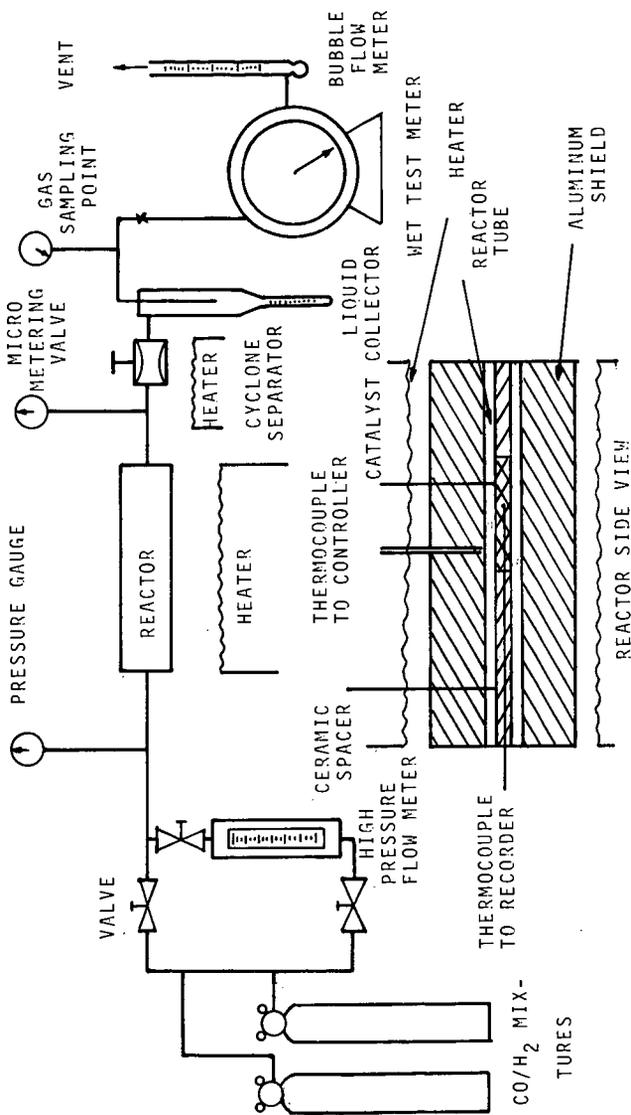


FIGURE I.- Reaction System Flow Diagram and Reactor Side View

"Studies on the Co-Cu-Al₂O₃ Catalyst System for
Conversion of CO and H₂ to Light Hydrocarbon Products"

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INTRODUCTION

Past research efforts on synthesis of hydrocarbons from CO and H₂ have been primarily devoted to two areas: synthesis of liquid hydrocarbons and production of methane (1). Early work was done mainly by Fischer, Tropsch and others in Germany. These researchers tested possible metal compounds in H₂/CO synthesis gas mixtures and they found that compounds of ruthenium, iron, nickel and cobalt were effective under various reaction conditions. They found that iron was the most effective catalyst for formation of liquid hydrocarbons when it was used under medium pressure reaction conditions (2). Recent methanation research showed that nickel was more selective for methane than cobalt, the latter producing more C₂⁺ for the same conversion of CO (3).

Light hydrocarbons can also be produced in the Fischer-Tropsch process (4). CO and H₂ synthesis gas can be produced from coal with existing technology (5,6). By choosing an appropriate catalyst, CO and H₂ can then be used to produce light hydrocarbons as raw materials for the petrochemical industry.

In a previous paper, extensive studies of different catalysts for the conversion of CO and H₂ to light hydrocarbons were reported (7). Among others, a catalyst consisting of cobalt and copper supported on alumina was found to be promising for achieving the above-mentioned objective. In this paper, we report additional studies on this catalyst system. Work included catalyst characterization and testing of various catalyst formulations.

EXPERIMENTAL

The catalysts employed in this study were prepared by a co-precipitation technique. A hot solution of Na₂CO₃ was added to a hot solution of the nitrates of Co, Cu and Al dissolved in distilled water. The precipitate was filtered, washed and finally dried in an oven at 110°C. It was then ground to pass 200 mesh sieve, pelleted, reground and finally sieved, the fraction 14-25 mesh being retained for charges to the catalytic reactor.

In some formulations cupric chloride was used and in others (NH₄)₂CO₃ or NH₄OH was used in the preparation. In two of the latter preparations, Na was added to the oven-dried catalyst by impregnation. A listing of the catalysts is presented in Table I.

Catalyst analyses for Co and Cu were made by a spectrophotometric method. This consisted in dissolving the oven-dried catalyst in concentrated HCl and measuring the solution absorbance for Co at 690 nm and for Cu at 380 nm. Standard solutions were prepared for calibration purposes.

Characterization of a number of catalysts was carried out in a flow micro-balance (8). These included measurement of degree of reduction and O₂ adsorption on reduced catalysts. The following sequence was adopted for this purpose:

- 1) Heat in H₂ flow to 450°C.
- 2) Switch to N₂ and cool to room temperature.
- 3) Switch to air and measure weight gain.
- 4) Switch to H₂ and heat to 450°C.
- 5) Switch to air and measure weight gain.

All steps except 3) were run until weight was constant. In step 3), a rapid weight gain was obtained followed by a slow continued gain; this step was terminated after 1/2 hour. The amount of O₂ adsorbed was taken at the break in the curve in step 3).

The amount of reduced metal was calculated from the weight gain in step 5), assuming complete oxidation of the reduced metal was obtained. Overall weight loss in going from the oven-dried state to the reduced state via step 1) was consistently very close to 50% loss for the catalysts tested.

The above sequence was varied to study the effect of reduction temperature and the effect of a low temperature (250°) hold prior to heating to the higher temperature. Also, some adsorptions in step 3) were determined at 0°C instead of room temperature; no difference in initial adsorption was obtained, but the small continued weight gain was suppressed at 0°C.

X-ray analyses were performed on several reduced samples after O₂ chemisorption. Average particle size was estimated by line broadening using the strongest Cu line. Electron microprobe was used to examine Co and Cu distributions in the catalyst. This was accomplished by forming a tablet of the crushed material which after subjecting to reduction, was sliced at the midpoint and carbon-coated. Selected areas were probed for Co and Cu concentrations.

Catalyst activities were measured in a fixed bed reactor. Details are given in the previous paper (7). Catalyst pretreatments were made in-situ in the reactor. Reactor feed consisted of mixtures of H₂ and CO. Product gases were analyzed by gas chromatography for H₂, N₂, CO, CH₄, C₂-C₄ hydrocarbons, C₅⁺ hydrocarbons and alcohols (predominantly CH₃OH). The C₅⁺ fraction consisted of hydrocarbons from C₅ to C₁₀ in decreasing amounts. Condensable liquid collected at room temperature was exclusively water, no measureable alcohols or hydrocarbons being detected.

CO conversion is defined as:

$$\text{CO Conversion} = \frac{\text{CO}_2 + \text{total hydrocarbons} + \text{alcohol}}{\text{CO} + \text{CO}_2 + \text{total hydrocarbons} + \text{alcohol}} \times 100$$

Hydrocarbon selectivities are defined as:

$$\%Y = \frac{Y}{\text{total hydrocarbons} + \text{alcohol}} \times 100$$

where Y represents C₁, C₂-C₄, C₅⁺ or ROH. All values are calculated on a carbon atom basis.

RESULTS

Catalyst Characterization

One CoCu formulation was examined to determine pretreatment conditions appropriate for reduction to the metal and to estimate metal areas. The results are presented in Table II, together with data on a Co catalyst and a Cu catalyst. All tests were carried out starting with oven-dried catalysts. Heating to 450° in H₂ was sufficient to essentially completely reduce the Cu and the CoCu catalyst to the metals; but the Co catalyst was only about one-half reduced under these conditions. Under comparable reduction conditions, the CoCu catalyst showed about a ten-fold larger O₂ chemisorption compared with either the Co or Cu catalyst. On a per gram reduced metal basis, these results translate into a three-fold increase over the Co catalyst and a five-fold increase over the Cu catalyst in surface metal area. A two-stage heating schedule gave larger metal areas (greater O₂ adsorptions) compared to a direct heat up to maximum temperature. This was especially marked at 500°.

Reoxidation of the reduced samples caused changes in metal dispersion. Thus, reduction of the reoxidized CoCu catalyst gave a five-fold loss in metal dispersion. A lesser loss was obtained for the Cu catalyst and no loss was observed for the Co catalyst. Evidently, reoxidation of the reduced catalyst caused sintering of the highly dispersed metal phase. Pretreatment with N₂ in place of H₂ at 450°, followed by reduction resulted in a much lower metal dispersion, being only slightly greater than the reoxidized sample. Also, total reduction was somewhat lower (79%). Assuming all the Cu had reduced, this corresponds to about 50% reduction of the Co,

close to that obtained with the Co catalyst. Evidently, N_2 pretreatment is equivalent to air oxidation in causing metal sintering and Co interaction with the support.

X-ray analyses of reduced samples exposed to air showed Cu metal to be the major component, with Cu_2O as a minor component. The amount of Cu_2O relative to Cu was greater for those catalysts which had high O_2 adsorptions and negligible for low uptake catalysts. This indicates some surface oxidation of Cu occurred during exposure to air. The Co catalyst contained appreciable amounts of $CoAl_2O_4$ in addition to Co metal, accounting for its incomplete reduction. On the CoCu catalysts, a separate Co metal phase was not detected by x-ray analysis.

Estimates of average particle size from x-ray line broadening generally agreed with the O_2 adsorption results. Although average particle sizes based on adsorption did not give good quantitative agreement with the x-ray values as seen in Table II, the trends are nevertheless in the same direction. Uncertainties in the exact stoichiometry of adsorption and possible oxidation beyond the monolayer probably account for these differences.

Electron microprobe examination of the CoCu catalyst showed the distribution of Co and Cu across the pellet to be quite inhomogeneous, with some areas high and others low in concentrations of metals. However, in general, Co and Cu were located in the same vicinity.

Catalyst Activity

A complete product analysis for a typical run is presented in Table III. Hydrocarbon products were predominately normal straight chain molecules, small amounts of isomers only appearing at high conversions. Generally, olefin/paraffin ratios were low for C_2 , about one for C_3 and low for C_4 compounds. The alcohol was exclusively methanol; small amounts of ethanol were only detected after prolonged reaction at high conversions.

Table IV shows the results of different pretreatments. The catalyst pretreated with H_2 at $520^\circ C$ was more active for converting CO than the catalyst air calcined at $520^\circ C$, then reduced in hydrogen at $275^\circ C$. The catalyst that was held in hydrogen at $225^\circ C$ for four hours, then at $520^\circ C$ for another four hours was even more effective. However, hydrogen at high pressure with the two-stage temperature schedule during the pretreatment had an adverse effect on conversion of CO. Different pretreatment methods did not have much effect on hydrocarbon product selectivities.

Table V shows that increased sodium on catalysts caused a decrease in CO conversion; however, the relationship between sodium content and CO conversion was not linear. The two percent addition of sodium had the largest effect on CO conversion. The product selectivities were likewise affected, alcohol decreasing and the C_5^+ fraction increasing with sodium content.

Catalysts prepared with $CuCl_2$ were less active than those with $Cu(NO_3)_2$. Table VI compares two pairs of otherwise identical catalysts. In both cases, the catalysts prepared from the chloride had lower conversions, and lower C_5^+ and ROH selectivities. However, they had higher CH_4 selectivities.

The effects of process variables on conversion were briefly studied with one catalyst formulation; the results are given in Table VII. Larger conversions were obtained at higher temperature and H_2/CO ratio, while pressure had little effect. Selectivity-wise, the following trends were observed: (1) increase in temperature - higher C_2-C_4 and C_5^+ and lower CH_4 and olefin/paraffin ratio; (2) increase in H_2/CO ratio - lower olefin/paraffin ratio; (3) increase in pressure - no effect.

The effect of catalyst composition was studied in some detail. Figures 1 and 2 give conversions and selectivities for one run condition. Other run conditions gave similar trends. Conversion was found to correlate best with total metal loading. Conversion reached a maximum at a total loading around 18%. Thereafter, conversion levelled off or decreased slightly with increasing metal content. Production of CO_2 appeared to be closely related to CO conversion. Hydrocarbon selectivities correlated best with metal ratio. At one extreme, the Co catalyst

produced a high percentage of CH₄ and no ROH. As the fraction of Cu increased, CH₄ decreased and ROH increased. Of significance, C₂-C₄ was higher over a wide range of catalyst compositions. The C₅⁺ fraction showed a similar trend. At the other extreme, the Cu catalyst gave high ROH with only a small percentage of CH₄ and C₂-C₄.

DISCUSSION

Catalyst Characterization

It is evident that Co and Cu interact during the prereduction step. The presence of Cu engendered reduction of the Co. The two together resulted in a much greater metal dispersion than each one separately. Sinfelt, (9) found a similar effect for RuCu and OsCu catalysts. Reoxidation caused appreciable sintering of the highly dispersed metals. Hence, air regeneration of aged catalysts would most likely cause a severe deactivation of the original catalyst activity.

The degree of dispersion was greatly affected by the pretreatment used. Oxidized and N₂ treated catalysts gave low metal dispersions after high temperature reduction, whereas direct treatment of the oven-dried catalysts with H₂ during heating gave much better dispersions. In the latter case, the heating schedule was important, viz., holding at 250° before subsequent high temperature heat-up resulted in even higher dispersions. Similar improvement in metal dispersion was found for Ni catalysts (10). Evidently, slow heating results in formation of small metals crystallites which are then stable at the higher temperatures. Increased metal dispersions were reflected in higher catalyst activities for CO conversion.

The increased dispersion found in H₂ pretreatment may be due to formation of an alloy phase or stable surface bimetallic clusters (11). The x-ray and electron microprobe results are in accord with this viewpoint. These states may be more stable towards sintering than crystallites of the individual metals. Further research along these lines is in progress and will be reported at a later date.

Catalyst Reactivity

Temperature had the most profound effect on catalyst activity and reaction path. Thus, at 250° and below, conversions were low and the major products were hydrocarbons and water; whereas at 275° and higher, conversions were high with formation of hydrocarbons and carbon dioxide. This is more or less typical of cobalt-containing Fischer-Tropsch catalysts (12).

At a given set of conditions, catalyst conversions increased with metal loading, as expected. However, the increase was not linear indicating that the amount of active metal surface area was not entirely proportional to the total metal present. Differences could reside in variations in degree of reduction and metal dispersion achieved for the various loadings. This is especially evident at the higher loadings, where conversions were found to tail off. The latter effect may be due to sintering of the basic metal crystallites to larger-sized particles.

The addition of copper as a promoter in Fischer-Tropsch catalysts was reported to facilitate reduction of the metal components, but not alter activity or selectivity (12). In addition to improving the reduction of Co, our CoCu catalysts also gave differences in selectivities. Thus, the Co catalyst gave selectivities relatively high in CH₄, low in C₅⁺ and no ROH; whereas, the Cu catalyst gave predominately ROH (Figure 2). In contrast, the CoCu catalysts gave moderate selectivities for CH₄ and C₅⁺ and low ROH. The significant selectivity improvement with the CoCu catalyst was in the C₂-C₄ range, which approached close to 50% of the hydrocarbon product. Although product selectivities changed somewhat with increase in Cu to Co ratio, the C₂-C₄ selectivity was relatively insensitive to this parameter. The major effect was to decrease the C₅⁺ and increase the ROH selectivities.

The addition of sodium to the catalyst had a depressing effect upon conversion. In addition, the C₅⁺ selectivity increased while the ROH decreased. Sodium

addition to a Co:Cu (9:1) catalyst was reported to be unfavorable (13), resulting in increased molecular weight of products and rapid catalyst decline. Since most of the catalysts were prepared using sodium carbonate as the precipitant, some sodium may have been retained by the catalysts after washing. Comparison of conversions (Figure 1) indicates that up to 1% Na may have been present in the normally prepared catalysts. It appears that the sodium-free catalyst is somewhat more active.

The use of CuCl_2 in place of $\text{Cu}(\text{NO}_3)_2$ in the preparation had an interesting effect on catalyst performance. A decrease in conversion was accompanied by a decrease in ROH selectivity, strangely parallel to the effect of added sodium. The reason for this effect is not known at present.

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Table I. Catalyst Compositions

No. ^a	wt. % ^b		Remarks ^c
	Co	Cu	
2	0	0	Al ₂ O ₃ only
3	8.5	0	
4	0	13.0	
5	7.8	11.0	
7	7.1	8.8	
10	5.1	4.0	(NH ₄) ₂ CO ₃ used
17	7.5	4.9	
18	8.1	16.1	
19	7.4	1.3	
33	7.3	0	
34	0	12.3	
37	9.8	8.1	
38	6.4	8.8	
42	5.5	15.5	
43	5.0	3.4	NH ₄ OH used
44	4.8	3.6	NH ₄ OH used, 2% Na ₂ O added ^d
51	5.6	3.9	NH ₄ OH used, 1% Na ₂ O added ^d

^aCatalysts above dotted line prepared with CuCl₂ and those below with Cu(NO₃)₂.

^bOven-dried basis

^cNa₂CO₃ used for precipitation except where otherwise noted.

^dImpregnation

Table II. Effect of Pretreatment on Metal Dispersions

Catalyst	Pretreatment ^a °C	Metal Reduced, %	Weight O ₂ Chemisorbed, b mg/g	Average Metal Particle Size, Å	Average Metal Particle Size, Å
				Adsorption	XRD ^d
2	-/450	0	0		
3	250/450	46	1.5(1.5) ^e		
4	250/450	94	2.5(1.5) ^e	130(220) ^e	90(150) ^e
5	250/450	96	19.0(3.5) ^e	25(140) ^e	50(100) ^e
5	250/400	-	22.0	20	30
5	-/400	-	16.5	30	40
5	250/500	-	24.0	20	40
5	-/500	92	10.8		
5	450 ^f /450	79	4.5	90	130

^aH₂ used; 2h hold at each temperature.

^bcatalyst charge basis (oven-dried).

^cbased on ratio of weights of O₂ chemisorbed to redox change assuming one O per metal site.

^dby x-ray diffraction line broadening.

^eafter high temperature oxidation-reduction cycle.

^fN₂ used.

Table III. Analysis of Reaction Products

<u>Component</u>	<u>Volume, %</u>	<u>Selectivity, %</u>
H ₂	55.3	
N ₂	0.18	
CO	22.6	
CO ₂	0.18	
CH ₄	3.06	46.0
C ₂ H ₄	0.021	}
C ₂ H ₆	0.135	
C ₃ H ₆	0.157	
C ₃ H ₈	0.178	
C ₄ H ₈	0.034	
C ₄ H ₁₀	0.108	28.4
C ₅ ⁺	0.30	22.3
ROH	0.22	3.3
H ₂ O	0.40	

CO Conversion % 23.2

CO₂, % 2.7

Olefin/Paraffin 0.53

Catalyst 38, 18.47 g charge

Reaction conditions: 235°, 750 psig, 3H₂/CO, 7.14 cc/sec

Table IV. Effect of Pretreatment on Conversion

Pretreatment ^a : Catalyst	CO Conversion, %			
	A	B	C	D
7 ^b	37	58		
38 ^c		17	38	16

^aPretreatments:

A - (1) air, 520°, 4 hr. (2) H₂, 275°, 2 hr., 5 psig.

B - (1) H₂, 520°, 4 hr., 5 psig.

C - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr., 5 psig.

D - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr. 60 psig.

^bReaction conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

^cReaction conditions: 250°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

Table V. Effect of Sodium on Catalyst Activity

Catalyst	43	51	44
Na ₂ O, %	0	1	2
CO Conv., % ^a	22	19	2
<u>Selectivity</u>			
C ₁	36	37	37
C ₂ -C ₄	36	40	33
C ₅ ⁺	18	21	30
ROH	10.	2	0

^aReaction conditions: 275°, 500 psig, 2H₂/CO, 0.77 cc/g sec.

Table VI. Effect of Copper Salt on Catalyst Activity

Pair	1		2	
	Catalyst	10	43	7
Cu salt ^a	Cl	NO ₃	Cl	NO ₃
CO Conv., % ^b	9	39	59	90
<u>Selectivity</u>				
C ₁	42	35	40	26
C ₂ -C ₄	45	38	41	42
C ₅ ⁺	13	19	18	26
ROH	0.2	8	2	6

^a Used in catalyst preparation

^b Reaction Conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec

Table VII. Effect of Process Variables on Conversion

Values are CO Conv., %

Temp., °C	235		250	
	H ₂ /CO	3/1	1/1	3/1
Pres. psig	750	34	13	77
	1000	41	10	37
			-	29

Catalyst 38, 0.38 cc/g sec

FIG. 1
 CATALYST CONVERSION VERSUS METAL LOADING - RUN 1

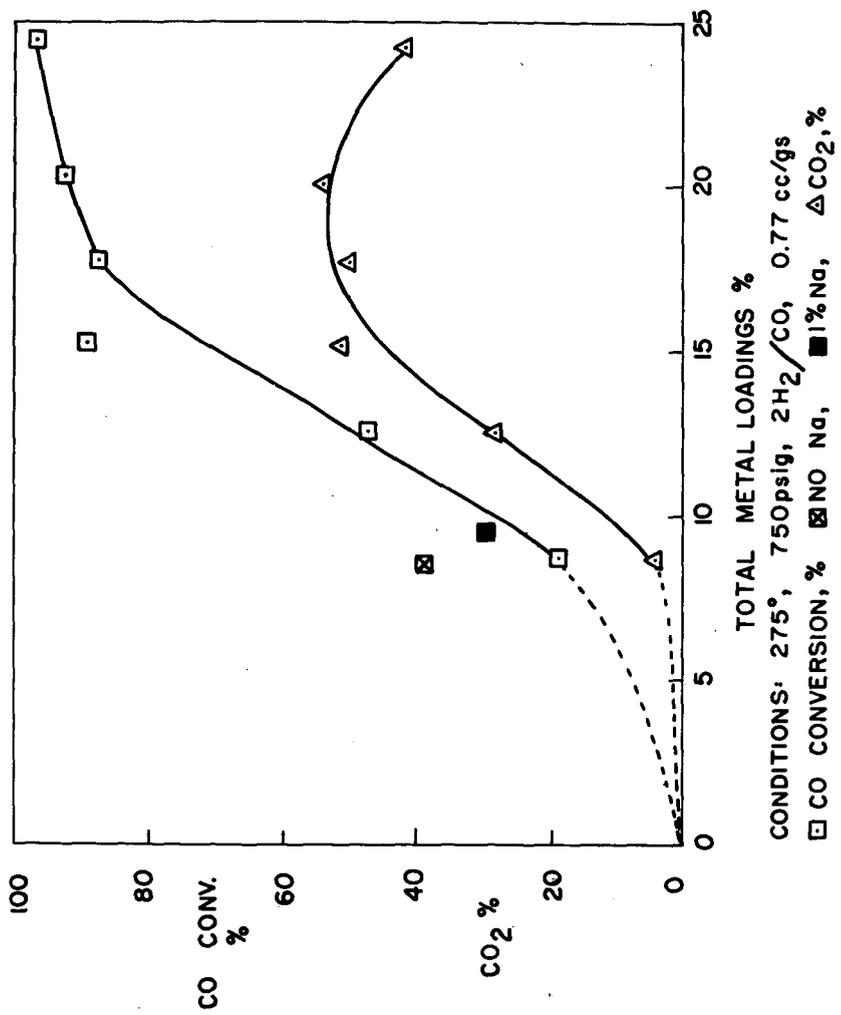
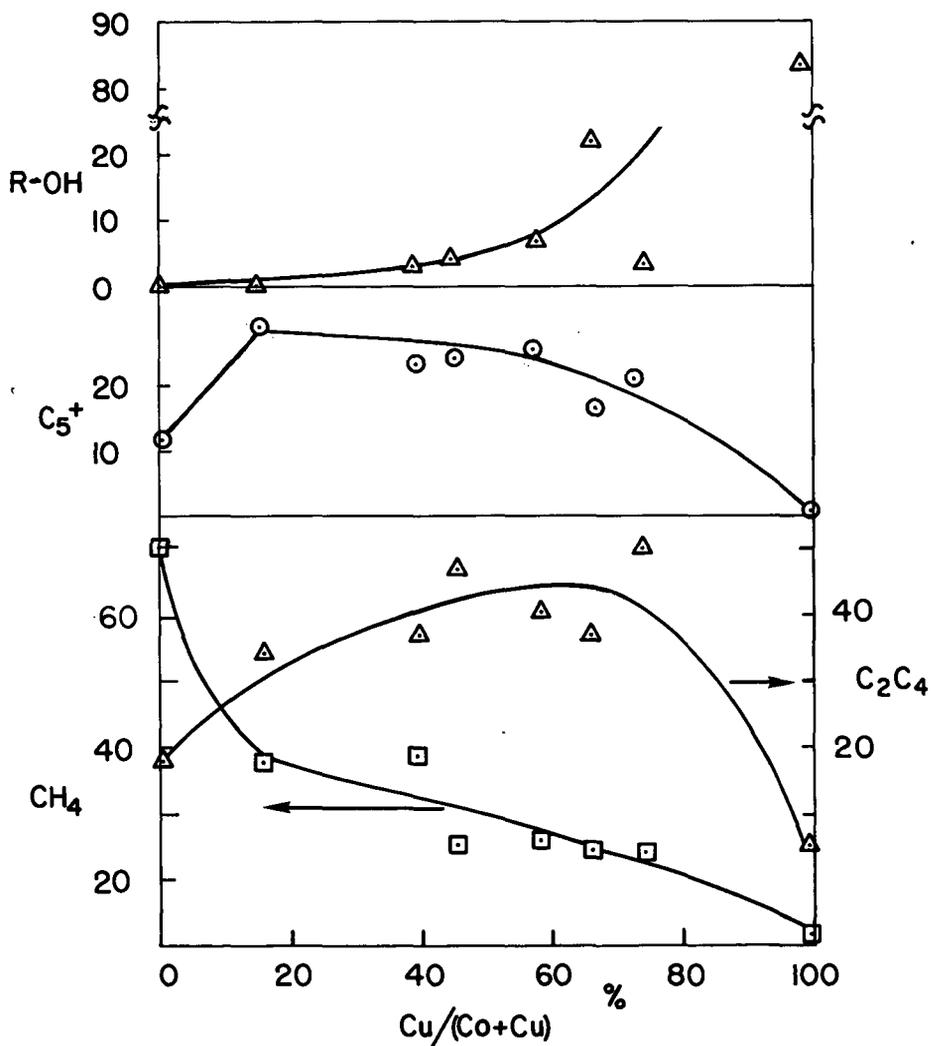


FIG. 2
 CATALYST SELECTIVITIES VERSUS WEIGHT FRACTION COPPER - RUN 1



CONDITIONS: 275°, 750psig, $2\text{H}_2/\text{CO}$, 0.77 cc/gs

DONOR SOLVENT REACTIONS WITH COAL IN A BATCH-RECYCLE SYSTEM

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INTRODUCTION

Numerous reports concerning kinetics of coal dissolution with hydrogen donor solvent are available. However, little knowledge about the primary products and the reactions which take place in experiments with short residence times have been reported until recently.

This study involved the dissolution of coal in hydrogen donor solvent (tetralin) in a rapid heat and rapid quench batch recycle system (Figure 1). The residence time of the coal-solvent slurry was in the range of a few seconds per pass in the slurry dissolver. The differential reactor system of batch recycle applied here had two main advantages compared with conventional autoclaves. 1) The rapid initial rate was expanded in the time scale of differential conversions; consequently, the initial conditioning period was minimized. In addition, continuous monitoring of data in a single run gave more definitive and smoother results which could probably not have been achieved by batch experiments. 2) A quench system was used which allowed only a few seconds of thermal exposure of the slurry (at the reaction temperature) per pass. This apparently reduced the reorganization and polymerization reactions of the primary reaction products and permitted the analysis of these primary fragmentation products from the dissolution process.

EXPERIMENTAL

A weighed amount of coal particles vehicled with small amounts of tetralin was vacuum fed into the slurry mixer. When addition of coal to the system was completed, hydrogen was used to purge and pressurize the system. Pumping of the coal-solvent slurry was carried out at room temperature for about 10 - 30 minutes while the slurry mixer was stirred at 1200 rpm to achieve complete suspension of the slurry throughout the system. The dissolver was heated to the reaction temperature to start the experiment. Less than three minutes was required to heat the slurry to 400°C in the dissolver. Flow velocity was 7.7 ft/sec when it was measured at the inlet to the preheater. Based on the conditions of 400°C and 1500 psig H₂, about six seconds of residence time of the slurry in the isothermal dissolver was achieved per pass. Slurry samples were taken at the mixer in sizes to minimize system disturbance. Slurry samples taken were weighed and centrifuged at 21,000 rpm for 40 minutes to separate solid residue and liquids. Liquid portions of the samples are subjected to gas chromatographic analysis to determine hydrogen transfer. Other methods of analysis were applied to the extracts from the reaction such as molecular weight and proton NMR.

Sequential washing of residual solids with fresh tetralin, benzene and pyridine was carried out to determine conversion data. Analysis of the ash content in the solid residues was used to determine the exact conversion figures. Gaseous products were collected in a liquid nitrogen double condenser in series at 77°K to trap the vapor products passing out through the gas vent. The rate of gas flow was kept to a minimum (approximately an average rate of 8 cc/sec at S.T.P.).

The following conditions were used for the system:

Temperature	
slurry dissolver	400°C ± 5°C
quench outlet	50-70°C

Note: Too low a temperature at the quench outlet was avoided to prevent wall deposition of products which could occur even at high turbulence (7.7 ft sec).

slurry mixer temperature	100°C ± 2°C
--------------------------	-------------

Note: Low temperatures were avoided here for the same reason as above.

H ₂ preheater inlet	1650 psig
dissolver	1500 psig
slurry mixer	1350 psig

Coal : solvent ratio = 1 : 9

Coal = Bituminous coal, Hiawatha, Utah
(V.M. =48.1%, F.C. =43.3%, ash =6.4%, S =0.7%)

particle size: 270/400 mesh, sp gr < 1.35

Figure 2 shows overall conversions data (pyridine soluble + gas, benzene soluble + gas and total gas) as a function of the residence time of the reaction. One set of numbers on the time scale (lower numbers) shows actual accumulated run time which is a time scale based on differential reaction. The upper numbers on the time scale represent the true residence time calculated as if reaction were carried out integrally. When coal particles are homogeneously suspended throughout the system, the relationship between these two time scale holds that,

$$t_i = \frac{w}{W} t_d$$

where t_i = residence time in integral conversion

t_d = residence time in differential conversion

w = mass hold up in dissolver

W = mass hold up in the remainder of the reactor system

Figure 3 shows net naphthalene and other tetralin derived compounds vs. percent conversion. Table 1 shows the gas composition from gas chromatographic analysis. Table 2 shows molecular weights of the products measured by vapor pressure osmometry.

As shown in Table 2 the average molecular weights of both the cyclohexane soluble portion and the tetralin soluble and cyclohexane insoluble portions gradually decreased as conversion proceeded.

DISCUSSION OF RESULTS

Figure 2 represents conversion-time data in real time and differential time. Figure 3 shows the same data in terms of naphthalene formation vs. conversion. Naphthalene formation was used here to indicate hydrogen transfer. From the data in both figures, two separate reaction regimes may be visualized. The kinetics are initially very rapid with minimal H₂ transfer. After about 1.5 minutes the conversion rate decreases and the transfer of hydrogen increases.

During the initial stages of the reaction, gas formation appears to predominate as shown by the gas production in Figure 2 and low H₂ transfer in Figure 3. The rate of gas production rapidly decreased after about 1 minute as shown by the nearly horizontal part of the curve in Figure 2.

Formation of gaseous products appeared to be concentrated in the first stage of the reaction. As can be seen in Figure 3 a negligible amount of hydrogen appears to have been transferred in the initial stages of the reaction. After the inflection point the following regime of reaction (after about 27% benzene sol. + gas) consisted of a slower overall reaction but one involving a rapid hydrogen transfer (up to around 60% of the benzene soluble fraction). Again there appeared to be a decrease in the rate of hydrogen transfer after about seven minutes of actual reaction time. These phenomena are strikingly similar to what Neavel (1) found except that inflections of the conversion curves were not observed in Neavel's experiments. This may point out one advantage of using the differential reaction system employed in our experiments. The fact that tetralin is consumed less than 20 parts per 100 parts of coal for benzene soluble conversion levels of around 80% shows considerable discrepancy from many previous results. (For example, some others have shown up to 40 parts of tetralin converted per 100 parts of coal.) Although our results cannot be directly compared for example to Neavel due to different experimental conditions such as a different tetralin:coal ratio (9:1 compared to 2:1) and a hydrogen atmosphere in our experiments, some of the same trends were observed.

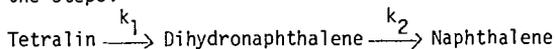
The initial regime of the dissolution reaction appeared to be controlled by thermal disintegration of the coal with evolution of gases. The lack of tetralin penetration into the micro (internal) pore structure of the coal (which is known to comprise about 80% of the total pores of the coal) seems to make the solvent-coal reaction less important during the initial stages. Also coal is known to be bimodal with sizes of the internal pores distributed around 5Å to 8Å which would make it difficult for tetralin molecules

(diameter about 10\AA) to enter these pores and make contact with internal reaction sites. Therefore, mere wetting of the external surface of coal may have taken place until opening of the micropores occurred by escaping trapped gases. An excess amount of solvent was supplied for the reaction (9:1 ratio of solvent to coal) since previous experiments by our laboratory and others showed that below approximately a 6:1 ratio of tetralin:coal the tetralin became the limiting reactant (2). Following the initial period of rapid donation of hydrogen from tetralin additional reaction paths may have been followed by introduction of tetralin into fresh reaction sites without restriction of diffusion into or out of the pores in the coal particles. The last stage of hydrogen donation appears to be controlled by diffusion either of fresh tetralin into the coal particles or products out of the particles. Even though the conversion rate is approximately constant (Figure 2) the hydrogen transfer rate after the initial rapid reaction is much less than the conversion rate as shown in Figure 3.

The data after about 10 minutes of actual reaction time for pyridine soluble and benzene soluble conversion were approximately the same. This is somewhat surprising since the initial reactions gave much higher benzene soluble yields. With the reaction system used the coal solvent mixture reached high temperatures followed by a quench which lowered the temperature to near ambient except during the time when the coal solvent mixture was in the reactor or heater. This gives some indication that perhaps this method of coal solvent interaction could improve product quality substantially.

The analysis of the gases which were released during the dissolution process which showed that methane formation was very small compared with that for other gases. This may or may not have implications as far as the linkages in the coal structure is concerned. As the carbon number of the molecules in the gas phase which appeared as products increased it is apparent from Table 1 that the fraction of the gases of a particular molecular weight which are normal straight chain hydrocarbon compounds decreased. This increasing ratio of unsaturates as the molecules became longer may be attributable to the longer lifetime of some free radicals which survive until the quench conditions change the temperature of the product mixture. As can be seen in Table 1 a substantial amount of isomers were formed for C4 compounds.

Substantial amounts of dihydronaphthalene were formed during the dissolution process. The formation of this dihydronaphthalene appears either to have been related to mild hydrogen transfer conditions or to have been an intermediate in the dehydrogenation of tetralin (or naphthalene formation). The majority of the dihydronaphthalenes were formed in a very short time in the initial stages of the reaction. The amount of these dihydronaphthalenes gradually decreased as conversion proceeded after giving a maximum at the first data point taken for the reaction at 400° (at about six seconds) as shown in Figure 3. In this tetralin excessive environment, dihydronaphthalene might follow the trends shown if it were an intermediate in a reaction path leading to naphthalene from tetralin. Such a consecutive reaction scheme would include the steps:



where the particular shape of the curves for dihydronaphthalene and naphthalene concentrations would depend on the relative values of k_1 and k_2 (assuming the reactions to be simple first order). The species resulting from the formation of dihydronaphthalene turned out to be over 99% of 1, 2-dihydronaphthalene. Hexa-, octa-, and decahydronaphthalene concentrations follow the same trends as given by Neavel (1) although he showed smaller quantities formed. This is probably to be expected since his conditions and coal/solvent ratio were different. The formation of cis-decalin always prevailed over trans-decalin. The results concerning dihydronaphthalenes and decalins needs mechanistic explanation and further experimental work will probably have to be done to explain the results obtained. Especially important is precise analyses of all of the chemical species present as a function of reaction time (or extent of reaction).

REFERENCE

1. R. C. Neavel, "Liquefaction of Coal in Hydrogen Donor and Non-Donor Vehicles", FUEL, Vol. 55, July, 1976.
2. W. H. Wiser and G. R. Hill, A Kinetic Study of the Thermal Dissolution of High-Volatile Bituminous Coal, Symposium of Science and Technology of Coal, Ottawa, Canada, 1967, p. 162-167.

Table 1. Gaseous Compounds
 (collected in liquid nitrogen at 77°K (-196°C))
 From reaction of tetralin with Hiawatha Coal at 400°C
 (Tetralin:coal = 9:1; weight basis)

Compound	%	% Composition in each Homologs	Composition sat/unsat.	% Composition of Homologs
C ₁	.3	100	100/0	.3
C ₂	32.6	82	82 / 18	39.7
C ₂ =	7.1	18		
C ₃	25.0	69	69 / 31	36.2
C ₃ =	11.2	31		
iC ₄	1.7	14*	60 / 40	12.1
C ₄	5.6	46		
1&iC ₄ =	.9	7*		
t,C ₂ C ₄ =	3.9	33		
n,iC ₅	3.5	56**	56 / 44	6.2
allC ₅ =	2.8	44		
allC ₆	5.1			5.1
allC ₇	.6			.6
allC ₈	.3			.3

* substantial amount of isomers

**mostly normal with small amount isomer on shoulder

Notes:

1. % Composition based on gaseous products up to C₈ vapors collected.
2. Gas chromatographic analysis with the following conditions:
 20 ft. activated alumina (F-1)
 program temperatures from 60°C to 280°C (8°C/min.)
 He carrier gas flow rate = 30 ml/min.

Table 2. Molecular Weight of Extraction Products
from Coal Extraction with Tetralin at 400°C

Conversion (benzene soluble)	Cyclohexane soluble	Cyclohexane insoluble Tetralin soluble
11.5	669	1506
27.7	539	15070
31.4	794	1368
42.5	504	1288
58.6	430	1126
77.5	436	1203

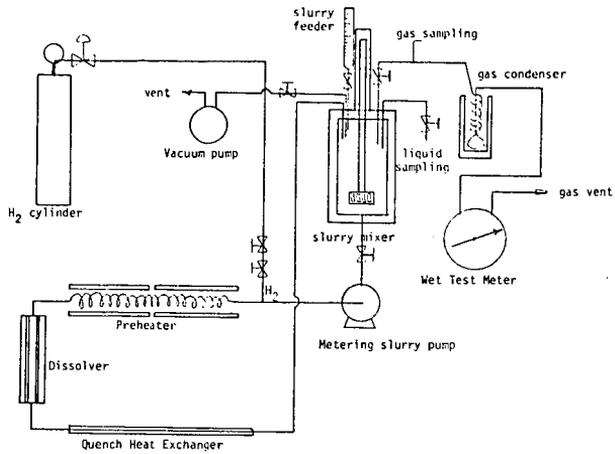
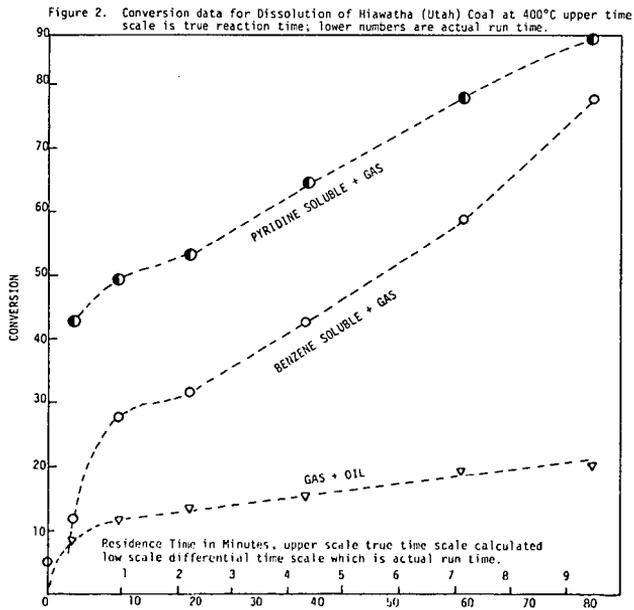


Figure 1. Batch recycle system for dissolution of coal in a hydrogen donor solvent.



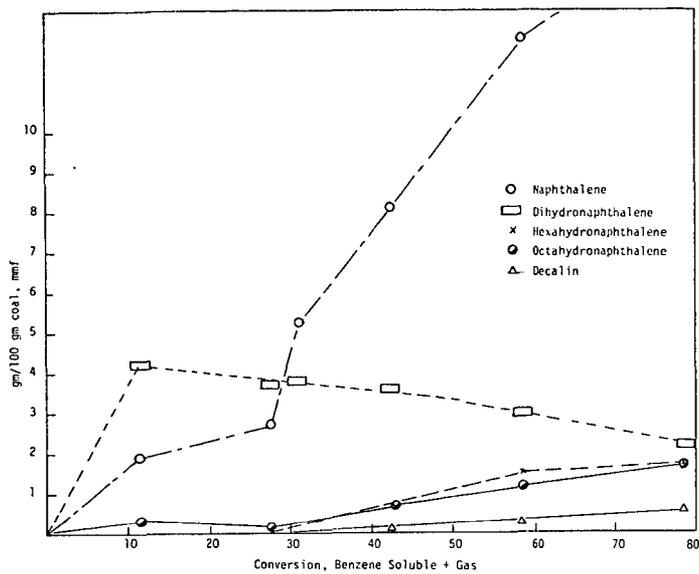


Figure 3. Hydrogen transfer as measured by tetralin derivatives from reactions with coal at 400°C (Hiawatha Coal)

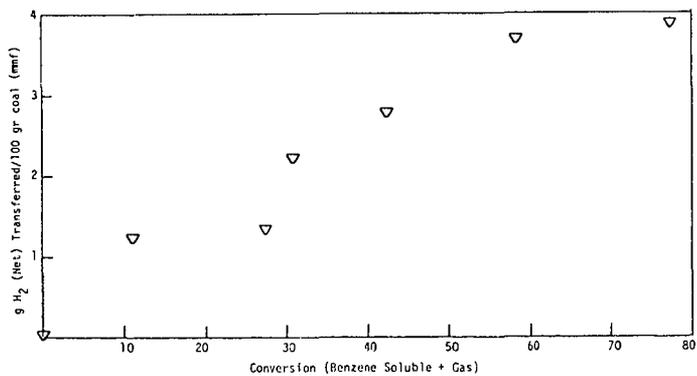


Figure 4. Net Hydrogen Transfer from Tetralin at 400°C in Reactions with Hiawatha Coal.

COMPOSITION OF SELECTED FRACTIONS FROM COAL TAR
PRODUCED FROM AN UNDERGROUND COAL GASIFICATION TEST

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INTRODUCTION

The remaining fossil energy resources contained within the United States are comprised primarily of coal. These resources have been estimated at 3.9 trillion short tons (1) or enough coal to provide this country with all of its energy needs for the next two hundred years. One drawback with this vast potential is the difficulty in utilizing this resource. Estimates indicate that only 10-25 percent (1) is recoverable using present day techniques. The remaining coal seams are either too deep or too low in quality to mine economically.

In an effort to develop this inaccessible resource ERDA has sponsored several different research programs in underground coal gasification. The Laramie Energy Research Center has been developing a technique called the linked vertical well (LVW) process to produce a low-Btu gas by gasifying a coal seam in situ.

The field tests conducted at Hanna, (2,3) Wyoming, have shown that a low-Btu gas can be produced and a great deal of control can be achieved in directing the underground reaction systems, thereby resulting in high utilization of the coal. The most recent field test conducted from April through July of 1976 showed a total of 6700 tons of coal utilized and production rates up to 12 MM scf/day. (4) The highest heating value obtained for a substantial period was approximately 175 Btu/scf. In addition to this low-Btu gas an organic condensate was co-produced with the gas. For lack of a better term, this organic liquid has been called a coal tar. Its composition has been studied for various reasons, one of which is to ascertain its value as a petrochemical feedstock or fuel.

Another consideration is the possible changes in composition due to changes in reaction conditions. Additionally, the possible environmental effects of such a by-product on groundwater quality must also be accounted for since the seam is considered to be a low-grade aquifer. With these thoughts in mind, the characterization was started to possibly answer these questions.

DESCRIPTION OF THE LINKED VERTICAL WELL (LVW) PROCESS

The coal seam at the Hanna site is 30 feet thick, approximately 300 feet deep and of subbituminous rank, a coal typical of most Western coals.

Numbers in parentheses refer to references at the end of the text.

The LVW process involves two distinct and separate steps. The first is a linkage step to achieve the desired permeability necessary for the subsequent gasification. This linkage is achieved through a reverse combustion process as shown in Figure 1 and then the gasification step using a forward combustion process follows. The produced gases flow through the previously formed linkage path to the production well and finally to the surface. The coal tars are produced within the reaction zone and carried to the surface with the produced gas.

The particular sample to be discussed in detail was produced during the first test at Hanna (collected on December 10, 1973) but reference to other samples from more recent tests will be made.

EXPERIMENTAL

Nonaqueous titration of nitrogen was performed in acetic anhydride and benzene with HClO_4 as described by Buell. (5) GLC analyses of tar acids were done on a 10' x .055" 10% SP-1200/1% H_3PO_4 on Chromosorb W AW column. With a helium carrier gas, a flow rate of 70 ml/min, isothermal for 2 min at 130° C, then 2° C/min increase to 200° C, a usable separation of components resulted. GLC analyses of the aliphatics were done on a 20' x .055" 3% SP-2100 on Supelcoport column. With a flow rate of helium carrier gas at 70 ml/min, isothermal at 50° C for 4 minutes, then a 2° C/min increase to 300° C, a usable separation was achieved. GC-MS data were collected on a system using a HP-5712 gas chromatograph interfaced to an AEI MS-12 mass spectrometer.

Simulated distillations were performed with use of gas chromatography with residue defined as any material that does not boil below 1000° F.

Fractionation into basic, acidic and neutral fractions was accomplished by aqueous mineral acid, sodium bicarbonate, and caustic soda extraction, pH adjustment to regenerate the species and extraction with diethyl ether. Neutrals were also separated into aliphatic and aromatic fractions with the use of silica gel. Hexane was used to elute the aliphatics and methanol to remove the aromatics.

PHYSICAL PROPERTIES

The following range of physical properties were determined from many samples collected during the three different tests conducted at Hanna, Wyoming.

Table 1 - Physical Properties

Specific gravity at 60° F	-	0.960 - 0.977
Viscosity at 100° F	-	3.5 - 13.2 centistokes
Heat of combustion	-	14,000 - 17,300 Btu/lb

As shown in Table 1 the physical parameters of these coal tars are desirable, in particular, they are very mobile compared to typical coal tars.

CHEMICAL PROPERTIES

The elemental analysis (Table II), for the sample collected on December 10, 1973, is typical for most of the tars produced from the underground coal gasification tests at Hanna.

Table II - Elemental Analysis

C	-	86.33 %
H	-	10.43
N	-	0.79
S	-	0.18
O ^a	-	2.27
^a Percentage determined by difference		

The maximum values for nitrogen and sulfur that have been observed are 1 percent and 0.5 percent respectively.

Another technique used for analysis is simulated distillations. The simulated distillation of the coal tar (collected December 10, 1973) is shown in Figure 2. The interesting point is the fact that none of the material boils above 950° F. When compared with the simulated distillation of a coal tar produced by laboratory carbonization (Figure 3), the obvious difference is in the boiling point distribution. With use of internal standard, it was determined that the carbonized laboratory sample was 24 percent (weight) residue or material boiling above 1000° F versus 0 percent for the UCG sample (Table III).

Table III - Boiling Range Distribution

<u>Sample</u>	<u>Amb- 400°F</u>	<u>400- 500</u>	<u>500- 600</u>	<u>600- 700</u>	<u>700- 800</u>	<u>800- 900</u>	<u>900- 1000</u>	<u>Residue</u>
Carbonized	0	11.3	16.3	13.1	15.2	12.4	7.5	24.2
UCG sample	6.2	16.9	25.6	28.2	16.0	5.3	1.8	0

This demonstrates an important point about the UCG coal tar. It is a fractionated portion of the total produced coal tar. The passage through the production path up to the surface from the reaction zone acts as a preliminary separation step before presenting the coal tar at the production wellhead. This also explains the rather low viscosity of the tar since the more volatile components are produced at the surface. This provides a rather unique product for characterization when compared to typical coal tars.

Non-aqueous titration of the sample is shown in Table IV.

Table IV - Non-Aqueous Titration Results

Sample from December 10, 1973	0.524% WB	0.186% VWB
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Strong, weak and very weak bases are defined by their half neutralization potential (HNP), with very strong bases having an HNP less than 150 mV, weak bases between 150 and 350 mV, and very weak bases greater than 350 mV. Pyridines and quinolines will titrate as weak bases and amides as very weak bases. Primary and secondary anilines titrate as very weak bases since they will acetylate and then titrate as amides.

The separation of numerous samples into tar bases, tar acids (strong and weak acids) and neutrals gave the following range of results (Table V).

Table V - Compositions Wt % of Tar

Tar Bases	2.5 - 8.0%
Tar Acids	.1 - 1% - Strong Acids 12 - 31% - Weak Acids
Neutrals	55 - 77% - 70% Aromatic 30% Aliphatic

In addition, the neutrals were separated into aliphatic and aromatic fractions. The interesting point was that after looking at many samples, the relative amount of aliphatics vs. aromatics was essentially constant (30:70). Previous work (6) on the bases indicate them to be primarily quinolines with some pyridines and anilines, much as would be expected in a liquid product produced from coal.

The results presented in this paper are concerned with the composition of the weak acid and aliphatic fractions of this one sample as identified by GC-MS and NMR analysis. Although complete analyses have not been finished on other samples, a comparison of the weak acid and aliphatic fractions from other samples will be made.

The sample from December 10, 1973, was 14.5 percent (by weight) weak acids and 23 percent (by weight) aliphatics.

WEAK ACIDS

The composition of the weak acid fraction is almost exclusively phenolic in nature. With the use of GC-MS a reasonable separation (Figure 4) and subsequent analysis was obtained. Table VI lists the resulting components determined. In some cases the GC resolution was adequate enough to provide a mass spectra "clean" enough to identify specific isomers but in most cases only enough information was available to determine molecular weight and/or degree of alkylation.

Table VI - Weak Acids

pheno
p - cresol
o - cresol
m - cresol
4 different xylenols
7 C ₃ - phenols
5 C ₄ - phenols
small amount of aromatic aldehyde or ketone

Additional spectral information was obtained by manually trapping peaks eluted from the GLC and using H^1 and C^{13} NMR techniques to identify the components. Without the presentation of the data, the H^1 and C^{13} NMR spectral data support the conclusions of the GC-MS analysis.

ALIPHATICS

The aliphatic fraction showed very little in the way of unsaturation or cyclic compounds but a very high concentration of saturate components. The results (Table VII) show a normal hydrocarbon series going from C_{10} all the way to C_{32} .

Table VII - Composition of Aliphatics

1. n- C_{10} through n- C_{32} series	
2. Branched Saturates	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">{</div> <ul style="list-style-type: none"> 2,11 - Dimethyl tridecane ($C_{15}H_{32}$) 2 - Methyl tetradecane ($C_{15}H_{32}$) 4,11 - Dimethyl pentadecane ($C_{17}H_{36}$) 6 - Methyl octadecane ($C_{19}H_{40}$) 7 - Methyl octadecane ($C_{19}H_{40}$) 3 - Methyl octadecane ($C_{19}H_{40}$) 3,6 - Dimethyl heptadecane ($C_{19}H_{40}$) two polybranched $C_{19}H_{40}$ 2,4 - Dimethyl octadecane ($C_{20}H_{42}$) </div>

A small amount of branched saturates are also observed with a rather large concentration of C_{19} branched saturates. As seen in Figure 5, the GLC trace for this sample shows the distinct normal series with the branched C_{19} series at about 70 minutes retention time. No C^{13} or H^1 NMR spectra were run on this sample since the GC resolution was sufficient to provide reasonable GC-MS analysis.

COMPARISON OF SAMPLES

Although analysis by GC-MS and NMR of other weak acid and aliphatic samples are not complete and ready for presentation, the author feels that the following evidence of similarity between samples will be of interest.

The only data presented is the very noticeable resemblance between GLC traces for the weak acids and aliphatics from different samples (Figures 6, 7, 8 and 9). The coal tars represented by these fractions were collected during different tests at the Hanna, Wyoming site. The sample previously discussed was collected in the first test during December of 1973. The next tar (Figures 6 and 8) was produced in the second test operated from April til August of 1975. The third sample (Figures 7 and 9) was collected during the most recent test from April through July 1976. Simple observation of the three GLC traces (Figures 4, 6 and 8) for the weak acids show a very strong similarity, indicating a very similar composition for the three fractions. A corresponding similarity is noticed for the aliphatics (Figures 5, 7 and 9) except for the concentrations of what appears to be the n- C_{25} component in the 6-25-75 sample (Figure 7). Other than that one difference, which the author cannot provide an explanation for, the fractions all have a normal saturate series from about C_{10} to C_{31} or C_{32} and a C_{19} branched series at 70 minutes retention time.

Other samples have shown this same general character within all their fractions although they are not presented here. The overwhelming conclusion is that the coal tar is fairly constant in composition, not only during the life of an experiment, but also from one test to another as long as the tests are in the same coal seam.

This would appear to be a very desirable by-product of the gasification process due to its constancy. Additionally, the consistency of composition would indicate a process approaching steady-state conditions since there does not appear to be variation in one of its products, the coal tar.

EXPLANATION OF COAL TAR FORMATION

The following discussion is based not only on the composition of the coal tars but also on the other available information pertaining to UCG and in particular the work conducted at Hanna, Wyoming.

The air reacts exothermically with the coal and/or char to provide heat for the then hot gases CO_2 and H_2O to react with the char to form CO and H_2 . The still relatively hot gases pass into or by fresh coal which is then devolatilized to produce the coal tars. These coal tars are then fractionated according to boiling point since they continue to cool as they flow with the product gas away from the combustion zone or heat source. The heavier components remain within the seam until they are eventually consumed or thermally cracked to lighter compounds. This fractionation is based on the temperature of the passage and the velocity of the gas stream since entrained droplets might also be carried to the surface.

This might also provide a very convenient method of disposing of these heavy molecular weight materials that would be hard to handle on the surface. It also helps to decrease the environmental effects on the ground water quality, if the more soluble products (the volatiles) are produced at the surface and the less water soluble (the heavy ends) remain behind and are eventually consumed. The actual fate of these organics in the ground water within the seam will be determined in a test to be conducted during the spring of 1977.

CONCLUSIONS

Analysis of the weak acid and aliphatic fractions of a coal tar produced from an underground coal gasification test reveal interesting results. The composition of the weak acids is much as would be expected, alkylated phenols. The aliphatics have a normal saturate series running from C_{10} to C_{32} with some branched saturates and a particularly heavy concentration of C_{19} branched saturates.

The most important point is the similarity of samples over the life of a system or from test to test. Referring to the three questions proposed earlier, this similarity or constancy would indicate the following:

1. As a fuel or petrochemical feedstock, a constant feedstock would be very desirable.

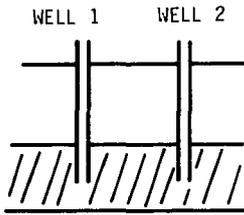
2. The unchanging composition suggests a system approaching steady-state conditions.
3. Environmental problems would be reduced if the effluent was constant in composition, thereby limiting the number of components to be monitored.

As a by-product, the coal tar appears to be advantageous which only increases the attraction of underground coal gasification as a commercial process.

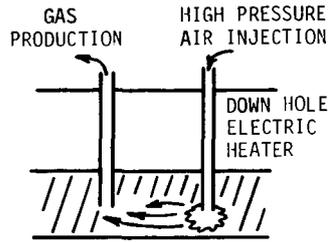
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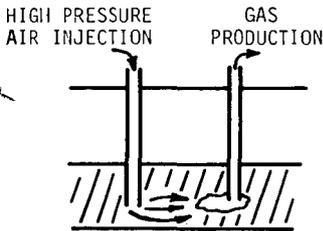
NOTE: Any reference to specific brand names does not imply endorsement by the Energy Research and Development Administration.



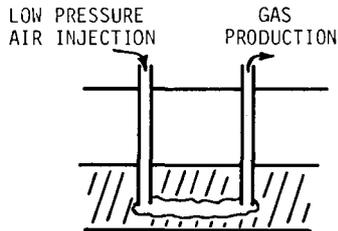
(A) VIRGIN COAL



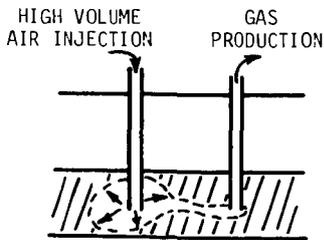
(B) IGNITION OF COAL



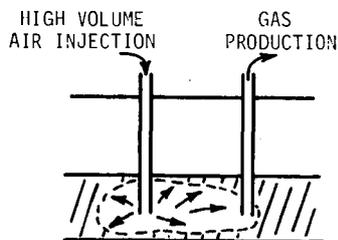
(C) COMBUSTION LINKING
FRONT PROCEEDS TO
SOURCE OF AIR



(D) LINKAGE COMPLETE WHEN
COMBUSTION ZONE REACHES
INJECTION WELL (SYSTEM
READY FOR GASIFICATION)

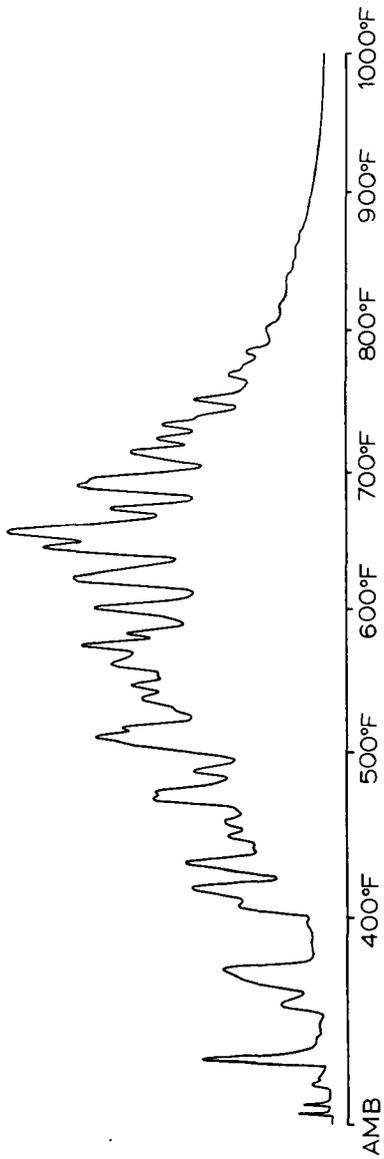


(E) COMBUSTION FRONT
PROCEEDS IN THE SAME
DIRECTION AS INJECTED
AIR



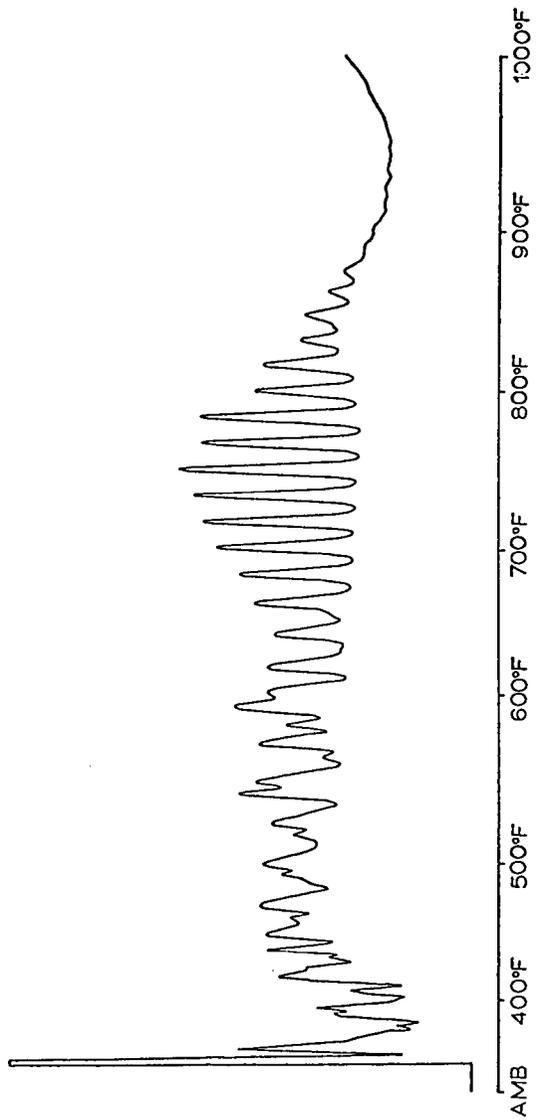
(F) COMBUSTION FRONT EVENTUALLY
REACHES PRODUCTION WELL

FIGURE 1



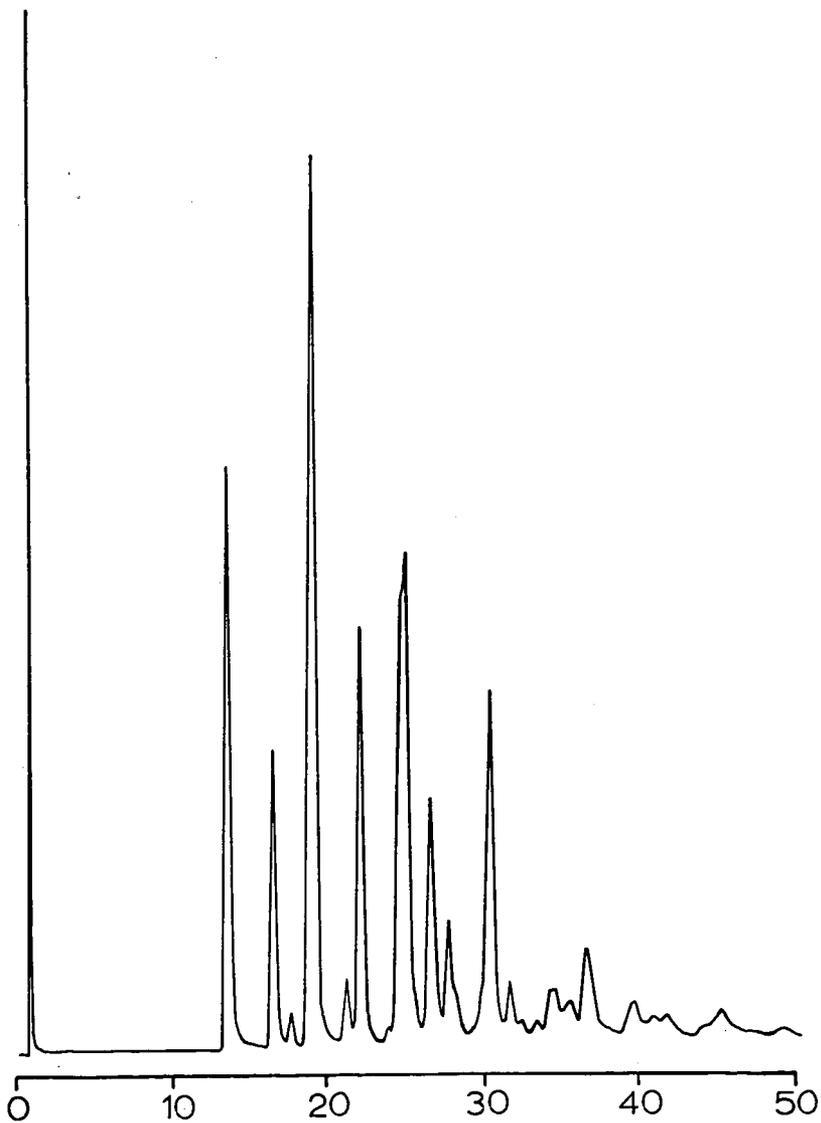
SIMULATED DISTILLATION OF TAR (12-10-73)

FIGURE 2

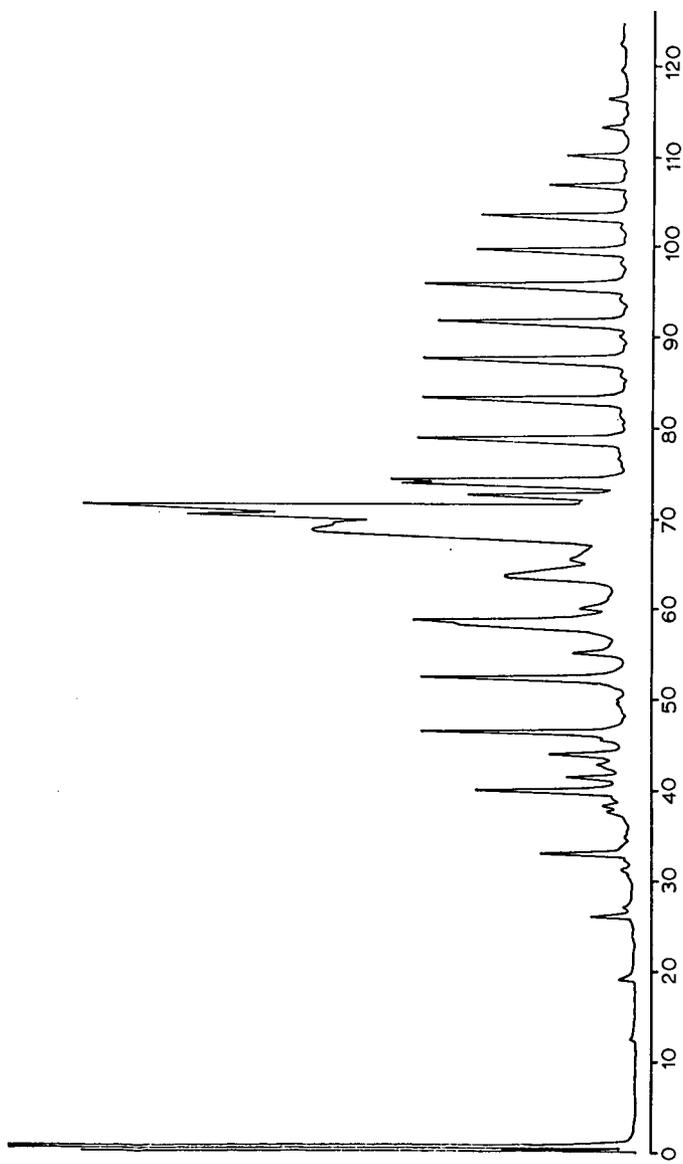


SIMULATED DISTILLATION OF COAL TAR
PRODUCED BY CARBONIZATION AT 500°C

FIGURE 3

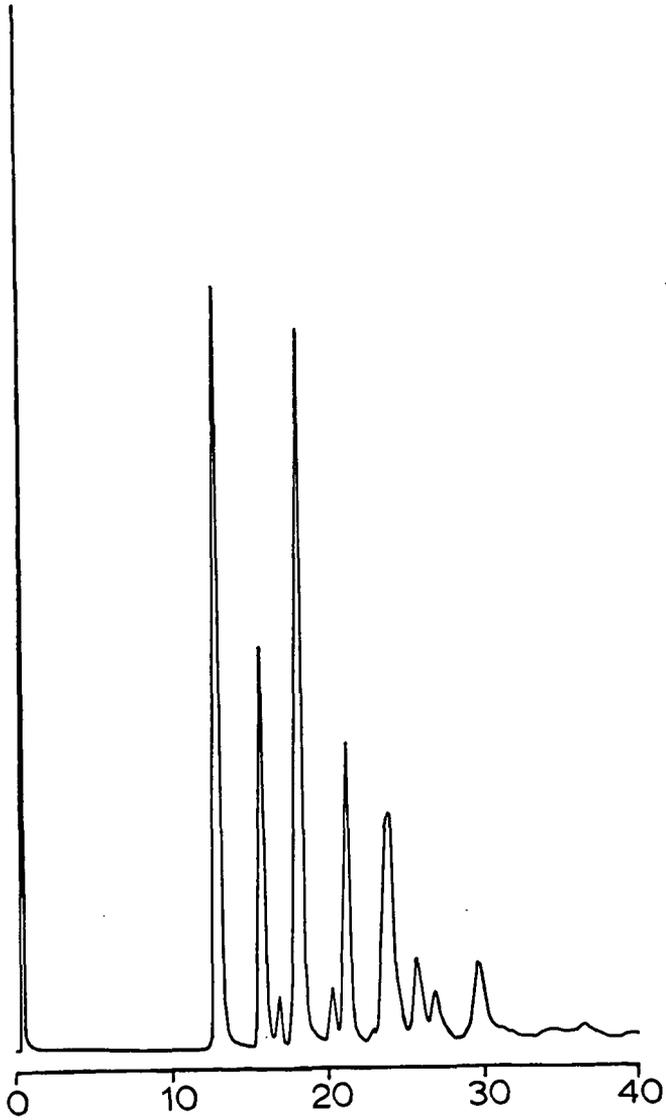


TAR ACIDS FROM (12-10-73)



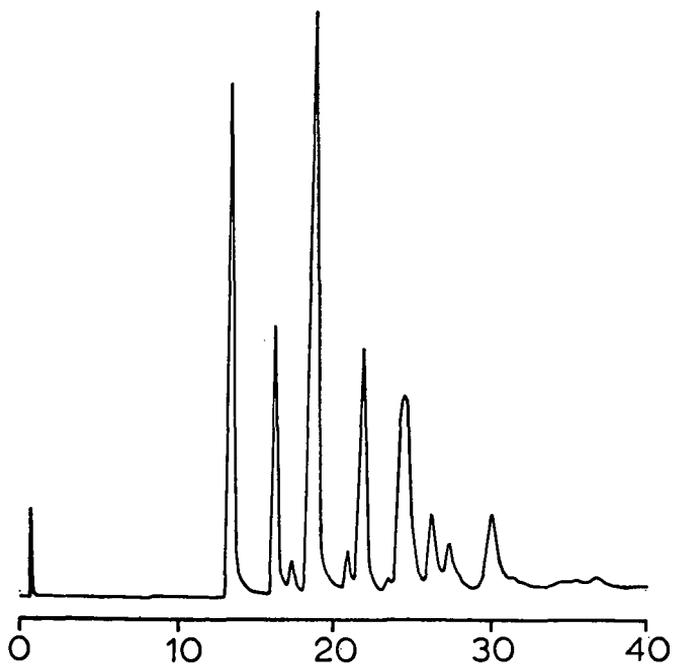
ALIPHATICS FROM (12-10-73)

FIGURE 5



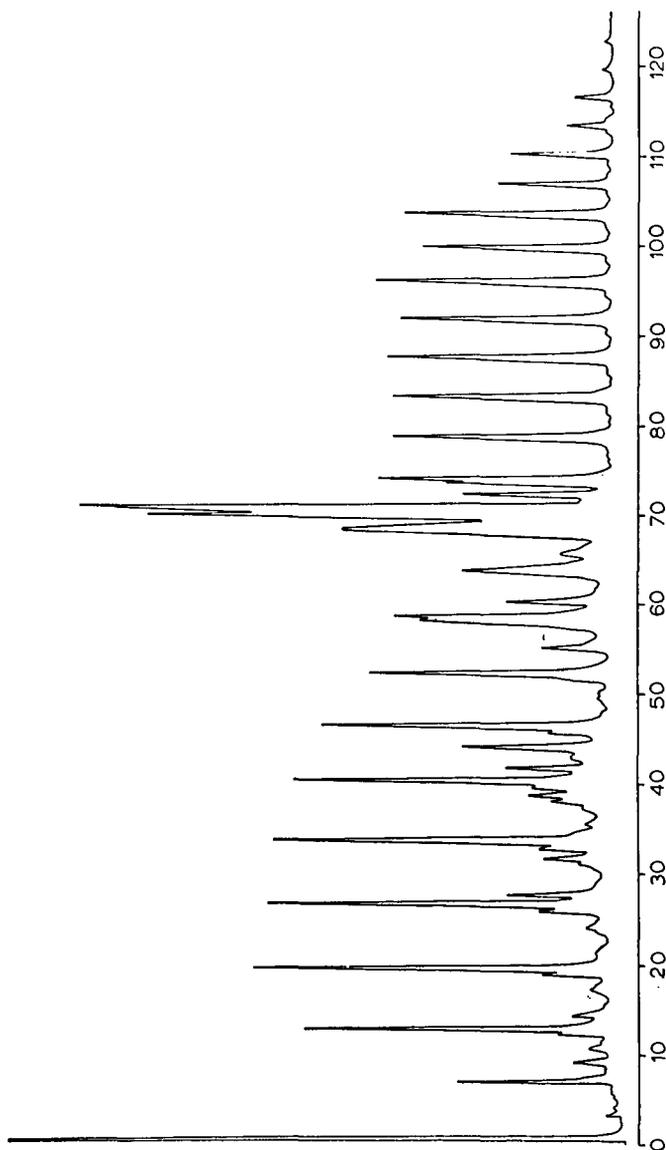
TAR ACIDS FROM (5-21-76)

FIGURE 6 131



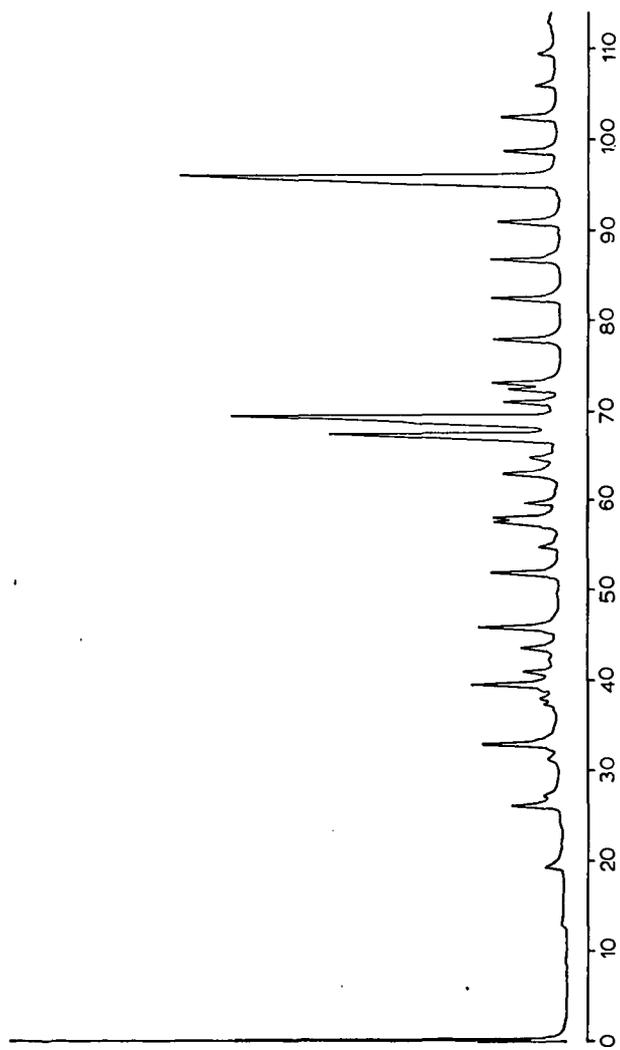
TAR ACIDS FROM (6-25-75)

FIGURE 7



ALIPHATICS FROM (5-21-76)

FIGURE 8



ALIPHATICS FROM (6-25-75)
FIGURE 9

COAL LIQUEFACTION UNDER HIGH-MASS FLUX AND SHORT-RESIDENCE
TIME CONDITIONS*

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INTRODUCTION

This paper describes progress made during the first year of a program directed toward developing and evaluating a concept for reacting pulverized coal with heated hydrogen to form hydrocarbon liquids suitable for conversion to fuels or for use as chemical feed stocks. The basic concept of the process is that high liquid yields are favored by rapid mixing, reaction, and subsequent quenching of the reacting mixture. The pulverized coal is being injected into the reactor by dense-phase transport, with a minimum amount of carrier gas required. A rocket engine-type injector is being used to rapidly and uniformly mix the coal with hydrogen that has been heated to 1200 to 2000 F. Reaction times of 10 to 1000 milliseconds at temperatures of 1500 to 1900 F and pressures of 500 to 1500 psi are being explored. The concept is being evaluated with a simple water-spray quench system.

The initial effort was directed toward cold-flow testing to develop suitable methods of transport, injection, and mixing of the pulverized coal. Subsequently, reactor testing was begun at a nominal coal flowrate of 0.2 tons per hour (tph). Preparations are also being made for testing at 1 tph.

COLD-FLOW TESTING

The purpose of the cold-flow testing was to develop effective means of feeding the pulverized coal into a reactor and suitably mixing this coal with incoming hydrogen. Dense-phase transport of the coal was chosen to minimize the gas requirement for feeding the coal and, thus, maximize the gas available for heating, because the process heat is supplied by heating the incoming hydrogen. Further, cold-flow mixing tests were made to allow selection of injector configurations and operating conditions that would produce a high level of mixing uniformity. This high mixing uniformity is needed to ensure that the coal particles are exposed to a uniform reaction environment and reaction time during their brief residence time in the reactor. Poor mixing would tend to cause some of the particles to be insufficiently reacted, thereby producing a poor yield, and others to react for too long a period of time, with attendant cracking of the oils into gases. This mixing optimization was accomplished by adapting mixing characterization techniques that are used for performance optimization of rocket engine injectors.

TRANSPORT AND FEEDING TESTS

Cold-flow tests were made with two simple pressurized feeders to evaluate the dense-phase feeding and transport characteristics of the pulverized coal. One of these feeders was made from a 4-inch-diameter Pyrex pipe 4 feet long and the second was made from a 10-inch steel pipe 17 feet long. A 30-degree included-angle cone was used in the bottom of each. Pulverized coal fed from each feeder through a ball valve and through steel tubing into a catch vessel. No fluidizing gas was provided other

*Program funded by ERDA Fossil Energy, Division of Coal conversion and Utilization
(Contract E(49-18)-2044)

than that associated with pressuring the feeder. The transport gas requirement was inferred from the rate of gas flow to the feeder during the flow of solids. Pressures were measured at the top of the feeder and at several points in the feed line.

Tests were made with two coal particle sizes--170 micron and 54 micron mass median (27 and 74 percent through a 200-mesh screen). In most cases, nitrogen was used as a carrier gas but tests were also made with helium and carbon dioxide to assess density effects. The coal was fed through 1/2-, 3/8-, and 1/4-inch tubing (inside diameters of 0.402, 0.277, and 0.180 inch, respectively).

Typical pressure gradient results are shown in Fig. 1. An approximate minimum pressure gradient is shown below which the coal would not flow. For each particle size, the pressure gradient results tended to fall along a single line irrespective of tube diameter. The coarser coal, which was used repeatedly because of a limited supply, produced an increased pressure gradient with increased usage, although the results still exhibited the same dependence on solids mass flux. The pressure gradient was unaffected by the substitution of helium or carbon dioxide for nitrogen as the transport gas. The difference in pressures between that measured in the feeder and that measured near the upstream end of the feed line exhibited a similar dependence, varying from 1.6 to 14 psi at solid mass fluxes of 400 and 1500 lbm/ft²-sec, respectively.

The transport gas requirement is shown in Fig. 2. The results indicate that the coal is leaving the feeder at near its static bulk density and only the gas carried in the interstices of the particles is required for transport.

The dispersed solids density was measured by simultaneously closing two ball valves in the line to trap the amount of solids being carried. For the 170 micron coal, this density exhibited a power law dependence on solids mass flux, varying from 50 to 30 lbm/ft³ at 150 and 700 lbm/ft²-sec for each carrier gas.

Results from this testing have shown that pulverized coal can be effectively fed from a simple pressurized feeder. The dense-phase flow is smooth and reproducible. Flowrates from ~0.1 to 1.0 lbm/sec were readily obtained. Flowrates ~10 lbm/sec were obtained with another pressurized feeder, used for loading the 10-inch pipe feeder.

COLD-FLOW MIXING TESTS

Cold-flow tests were also made to define coal/gas injector configurations and operating conditions which will give rapid and uniform mixing. Because techniques have been developed for achieving and characterizing injector mixing for liquid-propellant rocket engines, these techniques were adapted for the coal/gas case. Furthermore, injector configurations known to give high levels of mixing in rocket engines were considered primary candidates for the coal/gas case.

For this testing, nitrogen was chosen as a simulant for the heated hydrogen in the reactor. Both the gas injection velocity and density were modeled in the cold-flow case. The pressure in the cold-flow chamber was chosen to give a gas density corresponding to that of the hydrogen at injection conditions. To model hydrogen at 1000 psia and 1500 F, the nitrogen pressure should be 19.1 psia. Consequently, the use of nitrogen allowed the tests to be made at nearly atmosphere conditions.

A two-phase flow probe was used to characterize the flowfield created by the coal/gas injection. Similar probes have been used extensively to characterize gas/liquid

injection for rocket injectors (e.g., Ref. 1 and 2). These probes have been developed from that originally used by Dussourd and Shapiro (Ref. 3).

The cold-flow mixing tests were made with a single injection element in the cold-flow chambers. A secondary flow of gas was also used in the chamber to suppress recirculation. Data from the probe tests were analyzed to calculate the local mass fluxes of a gas and coal. The local mass flux values were numerically integrated to obtain collection efficiencies by comparison with measured injection flowrates.

The resultant mass flux distributions were plotted for qualitative assessment; also, a mixing efficiency was calculated. The mixing efficiency used was one developed for rocket engine injector characterization by Rupe (Ref. 4). This mixing efficiency is usually expressed as

$$E_m = 1 - \sum_{r_i < R} MF_i \left(\frac{R-r_i}{R} \right) - \sum_{r_i > R} MF_i \left(\frac{R-r_i}{R-1} \right) \quad 1)$$

$$\text{where } MF_i = \frac{(m_c + m_g)_i}{\sum (m_c + m_g)_i} \quad \text{and } R = \frac{\sum m_{ci}}{\sum (m_c + m_g)_i} \quad \text{and } r_i = \frac{m_{ci}}{m_{ci} + m_{gi}} \quad \text{and } m_{ci}, m_{gi}$$

are the local mass flowrates of coal and gas, respectively, in the i^{th} steamtube. A relatively simple interpretation of Eq. 1 can be obtained by recognizing that the terms in parenthesis in the equation represent local deficiencies of the fractional mass fluxes. The flowfield data were numerically integrated to obtain the mixing efficiencies.

Two coal/gas injector configurations were chosen for cold-flow evaluation: a concentric tube configuration and a 4-on-1 impinging configuration. Both of these yield high mixing efficiency in rocket applications. Further, they were not expected to result in substantial impingement of coal on the walls. The concentric tube element involves coaxial flow of the two streams with coal in the central tube and gas flowing in the annulus. The 4-on-1 element involves impingement of four gas streams on a central coal stream. The dimensions of the injection elements were also selected on the basis of rocket engine experience.

Results from the cold-flow mixing tests are summarized in Fig. 3 and 4. High levels of mixing efficiency have been obtained, with both types of elements. In rocket engines, mixing efficiencies greater than 80 to 90 percent lead to very high combustion efficiencies (>95 percent).

The mixing results obtained with the concentric tube element exhibit different trends from those obtained with gas/liquid injection element, probably because of differences in the shear interaction in the element. Conversely, the coal/gas 4-on-1 injector exhibits qualitatively similar characteristics to a gas/liquid or liquid/liquid injector. Optimum mixing was obtained with two different diameter ratios, although in each case, the mixing on only one side of the optimum has been defined.

These two results may be used to obtain a diameter ratio dependence as:

$$\left[(\rho u_g^2) / (\rho u_c^2) \right]_{\text{optimum}} = 12.6 (D_g/D_c)^{2.1} \quad 2)$$

or

$$\frac{D_g}{D_c} = \left[\frac{1}{12.6 (4^2)} \left(\frac{m_g}{m_c} \right)^2 \frac{\rho_{ds}}{\rho_g} \right]^{1/6.1} \quad 3)$$

High levels of mixing have been demonstrated with both the concentric-tube and 4-on-1 element configurations. The highest levels of mixing were obtained with the 4-on-1 configuration, although either type appears suitable on the basis of mixing for reactor testing. Furthermore, the ability to use a two-phase flow probe to characterize coal/gas mixing has been demonstrated.

REACTOR TESTING

Reactor testing currently under way is directed toward evaluation and development of a reactor based on the short-residence time concept. The reactors are being designed to promote rapid mixing (based on the cold-flow results) and to obtain relatively high gas velocities, to promote interaction (mass transfer and reaction) of the gas with the particle. The hydrogen is being partially heated by indirect heating and by partial combustion with oxygen as necessary to supply the required process heat. The reactor is being operated with high internal wall temperatures to minimize a tendency for adhesion of the partially reacted coal particles on the wall. The amount of hydrogen fed is being kept as low as practical because of the recycle implication for a complete process. A simple water-spray quench system is being used.

Reactor testing was begun with a system capable of feeding 35 lbm of coal at a planned flowrate of ~ 0.1 lbm/sec (~ 0.2 tph). The 0.2 tph reactor assembly is illustrated in Fig. 5 and a schematic flow diagram of the test system is shown in Fig. 6. The reaction chamber for most tests was a 1-1/2-inch-diameter, 0.049-inch-wall stainless steel (type 321) tube, 36 inches long. This reaction chamber is contained within an insulated pressure vessel made from 8-inch pipe. Coal is fed in dense phase to the reactor from a pressurized feeder of the type used during the cold-flow testing. The feeder is a 6-inch diameter vessel with a conical (15-degree half angle) exit. Reaction products pass from the reaction chamber into a quench section, which has a set of water spray nozzles, and into a char receiver. The hydrogen is heated in a 260-inch-long coiled tube that is heated by passing an electric current through the tube. Up to 150 kilowatts of power is supplied to this tube by seven motor-generator sets. Nearly all of this power is transferred to the hydrogen as heat.

Two types of injectors have been used: a concentric tube and a 4-on-1 configuration. The 4-on-1 injector configuration is shown in Fig. 7. The body of this injector is made from a 1-1/2-inch tube fitting tee. The heated hydrogen enters the injector from the side, flows around the insulated coal feed tube, and through four injection orifices. The four hydrogen streams impinge with a 30-degree half angle at a point 0.400-inch from the injector face. Also included are four oxygen injection orifices which also impinge with an angle of 30 degrees but at a distance of 0.700 inch from the injector face.

Initial testing was directed toward solving operational problems with the system. The initial tests were made with the concentric tube injector and without oxygen addition. The reactor temperature was found to be lower than anticipated during these tests. The reaction process appeared to exhibit thermally neutral character whereas exothermic character was anticipated. Hydrogen-to-coal flowrate ratios near 0.36 were required to obtain a reactor outlet temperature 1100 F. A reactor outlet temperature ~ 1500 to 1800 F was believed to be needed for high conversions. Further, it was found that the char in the reactor tended to agglomerate and adhere to the walls of the reactor. The latter problem was believed due to a low reactor wall temperature, which was ≤ 1000 F during initial tests. Feldmann et al. (Ref. 5) report that wall temperatures of 1340 to 1470 F were required in the Hydrane reactor to avoid wall adhesion. The system and operating procedures were modified to minimize heat losses from the reactor tube and, also electric wall heaters were tried. However, the wall temperatures were not increased sufficiently to eliminate the wall adhesion problem. Therefore, the system was modified to allow the addition of oxygen to raise the temperatures by partial combustion.

Two methods of oxygen addition were tried: (1) injection in a small combustor upstream from the injector, and (2) injection directly into the reactor. Relatively small amounts of oxygen are required to increase the gas temperature to near 2000 F. Both methods were successful, although some difficulties were encountered with overheating the injectors and preburners with the preburner approach. Agglomeration was largely eliminated for reactor temperatures greater than ~1600 F and reactor plugging due to wall adhesion did not occur with reactor temperatures above ~1500 F.

A series of tests was made to assess the effects of reactor temperature, location of oxygen addition, residence time, and velocity.

The raw char gas samples, and aqueous samples from the tests have been analyzed to determine the composition of the products and to allow calculation of material balances. The gas samples were analyzed by gas chromatography for N₂, H₂, O₂, CO, CO₂, and C₁ to C₄ hydrocarbons. A gas chromatographic analysis is used also for benzene, toluene, and xylene. The latter procedure was confirmed by mass spectrometric analysis. Also, the sample bottles are washed with a solvent to remove tar-like materials.

Aqueous samples from the cyclone and secondary separators and the water removed from the char receiver have been analyzed for carbon content with a total carbon analyzer.

The raw char samples are weighed, air dried, and reweighed after which a portion of the sample is dried in an oven at 221 F for 1 hour. A portion of the air-dried sample is sent to an outside laboratory for proximate and ultimate analyses. Also, an analytical benzene extraction, employing a Soxhlet apparatus, is used to determine an extractable fraction. Most of the extractions have been made with material dried at 221 F for 1 hour. An ash analysis is also made.

Typical results from the 0.2 tph testing are shown in Tables 1 through 3, which summarize the test conditions and product composition from four tests made with the 4-on-1 injector.

Carbon conversion results from the 0.2 tph testing are shown in Fig. 8, which shows overall and gas conversions. Results are shown from tests made with a basic reactor size of 1.402 inch diameter x 36 inch long and also with 0.995 inch diameter x 36 inch, 1.995 inch diameter x 36 inch and 1.402 diameter x 18 inch reactors. Thus, the reactor residence time was increased and decreased by a factor of 2.0 from the base case. The overall conversion has been calculated with the ash in the coal being used as a tracer. In most cases the ash recovery was in the range of 90 to 100 percent. The overall conversions appear to vary most strongly with temperature and residence time, while changes in the location of oxygen addition (preburner or reactor) and injector (concentric tube or 4-on-1) had relatively small effects. The effect on conversion to gas of changing the location of oxygen addition was significant. The increase in gas formed with oxygen addition in the reactor appears to result from oxidation of liquid products.

Carbon conversion to liquids is shown in Fig. 9. Not all of the carbon was recovered during many of the tests. This lost material is believed to be liquid, probably a mist of small droplets not removed by the cyclone separator and settling tank. Some tarry material was recovered from the gas sample bottles but the accuracy of that sample is not sufficient for it to be used to account for the carbon deficit. Tar quantities ranging from a few milligrams to a few grams have been obtained while samples in the middle of this range would account for the loss. The carbon fraction corresponding to the liquid obtained by benzene extraction of the char and tar removed from the separators is shown in Fig. 9 along the fraction inferred by difference. The carbon deficit is shown in Fig. 10.

Current effort is directed toward improving the carbon recovery and preparation for reactor testing at 1 tph.

CONCLUSIONS

Results from the testing are regarded as highly significant and encouraging. Effective methods of feeding the coal and of injection and mixing of the hydrogen and coal have been developed. Significant progress has been made on developing the desired reactor process and feasibility has been demonstrated. For comparable flowrates, the size of this reactor is several orders of magnitude smaller than some of the other liquefaction reactors being developed.

The test results indicate high overall conversion, approaching that required for a balanced plant operation. Liquid yields also appear high, although the lack of total recovery leaves some uncertainty.

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TABLE 1. TEST CONDITIONS FOR TYPICAL TESTS

Test Number	Total Coal, lbm	Duration, seconds	Flowrates, lbm/sec			Average Temperatures, F			Injector
			Coal	H ₂	O ₂	Wall	Reactor	Calculated Reactor	
23	19.7	234	0.084	0.0383	0.0226	1780	1780	1830	4-on-1 ↓
24	15.6	210	0.074	0.0380	0.0230	1820	1700	1920	
25	17.0	155	0.110	0.0372	0.0149	1430	1400	1590	
26	19.2	240	0.080	0.0386	0.0196	1550	1500	1770	

NOTES: (1) Tests 23, 24, and 26 were made with oxygen injection in the reactor.
(2) Test 25 was made with oxygen injection in the preburner.
(3) Calculated reactor temperatures correspond to mixing with no heat of reaction.

TABLE 2. COMPOSITION OF COAL, CHAR AND LIQUID PRODUCT FROM TYPICAL TESTS

Constituent	Composition, percentage by weight					
	Coal	Raw Char				Benzene Extractable Material
		Test 23	Test 24	Test 25	Test 26	
Moisture	2.05	2.83	5.96	7.49	5.17	85.70 5.67 1.08
Ash	10.56	18.54	18.95	14.71	15.89	
Carbon	69.25	69.97	67.15	67.94	71.01	
Hydrogen	4.87	2.82	2.64	2.78	2.66	
Nitrogen	1.46	0.58	0.71	1.38	0.95	
Chlorine	0.01	0.01	0.01	0.02	0.01	
Sulfur	4.26	3.28	3.11	3.16	2.65	
Oxygen (Diff.)	7.54	1.97	1.47	2.52	1.66	
Benzene Extractable Fraction	0.5	15.5	9.9	18.3	23.2	

TABLE 3. COMPOSITION OF PRODUCT GAS FROM TYPICAL TESTS

Component	Mole Fraction, percent			
	Test 23	Test 24	Test 25	Test 26
N ₂	2.6	0.9	1.3	2.5
H ₂	89.4	91	93	89
CO	4.7	3.4	0.3	1.8
CO ₂	0.2	0.2	0.1	0.1
CH ₄	2.2	4.0	1.6	1.1
C ₂ H ₄	-	<0.1	<0.1	<0.1
C ₂ H ₆	0.2	0.1	0.4	0.2
C ₃ H ₈	-	-	<0.1	-
C ₄ H ₁₀	-	-	-	-
Benzene	7.7(10 ⁻⁴)	7.3(10 ⁻⁴)	2.5(10 ⁻⁴)	5.1(10 ⁻⁴)
Toluene	3.8(10 ⁻⁵)	1.3(10 ⁻⁵)	1.3(10 ⁻⁴)	4.8(10 ⁻⁵)
Xylene	-	-	2.8(10 ⁻⁵)	1.2(10 ⁻⁶)

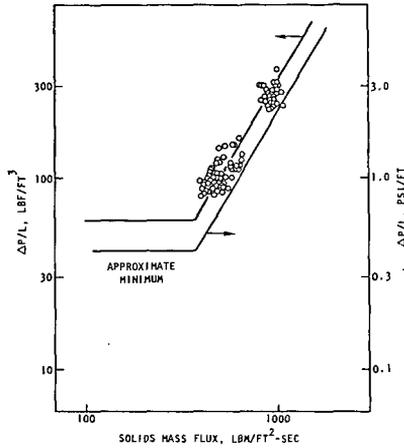


Figure 1. Measured Transport Line Pressure Gradient Obtained From Mixing Test Facility

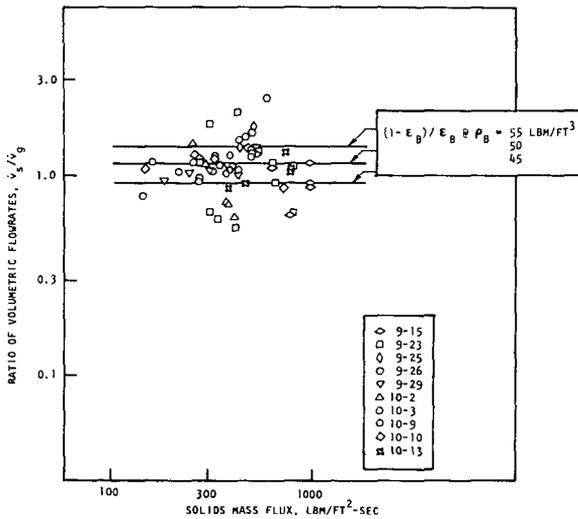


Figure 2. Ratio of Solid-to-Gas Volumetric Flowrates Obtained From Transparent Feeder Data

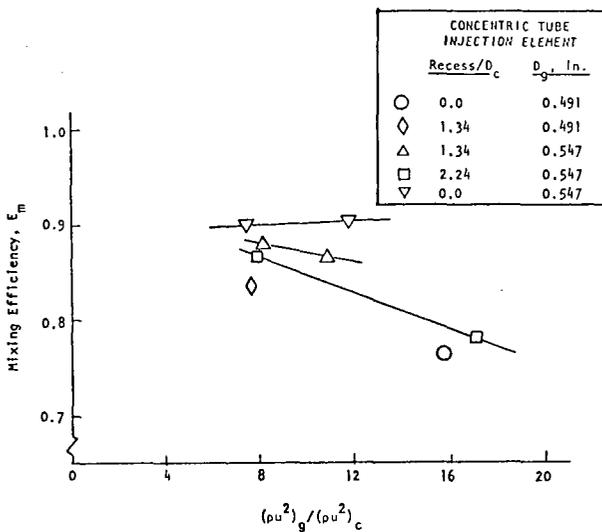


Figure 3. Cold-Flow Mixing Results From Concentric Tube Injection Elements

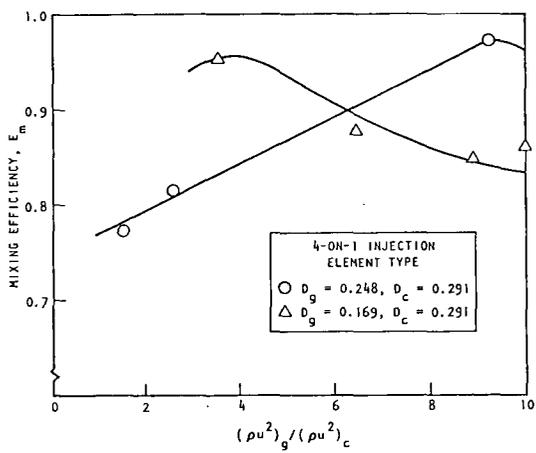


Figure 4. Cold-Flow Mixing Results From 4-on-1 Injection Elements

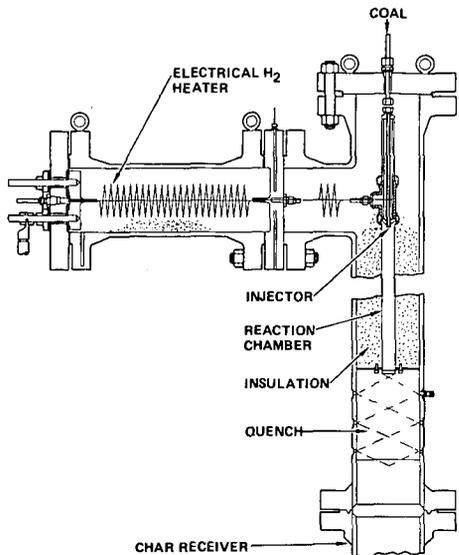


Figure 5. Schematic Diagram of 0.2-tph Reactor Assembly

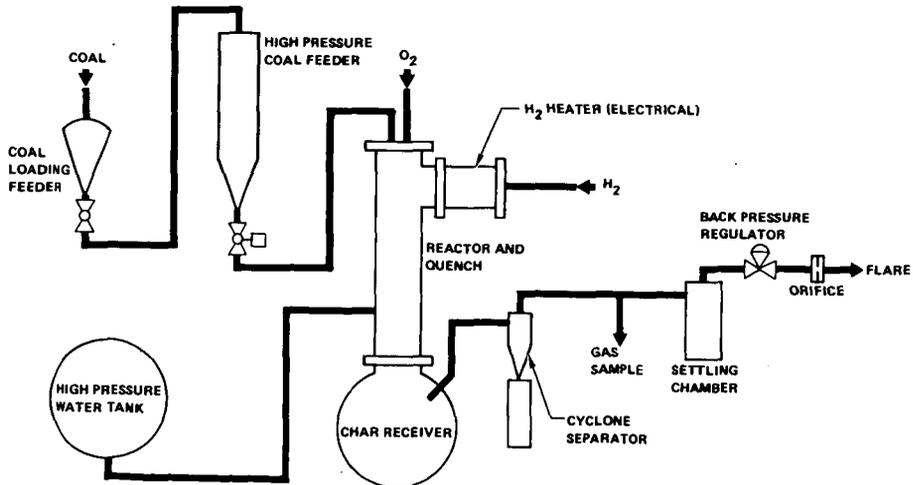


Figure 6. Flow Diagram of 0.2-tph Reactor Test System

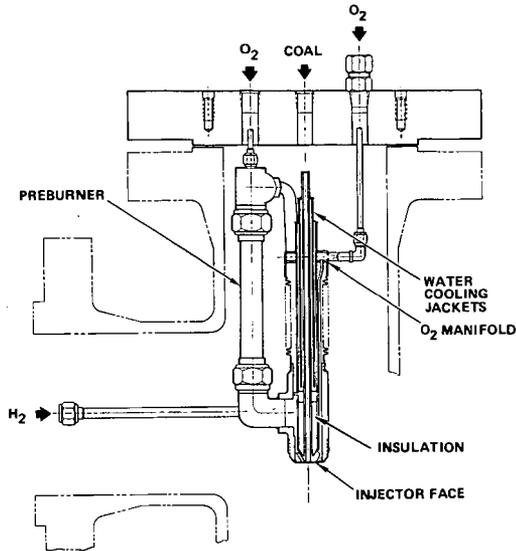


Figure 7. 0.2-tph 4-on-1 Injector and Preburner With Oxygen Injection Capability

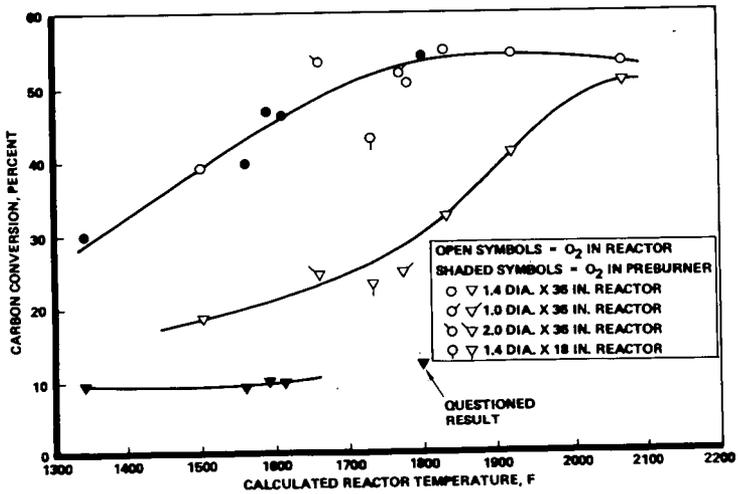


Figure 8. Carbon Conversion Results From 0.2-tph Reactor Testing

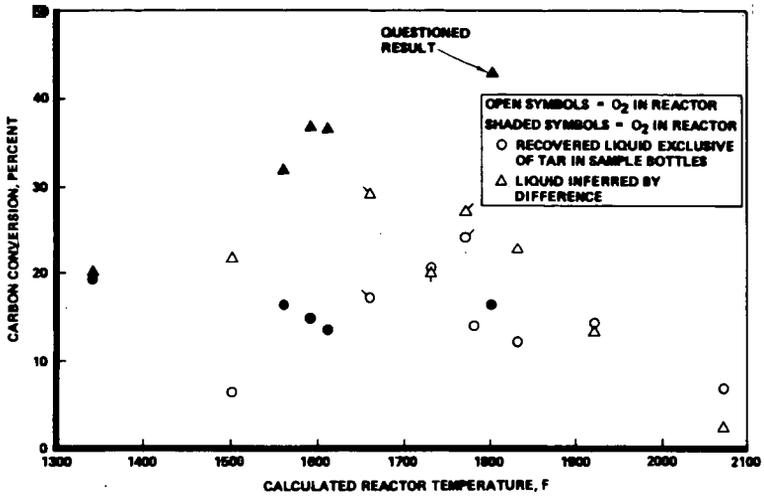


Figure 9. Carbon Conversion to Liquids From 0.2-tph Testing

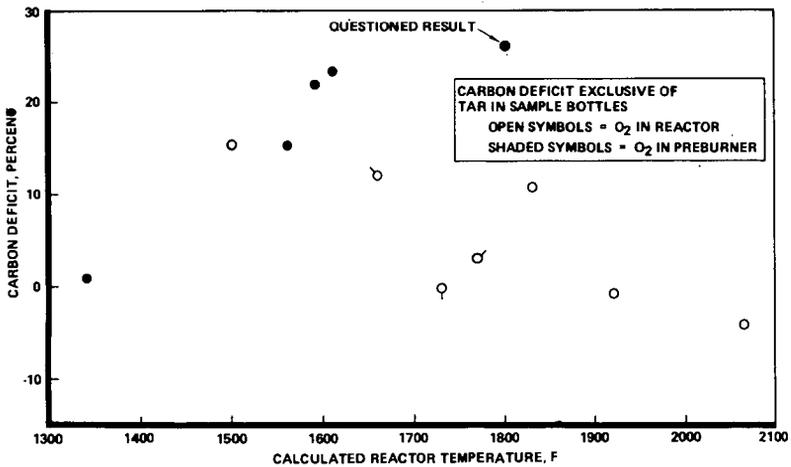


Figure 10. Carbon Deficit in Products From 0.2-tph Testing

Gasification of Iowa Coal in the SYNTHANE PDU Gasifier

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Introduction

Vast deposits of high sulfur caking coals found in the eastern and midwestern United States can be converted to clean gaseous energy by gasification. In the 1980's many coal gasification plants are expected to be constructed in the United States to produce a high-Btu gas as a supplement to the dwindling supply of natural gas. One important consideration in the development of a coal gasification process is the acceptability of various coal feedstocks. The SYNTHANE process is one such process for the manufacture of high-Btu gas from coal. This report demonstrates the capability of using the SYNTHANE process for the gasification of the mildly caking high sulfur₉ coal from Iowa. This coal is not only present in substantial reserves (7.2×10^7 tons) (1) but is also convenient to the large energy markets of the Midwest. The Iowa coal for this study is from the Iowa Coal Project Demonstration Mine #1 of Iowa State University. This coal bed is located in the southwest corner of Mahaska County and is part of the Cherokee Group.

Experimental Equipment

A schematic flow diagram of the SYNTHANE PDU gasification system is shown in figure 1. This system combines the steps of fluidized-bed pretreatment, free-fall carbonization and fluidized-bed gasification. The pretreater is an 8-foot long, 3/4-inch diameter pipe with a 2-1/2-foot long, 1-inch diameter expanded zone. Both sections of pipe are schedule 80 and made of 304 stainless steel. The pretreater is enclosed by four individually controlled heaters that supply heat for startup and to counter radiation losses. The carbonizer is a 6-foot long, 10-inch diameter schedule 40 pipe made of 304 stainless steel located directly above the gasifier. Electric heaters surrounding the carbonizer maintain the temperature at 1000° F. The gasifier is a 6-foot long, 4-inch diameter schedule 40 pipe made of 310 stainless steel. Surrounding the gasifier is a 10-inch schedule 40 pipe made of 304 stainless steel which acts as a pressure shell. In the annulus three individually controlled electric heaters, wrapped in a 2-inch thick blanket of insulation, supply heat for startup and to counter radiation loss during operation. A 1/8-inch pipe entering the base of the gasifier serves as the gas distributor. A thermowell made of 3/8-inch pipe located in the center of the gasifier extends from 1-inch above the gas distributor to the top of the carbonizer. Twelve thermocouples inserted into the thermowell detect internal temperatures from the base of the gasifier to the top of the carbonizer. A variable speed extractor screw located at the base of the gasifier maintains the bed height by removing reacted char. The raw product gas leaving the top of the gasifier is filtered to remove fine particles and cooled in a series of two water-jacketed condensers. Effluent water and tar are collected in a receiver. The dry gas is then analyzed by mass spectrometric and chromatographic methods prior to metering the flow rate.

Experimental Procedure

The caking Iowa coal (analysis shown in table 1) was crushed and sized to an average size of 240 microns with a U.S. Standard mesh range of 20 X 0. The pulverized coal was fed to the base of the pretreater under pressure (40 atm) at a rate of about 20 lb/hr. The coal then moved through the pretreater in a fluidized state with nitrogen

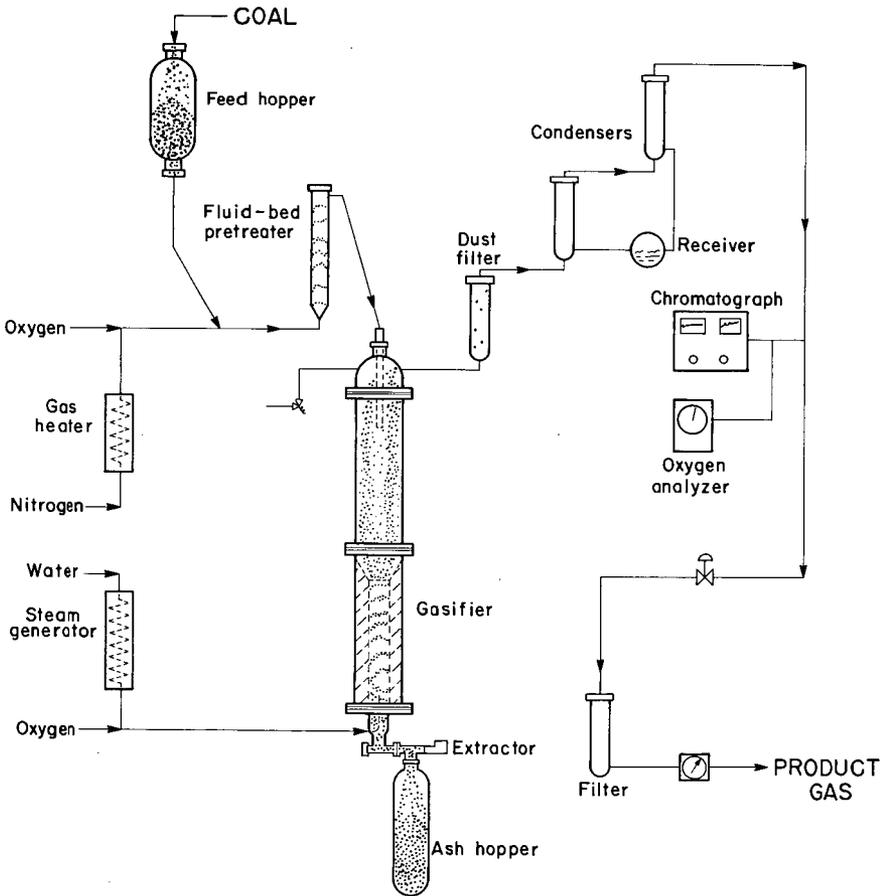


Figure 1-SYNTHANE PDU GASIFIER.

10/6/76 L-15077

and oxygen. The pretreating conditions were the same as those developed for the pretreatment of Illinois No. 6 coal as reported by Gasior (2). The decaoked coal emptied from the top of the pretreater and was gravity fed into the gasifier through the carbonizer, countercurrent to the exiting product gas. A mixture of steam and oxygen entering the base of the gasifier provided both the reactant and fluidizing gases. Gasifier temperatures were maintained by varying the flow rate of oxygen to the reactor. A fluidized-bed height of about 68 inches was maintained by adjusting the char extraction rate to coincide with the coal feed and gasification rates.

Discussion and Results

The operating conditions and results for the three experimental gasification tests are shown in table 2. Coal feed rates for these tests ranged from 17.6 to 19.9 lb/hr, which are equivalent to coal throughputs of 37.4 to 42.4 lb/hr ft³ of gasifier volume. Average gas inputs of 0.35 lb oxygen/lb coal and 1.8 lb steam/lb coal resulted in a superficial gas velocity of 0.29 ft/sec at 40 atmospheres pressure in the 4-inch gasifier. No difficulty was experienced in maintaining temperature control in the fluidized-bed with the average of the maximum gasifier temperatures ranging from 1761° to 1832° F, and no slag-sintering problems occurred at peak gasifier temperatures of 1850° F.

The results of the three tests showed that carbon conversions ranged from 77.0 to 80.2 percent and steam conversions or decomposition ranged from 14.3 to 16.9 percent. Raw gas analysis showed that the hydrogen sulfide yield was 0.77 SCF/lb coal, maf, for the 8 percent sulfur coal, while product gas yields ($H_2 + CO + CH_4 + C_2H_6$) averaged 13.6 SCF/lb coal, maf, with equivalent methane yields ($CH_4 + C_2H_6$) ranging from 3.45 to 3.60 SCF/lb coal, maf.

Comparing test results using Iowa coal to similar test results using Illinois No. 6 coal, as reported by Forney (3), the Iowa coal results showed higher carbon conversions (78.6 vs. 71.8 percent), lower product gas yields (13.6 vs 14.9 SCF/lb coal, maf) and higher hydrogen sulfide yields (0.77 vs. 0.36 SCF/lb coal, maf). The higher temperature accounted for the high carbon conversion while the high sulfur content of the coal resulted in high hydrogen sulfide yields and slightly lower hydrogen yields. The high steam to coal ratio (1.8/1) resulted in a high hydrogen to carbon monoxide ratio (3.3/1). Calculations indicate that shift equilibrium for all tests is achieved between the average temperature and the temperature at the top of the bed. The high hydrogen to carbon monoxide ratio would eliminate the need for a shift reactor and can be controlled to give the desired ratio for methanation (~3.05/1) by adjusting the steam to coal ratio.

Table 3 shows the distribution of sulfur forms in the coal and char. Sulfur forms are determined by extraction of the coal and char samples with hydrochloric and nitric acids. The analysis and a weight balance between the coal fed and char produced indicates that most of the sulfur in the coal is converted to hydrogen sulfide and trace sulfur compounds in the gas and tar. About 0.7 weight percent of the sulfate sulfur, 0.3 weight percent of pyritic sulfur and 26.9 percent of the organic sulfur found in the coal remain in the char after gasification. Pyritic sulfur is easily removed by its reaction with hydrogen. (4) The sulfate sulfur is also converted to hydrogen sulfide.

As shown in table 4, there are a number of trace sulfur compounds in addition to the large quantities of hydrogen, carbon monoxide, carbon dioxide, methane, ethane and hydrogen sulfide produced in the gasifier. These trace compounds are separated from the product gas by cryogenic distillation and by measured mass spectrometric analysis. The product gas contains 3.2 volume percent sulfur compounds and would require a sulfur clean up prior to methanation.

The analysis and fusibility of ash for Iowa coal and char are shown in table 5. Certain compounds contained in the ash of coals undoubtedly contribute to the carbon conversion, gasification rates, the quantity and the quality of gas produced. (2, 5, 6) According to Grossman (7) and Ely (8) iron is the major contributor in lowering the fusion temperature of coal ash under reducing conditions. Gasior (2) also found that coals having the greatest percentage of calcium and magnesium compounds have the lowest sintering temperature. Results of these Iowa coal gasification tests appear to confirm these findings since no sintering was observed.

The major effluent problem associated with the steam-oxygen gasification of Iowa coal is the unreacted steam leaving the gasifier as contaminated water condensate. The analysis of this water is shown in table 6 along with a coke plant water analysis for comparison. The amounts of the contaminants vary greatly, but the cyanide and thiocyanate content of the gasification effluent is much smaller than in the coke plant effluent while the phenol and COD content are greater. It is believed that the high steam partial pressure in the SYNTHANE gasifier causes conversion of nitrogen compounds to ammonia. Coke plant water pollution has been alleviated to some extent (9), but some problems still remain. The Iowa coal effluent water analysis shows no significant difference from other reported analyses of SYNTHANE effluent waters. (10)

A coal tar byproduct is also produced from the gasification of Iowa coal. This tar leaves the gasifier as a vapor with the unreacted steam and is easily separated from the effluent water condensate by decanting. The tar is heavier than water and negligible amounts of a lighter-than-water phase are produced. Table 7 shows the analysis and physical properties of the tar produced. For the gasification of Iowa coal, tar yields averaged 7.3 percent of the coal fed, compared to 4.0 percent for Illinois No. 6 coal. Gasior (2) and Nakles (11) have found that feeding the coal below the top of the fluidized-bed can significantly reduce the tar yield. A simulated ASTM distillation of this tar shows that less than 50 percent of the tar boils below 940° F. The high percentage of sulfur (3.2%), however, could drastically limit the direct use of these tars as a fuel. With an effective desulfurization process, the desulfurized tar could be used as a nonpolluting boiler fuel or an oil refinery feedstock.

Conclusions

Overall results from an exploratory study to gasify a mildly caking, high sulfur Iowa coal in the SYNTHANE PDU gasifier have shown that carbon conversions of 80 percent and steam conversions of 16 percent can be achieved at average maximum gasifier temperatures of 1832° F and coal throughputs of 40 lb/hr ft². These results confirm published findings that coals having the largest amount of calcium and magnesium compounds have the lowest sintering temperatures and that the amount of sulfur in the tar and gaseous products is generally related to the amount of sulfur in the coal. The effluent water shows no significant difference from other SYNTHANE gasifier condensates, and is generally similar to coke-oven byproduct water.

Acknowledgment

We especially thank F.R. Schmidt, Metallurgist of ERDA's Ames Laboratory, Iowa State University, Ames, Iowa who provided the coal used in these experiments and performed the coal and char analyses required for the material balance calculations.

Table 1. - Analysis and free-swelling index of Iowa coal

Class	High-Volatile C
Analysis (as received), %	
Moisture	2.9
Volatile Matter	36.2
Fixed carbon	41.2
Ash	19.7
Hydrogen	4.4
Carbon	59.2
Nitrogen	0.8
Oxygen	8.0
Sulfur	7.9
Free-swelling index	1.5

Table 2. - Operating conditions and results for Iowa coal gasification tests in a fluidized-bed at 40 atmospheres pressure

Test No.	209	210	211
Operating time, hrs.	6.0	6.0	6.0
Coal feed rate, lb/hr	17.6	19.5	19.9
lb/hr ft ³ gasifier	37.4	67.0	68.0
Bed height, in.	68.4	67.9	68.0
Steam rate, lb/hr	35.3	35.1	35.3
Oxygen rate, SCFH	75.5	81.5	76.9
Temperature, °F			
peak	1844	1850	1850
average maximum	1761	1832	1832
average	1664	1691	1702
top of bed	1572	1576	1601
Superficial gas velocity at avg. max. temp., ft/sec	0.28	0.29	0.29
Yields and conversions			
Carbon conversion, weight percent	80.2	77.0	78.6
Steam decomposition, weight percent	14.3	15.4	16.9
Product gas ^{1/} yield, SCF/lb coal, maf	13.7	13.5	13.6
Equivalent methane ^{2/} yield, SCF/lb coal, maf	3.60	3.53	3.45
Tar yield, % of coal ^{3/} fed	7.6	7.0	7.4
Product gas analysis, dry, N ₂ free (%)			
H ₂	33.6	33.2	33.7
CO	9.2	10.3	10.7
CH ₄	11.9	12.1	11.9
CO ₂	40.7	39.8	39.1
C ₂ H ₆	1.4	1.4	1.4
H ₂ S	3.2	3.2	3.2

^{1/}H₂ + CO + CH₄ + C₂H₆.

^{2/}CH₄ + C₂H₆.

^{3/}As received after air drying.

Table 3. - Distribution of sulfur forms in Iowa coal and char and the sulfur conversion

	<u>Sulfate</u>	<u>Pyritic</u>	<u>Organic</u>
% S in Coal	0.41	5.18	2.35
% S in Char	0.01	0.05	2.55
lb char/lb coal	0.29	0.28	0.26
% Converted	99.3	99.7	73.1

Table 4. - Trace components in dry product gas^{1/} from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres pressure

Test No.	209	210
Hydrogen Sulfide	11,040	12,000
Carbonyl sulfide	250	250
Methyl mercaptan	<5	<5
Thiophene	<5	<5
Sulfur dioxide	-	-
Benzene	100	N.D. ^{2/}
Toluene	100	N.D. ^{2/}
Xylene	-	-

^{1/}All values in ppm by volume.

^{2/}Not determined.

Table 5. - Analysis and fusibility of ash^{1/} of Iowa coal and char

<u>Major Elements in Ash</u>	<u>Coal, %</u>	<u>Char, %</u>
SiO ₂	35.4	34.1
Al ₂ O ₃	14.0	14.7
Fe ₂ O ₃	39.5	44.0
TiO ₂	0.8	0.6
CaO	3.6	2.8
MgO	0.4	0.3
Na ₂ O	1.3	0.4
K ₂ O	0.9	0.7
SO ₃	1.5	0.1
Fusibility of ash, °F		
Initial deformation temp.	1900	1930
Softening temperature	1950	1980
Fluid temperature	2040	2030

^{1/}Staff, Office Director of Coal Research Methods of Analyzing and Testing Coke and Coal, BuMines Bull. 638, 1967, 82 pp.

Table 6. - Effluent water analysis^{1/} from the fluidized-bed gasification of Iowa coal with steam_{2/} and oxygen at 40 atmospheres pressure^{2/}

Test No.	209	210	211	Coke Plant
pH	9.0	9.2	9.1	9.0
Suspended solids	6	16	15	50
Phenol	2060	2340	2180	2000
COD	14500	17400	16800	7000
TOC	4600	4970	4850	N.D. ^{3/}
Thiocyanate	108	129	135	1000
Cyanide	0.029	0.027	0.122	100
Chloride	22	40	118	N.D. ^{3/}
Ammonia	N.D. ^{3/}	N.D. ^{3/}	N.D. ^{3/}	5000

^{1/}Standard method for the examination of water and waste water according to the American Public Health Association; American Water and Waste Water Association, and Water Pollution Control Federation, 13th Edition, 1971.

^{2/}All values in ppm except pH.

^{3/}Not determined.

Table 7. - Product tar analysis and physical properties of dewatered tar from the fluidized-bed gasification of Iowa coal with steam and oxygen at 40 atmospheres

Test No.	210	211
Ultimate analysis of tar, ^{1/} weight percent		
C	83.7	83.8
H ₂	6.6	6.4
N ₂	0.9	1.0
S	3.2	3.2
O	5.6	5.6
Benzene insolubles, weight percent	0.8	1.1
Viscosity, SSU @ 180° F ^{2/}	132	152
Specific Gravity @ 60/60° F ^{3/}	1.151	1.150
ASTM Distillation, weight percent boiling/°F	48.8/940°	40.2/928°

^{1/}ASTM D271.

^{2/}ASTM D88.

^{3/}ASTM D70.

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CHEMICAL BOND CLEAVAGE DURING ASPHALTENE FORMATION¹

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An important question arising from experiments involving coal liquefaction processes is "which bonds are broken when solid coal is converted to liquids, or to soluble oils, asphaltenes, and preasphaltenes?" In earlier work² it was proposed that ether linkages were cleaved and hydrogenolysis occurred during treatment of coal with hydrogen-donor solvents at elevated temperatures. Thus, a limited number of model ether structures were shown to break in the presence of tetrahydroquinoline at 309°. It was also reported^{2,3} that solubilization could not be due to cleavage of single methylene bridges in coal. However, structures containing one methylene group in the bridge, such as diphenylmethane, are stable under the above conditions.

We presented data in a recent manuscript⁴ showing that other structure types undergo thermolysis under the conditions of asphaltene formation. A variety of diaryl- and triarylethanes and ethylenes were found to cleave at the central C-C bond; the derived products were characterized. Certain ethers were found to cleave accompanied by the formation of water.

We have now investigated a large variety of compounds containing structural linkages chosen, partly, from coal models suggested by Given,⁵ Weiser,⁶ and Hill and Lyon.⁷ Some bond types appear to cleave rapidly, others with difficulty, and some not at all. These compounds are arranged in groups and their relation to coal liquefaction is considered. Examples of bonds which break easily are those attaching large groups to the aromatic nucleus of phenols and phenol ethers. Parabenzylphenol is rapidly converted, principally, to toluene and phenol with a little benzene and *p*-cresol. Several products are produced from phenylethyl ether; benzene, toluene, ethylbenzene, phenol, ethane, ethylene, and water.

Implicit in a portion of the above discussion is another important question relating to the structural units in coal. For example, "does it contain any isolated, nonaromatic double bonds?" Hydrogen nmr does not show olefinic structure and carbon nmr is ambiguous. Our solution is based on the stitching and riveting reactions developed by H. C. Brown.⁸ Vitrinite, or a pyridine-soluble fraction of it, was reacted with diborane. Then the hydroborated coal was converted to a trialkylborane derivative by treating it with ethylene gas. Any trialkylborane formed within the coal structure was finally converted to a radioactive-labeled ketone by treatment with radioactive carbon monoxide, or with labeled cyanide ion, followed by hydrolysis. A determination of the specific carbon-14 activity enabled us to calculate the number of double bonds originally present. We are presently applying the above technique to other coal-derived materials. A summary of our data follows:

<u>Sample</u>	<u>Radio. Equiv., Wt.</u>	<u>No. of Carbons Per Double Bond</u>
Vitrinite (Ill. #6)	7300 g.	498
Pyridine-soluble Vitrinite	1500 g.	102
Blank	61000 g.	

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ISOPROPYL ALCOHOL AS A COAL LIQUEFACTION AGENT

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The use of Tetralin and similar H-donor solvents in the hydroconversion of coal to liquid fuels is well known (1), and is important in large-scale coal conversion processes (2). We present here evidence that isopropyl alcohol can act as an H-donor solvent, yielding products similar to those generated in Tetralin-based systems. Contrary to the case for Tetralin, it appears that the action of the isopropyl alcohol can be promoted by the presence of bases. This report presents initial data from a research program still in progress; a full account of the work will be presented in a subsequent manuscript.

EXPERIMENTAL PROCEDURES

The experiments described here were carried out in a 300-ml MagneDrive, stainless steel autoclave from Autoclave Engineers. The substrate was beneficiated Illinois No. 6 coal supplied by Pennsylvania State University (PSOC 26), and ground under nitrogen in a ball mill to -60 mesh. In each run, 5-g samples of the coal were used, in addition to 75 to 150 g of alcohol solvent. These experiments were run at 335°C for 90 min, with typically 45 min heat-up and 60 min cool-down periods. No hydrogen was used in any of the experiments described, and the pressures are those generated by the solvents themselves. The reaction temperature of 335°C was above the critical temperatures of the alcohols used.

In these experiments the product mixture was filtered, the residue washed with more solvent until the washings were colorless, and the filtrate recovered by evaporation of the solvent under vacuum. For those cases in which alkoxide salts were used, all fractions were appropriately neutralized with concentrated HCl. Both the filtrate and residue were then dried to constant weight at 110°C under < 1 torr pressure. Mass balances were generally greater than 95%. In all cases the isolated filtrate was found to be fully pyridine-soluble. Pyridine solubilities of the residues were determined at room temperature, with 0.5 g of a product coal fraction stirred for 1 hr in 50 ml pyridine. The pyridine solubilities of the residues were established for all cases and recorded as the fraction of the residue soluble in pyridine. For some cases, it was convenient to refer to the composite pyridine solubilities and elemental composition values, that is, these values for the entire coal sample. In these instances the individual values for both the filtrates and residues were appropriately summed and recorded.

H_{al}/H_{ar} ratios were obtained from the proton NMR spectra, which were run on a Varian EM 360 spectrometer using nearly saturated solutions of sample in pyridine- d_5 or CS_2 /pyridine- d_5 mixtures. The SRC used was supplied by Catalytic, Inc., Wilsonville, Alabama, sample number 16573, derived from an Illinois No. 6 coal and processed to K109 SRC specification.

RESULTS AND DISCUSSION

Autoclave Experiments

The results of a series of experiments run at 335°C with a number of solvents are summarized in Table 1. The figures for the pyridine solubilities and elemental analyses are composite values, calculated from the respective values for both the filtrate and residue from each run.

Table 1
TREATMENT OF BENEFICIATED ILLINOIS NO. 6 COAL
AT 335°C FOR 90 MINUTES^a

Run No.	Conditions ^b	Pyridine ^c Solubility (%)	Elemental Analyses ^d			
			H/C (molar)	O/C (molar)	N (%)	S (%)
-	Untreated coal	17	0.79	0.117	1.58	2.20 ^e
21	iPrOH ($\rho = 0.5$)	50	0.81	0.086	1.63	1.82
53	iPrOH + Al(OiPr) ₃ ^f ($\rho = 0.3$)	61	0.87	0.073	1.64	1.81
54	iPrOH + K(OiPr) ^g ($\rho = 0.3$)	97	0.95	0.090	1.69	0.11
62	iPrOH + K(OiPr) ^g ($\rho = 0.3$)	89	0.83	-	1.33	-
36	tBuOH ($\rho = 0.2$)	13	-	-	-	-
61	tBuOH + K(OtBu) ^f ($\rho = 0.5$)	12	-	-	-	-
48	Tetralin ^h	48	0.81	0.079	1.58	1.83

^aNo hydrogen is added to the system; the pressure during a run is in the range of 2000 psi, and due only to the vapor pressure of the medium. The starting coal has been beneficiated to about 2% ash.

^bSince 335°C is above the T_c of both alcohols, the amount of solvent present is expressed as ρ , the number of g of alcohol per ml of reactor volume (285 ml).

^cSolubility of recovered material in pyridine, based on ash free weight of the starting coal. Composite values, as discussed in the text.

^dAsh-free basis. Composite values, as discussed in the text.

^eThis value represents the organic sulfur in the starting coal.

^f1 g metal alkoxide/5 g coal was used.

^g0.5 g potassium salt/5 g coal was used.

^hThe critical temperature of Tetralin is $484 \pm 32^\circ C$. Thus the medium here was subcritical.

The table shows that the untreated coal has a pyridine solubility of 17%. In Run 21, in which the coal is treated with isopropyl alcohol, the resulting product coal displays a solubility in pyridine of 50%. This result is clearly significant, and is comparable to the results for a similar experiment with Tetralin, Run 48,

where the resultant coal product shows a 47% pyridine solubility. The surprising similarity of the elemental analyses for the products in both cases leads us to conclude that, like Tetralin, isopropyl alcohol acts as an H-donor under these conditions.

An alternative possibility is the introduction of isopropoxy groups to the coal, which would possibly increase both the solubility and the H/C ratio. This route is most likely ruled out for Run 21, however, on the basis of the decrease in the O/C ratio with respect to the starting coal.

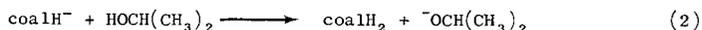
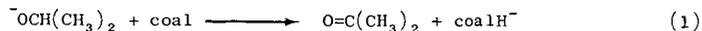
This point is confirmed by the results of Run 36, where t-butyl alcohol was used. The structural differences between isopropyl and t-butyl alcohols are insignificant for work at these temperatures, and if alkoxylation were important, it would take place with both alcohols. The pyridine solubility of the product coal from the t-butyl alcohol experiment, however, is somewhat less than that of the starting coal, and significantly less than the results for Runs 21 and 48. These data thus support our contention that for the isopropyl alcohol case no incorporation of solvent into the coal has taken place. On the other hand only the isopropyl alcohol can provide hydrogen, perhaps as hydride, as discussed below. The large difference in the results is thus consistent with H-donation by isopropyl alcohol.

These results suggest a similarity in general mechanism to the known Meerwein-Ponдорff reduction of carbonyl groups with isopropoxide salts, most commonly aluminum isopropoxide in isopropyl alcohol (3). In this reaction hydride ion from the oxygen-bearing carbon in the alcohol is transferred to a carbonyl group, thereby reducing it. To test this possible mode of reaction, aluminum isopropoxide was added to the reaction mixture in Run 53 and potassium isopropoxide was added in Run 54.

For Run 53, the product is 61% soluble in pyridine, somewhat enhanced relative to the value for isopropyl alcohol alone. For the potassium isopropoxide case the result is striking. The product coal is essentially fully pyridine-soluble, and additionally, the organic sulfur in the coal has been reduced to the low value of 0.41%.

While these data strongly support a hydride transfer process, it might be proposed that the results were due to some kind of base-promoted dissolution. This possibility was eliminated by the data from Run 61, in which potassium t-butoxide in t-butyl alcohol was used. Here the result is little different from that for t-butyl alcohol alone.

Thus it can be concluded that isopropyl alcohol can act as an H-donor solvent for coal conversion in a process involving hydride transfer from the alcohol, or alkoxide salt, to the coal. The net transfer of H₂ to the coal could involve a chain process, such as



in which the alkoxide ion is regenerated with each cycle, H_2 has been transferred to the coal, and acetone is formed. The formation of acetone has in fact been confirmed qualitatively, and experiments are currently under way to assess the quantitative nature of the process.

Product Characterization

While we have written reaction (2) with the notation $coalH_2$, we do not wish to imply that simple hydroaddition to multiple bonds has necessarily occurred. The question of the specific site of hydrogen reaction remains open, and it is of interest to establish the degrees to which hydroaddition and hydrocracking have taken place.

Accordingly, it is convenient to look at our product data in more detail, namely in terms of the separated fractions of the product coal. Table 2 presents data for the fraction of the starting coal isolated from the solvent after reaction, the H/C and H_{al}/H_{ar} ratios for that fraction, the H/C ratio of the residue, and the solubility of the residue in pyridine. Also given are H_{al}/H_{ar} for the starting coal, for the residue from the potassium isopropoxide experiment, and for an Illinois No. 6 SRC. The values for pyridine solubility of the residue are given as the fraction of the residue soluble in pyridine. For example for Run 21, of the starting 5 g of coal, 1.0 g, or 20%, was recovered from solution in isopropyl alcohol at the end of the run. Of the remaining 4.0 g of residue, 1.5 g, or 37.5% was soluble in pyridine.

Table 2
ILLINOIS NO. 6 COAL WITH VARIOUS MEDIA
AT 335° FOR 90 MINUTES

Run No.	Medium	Filtrate ^a			Residue		
		Fraction of Starting Coal ^b (%)	H/C	$\frac{H_{al}}{H_{ar}}$	H/C	$\frac{H_{al}}{H_{ar}}$	Pyridine Solubility ^c (%)
Untreated coal	-	-	-	-	0.79	5.2 ^d	17.0
25	Heptane	1.7	1.20	3.2	0.79	-	6.9
48	Tetralin	17.5	0.95	2.2	0.79	-	35.8
21	i-Propyl alcohol	20.0	0.95	2.1	0.78	-	37.5
54	KO _i Pr/ i-propyl alcohol	40.0	1.08	3.4	0.87	1.8	95.0
SRC	-	-	-	-	0.75	1.2	99.0 ⁺

^aThe solubilities of the untreated coal in the media are $\leq 1\%$ for all cases.

^bThese values represent the solubilities of the resultant coal products in the respective media. The filtrates were found to be completely pyridine soluble in all cases.

^cThese values represent the fraction of the isolated residue soluble in pyridine.

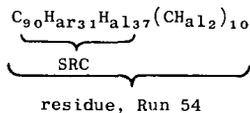
^dG. Hill, H. Hariri, R. Reed, and L. Anderson, *Advances in Chemistry Series 55*, 427 (1966).

Results for an experiment with heptane (Run 25) are presented in the table for comparison. Clearly the heptane run did not result in much coal dissolution, nor did the residue display any unusual behavior.

For Runs 48 and 21, however, with Tetralin and isopropyl alcohol, respectively, about a fifth of the starting coal is converted to material soluble in the media themselves, and the H/C ratios are enhanced. The residues for both cases have also undergone chemical change. For both the Tetralin and the alcohol experiments the residues are 35-40% pyridine-soluble. The H/C values for these fractions, however, are essentially the same as that for the starting coal. Thus it would appear that, for both solvents, a chemical process is taking place that (1) adds hydrogen to some fraction of the coal, converting it to material soluble in the respective media, and (2) generates a residue with a large pyridine solubility, but with no significant increase in hydrogen content.

The results for Run 54 with potassium isopropoxide show that 40% of the starting coal is converted to a product soluble in the reaction medium. That fraction is considerably enriched in hydrogen, and a substantial fraction of the added hydrogen is aliphatic, comparable to the small quantity of material isolated from the filtrate of the heptane experiment. The residue in this case is essentially fully pyridine-soluble and, in contrast to those for Runs 21 and 48, has been enriched in hydrogen. The H/C and H_{al}/H_{ar} data are reasonably similar to those shown in the table for SRC, although it is clear that our product has more overall aliphatic character than the SRC. Both are also considerably more aromatic in character than the starting coal, although the H_{al}/H_{ar} value for the coal is for an "average coal" and is probably only a rough, semiquantitative value of the ratio for our starting coal.

If just the hydrogen and carbon contents are considered, the values for both the Run 54 residue and the SRC permit the calculation of an average molecule for both. Interestingly, the data for both can be accommodated by



This result includes number average molecular weight data in the range 1000-1300, which we have obtained for both materials. It appears that the two may be simply related, with additional polymethylene bridges, or hydroaromatic components, present in our product. The implications of this result await further study.

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HYDRODESULFURIZATION IN THE SOLVENT REFINED COAL PROCESS

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The Solvent Refined Coal (SRC) process is currently recognized as one of the more promising processes for producing an environmentally acceptable boiler fuel from coal. In the SRC process, coal is liquefied to allow removal of entrained mineral matter by physical separation methods and reacted with hydrogen to remove chemically part of its organic sulfur. Liquefaction of coal has been shown to occur almost instantaneously upon reaching reaction temperatures while in the presence of a hydrogen-donor solvent, the overall rate limiting step in liquefaction being rehydrogenation of process solvent - which may be performed separately in the recycle stream - to replenish hydrogen-donor species (1,2). Based on data collected in this laboratory hydrodesulfurization (HDS) of coal, on the other hand, appears to be a much slower reaction. As a result, the kinetics of HDS will be a primary, if not the controlling factor in the design and operation of the dissolver/reactor in the SRC process.

In the present work, an experimental evaluation is made of the feasibility for accelerating HDS of coal by simply varying reaction conditions and utilizing coal mineral matter and/or other cheap regenerable catalysts. The rate data reported were all obtained in a batch system; and, except for one series of experiments, only one coal type, a bituminous Kentucky No. 9/14, was used. Experimental methods and materials are given in (2), except as noted herein. A reaction model was developed that gives an excellent fit to the experimental data. The model, as well as other results of the comparative studies performed, is intended to assist in predicting and interpreting results from pilot studies of the SRC process, such as those at Wilsonville, Alabama, and Tacoma, Washington. The model provides also a useful design tool; but, for a reaction system as complex as the one dealt with here, it would be presumptuous to suggest that it represents the true mechanism.

In a previously reported catalyst screening study (5), several minerals indigenous to coal were shown to have a catalytic effect on the HDS of creosote oil. Of particular interest was the observation that in the presence of reduced metallic iron the HDS rate of the oil was significantly higher than that resulting when no mineral was present; whereas, in the presence of pyrite the HDS rate was about the same as it was when no mineral was present. These observations were surprising in that both reduced iron and pyrite are converted into the sulfide form (pyrrhotite) within the first fifteen to twenty minutes of reaction. Based on these observations, to further examine the practicality of coal mineral catalysis, a series of experiments was performed to ascertain whether the acceleration of the HDS rate in the presence of iron was predominantly thermodynamic or catalytic in nature. It is possible that iron, by removing H_2S , promotes HDS by Le Chatelier's principle, or simply prevents the H_2S from reducing the activity of catalytic sulfides by preferential adsorption.

Basic Nature of Reactions

The influent coal/oil slurry to the reactor/dissolver in the SRC process includes a wide variety of sulfur-containing compounds; thiols, disulfides, sulfides, thioethers, γ -thioopyrone, thiophenes, dibenzothiophenes, and other heterocyclic sulfur compounds. In general, thiols, disulfides, sulfides, thioethers, and γ -thioopyrone are very reactive - undergoing hydrogenolysis at an appreciable rate, forming H_2S and hydrogenated compounds, without the aid of a catalyst; whereas, heterocyclic sulfur compounds are much less reactive - requiring a catalyst to achieve an acceptable HDS rate. As a result of the large difference in reactivity of these two groups of sulfur-containing

compounds and to simplify analysis, the HDS reactions involving individual compounds in each of these two groups sometimes are lumped together; and HDS of a coal/oil slurry is often treated as if there were only two reactive compounds (3,4).

In addition to HDS reactions, under reaction conditions used in the SRC process, hydrocracking (i.e., breaking of C-C bonds) and hydrogenation reactions also occur. It is by means of these reactions - particularly cracking reactions - that coal solids are converted into lower molecular weight components that are soluble in SRC process solvent, allowing removal of entrained mineral matter by subsequent physical separation methods. These reactions take on importance, other than liquefaction of coal solids, by consuming hydrogen in the process without removing sulfur. Only that amount of hydrogenation, or cracking, required to liquefy coal solids and allow mineral matter removal is desired. Any excess hydrogenation beyond this amount, such as in the formation of C₁ - C₄ gases, etc., results in inefficient use of hydrogen, thus higher operating costs. This should be avoided as much as possible. Actually SRC product contains a slightly lower hydrogen/carbon ratio (H/C = 0.75) than the feed coal itself (H/C = 0.8). Furthermore, the stoichiometric amount of hydrogen required solely for removal of an acceptable amount of sulfur as H₂S in the SRC process is an order-of-magnitude less than the total amount of hydrogen currently consumed (two weight per cent of MAF coal feed) at the Wilsonville, Alabama, and the Tacoma, Washington, SRC pilot plants. Excess hydrogenation therefore accounts for most of the hydrogen consumed in producing solvent refined coal.

The rate of noncatalytic (except for mineral matter) HDS, unlike that of hydrogenation, appears to be relatively insensitive to hydrogen concentration, in the form of either dissolved molecular hydrogen or readily transferable hydrogen such as that attached to donor species (e.g., tetralin) contained in the process solvent. Variation, for example, in initial hydrogen partial pressure from 1000 to 2600 psig at reaction temperature had no significant effect on the final organic sulfur content of a coal/creosote-oil reaction mixture, even after two hours of reaction (Table 1). Also, as shown in Table 2, the reduction in total sulfur content of the coal was essentially the same after fifteen minutes of reaction when slurried with creosote oil - which contained only trace amounts of tetralin and other known hydrogen-donor species - as when slurried with pre-hydrogenated creosote oil - which, like the SRC recycle oil used, contained significant amounts of tetralin and 9,10-dihydrophenanthrene. The rate of liquefaction, on the other hand, was significantly higher when the coal was extracted in prehydrogenated creosote oil. When reacted in an inert nitrogen atmosphere, the cresol-soluble yield was almost twice that obtained when the coal was extracted with untreated oil. The high sensitivity of the rate of liquefaction, as opposed to the relative insensitivity of HDS to hydrogen concentration is further evidenced in that the cresol-soluble yield was significantly higher when the coal was reacted in an initial 2000 psi hydrogen atmosphere, both when slurried with creosote oil and also when slurried with pre-hydrogenated creosote oil. Also, solvent-to-coal ratio had no significant effect on HDS rate relative to that of liquefaction (Table 3).

The rate limiting step in liquefaction has been shown to be the reaction of dissolved molecular hydrogen with the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly (1,2). In fact, when extracted in a highly active hydrogen donor solvent such as hydrogenated creosote oil, coal solids have been observed to liquefy almost instantaneously upon reaching reaction temperature (1). Thus the observed sensitivity of the rate of liquefaction to hydrogen concentration should be expected. Furthermore, as long as solvent quality (i.e., a sufficiently high hydrogen-donor concentration) is maintained - which can be done independently by hydrogenating the recycled process

solvent as is done in the Exxon process - with liquefaction occurring almost instantly. HDS should be the controlling factor in the design and operation of the dissolver/reactor. HDS kinetics thus take on a special importance for the commercialization and development of the SRC process.

Coal Mineral Catalysis

A limited experimental evaluation of process advantages and disadvantages of coal mineral catalysis was presented in an earlier work (5). As part of this evaluation, twelve different coal minerals and, also, actual SRC mineral residue as well as coal ash were individually screened to rate their catalytic activity on the HDS rate and hydrogenation of creosote oil relative to that of a commercial Co-Mo-Al catalyst. Some results of this earlier work are given in Table 4 and in Figures 1 and 2. Reduced iron, reduced pyrite (presumably pyrrhotite), and pyrite had decreasing effects on sulfur removal during hydrogenation/hydrodesulfurization of creosote oil at 425°C, with reduced iron being second only to Co-Mo-Al in catalytic activity for HDS and with pyrite, despite its pronounced effect on hydrogenation, having essentially no apparent catalytic activity for HDS. The relatively insignificant effect of pyrite on HDS rate was further evidenced in that the rate of organic sulfur removal from coal slurried in creosote oil remained essentially the same even after about seventy-five per cent of its pyritic content had been removed physically by magnetic separation prior to reaction (Figure 3). Reduced iron, on the other hand, was found to have a significant effect on HDS reactions when present in only trace amounts (Table 5).

The stable form of iron in the presence of hydrogen and hydrogen sulfide in the temperature range of 400 to 500°C is pyrrhotite (6,7). As shown in Figure 4, pyrite is reduced to the sulfide (presumably pyrrhotite) within about fifteen minutes of reaction at 425°C. Rapid reduction of pyrite coal minerals has also been observed to occur in the dissolver/reactor at the Wilsonville SRC pilot plant (8). H₂S product from the reduction of pyrite is thus generated in the early stages of HDS. H₂S is known to inhibit catalytic HDS of petroleum feedstocks; thus, since some of the same sulfur-containing components in petroleum feedstocks exist also in coal/oil slurries, H₂S may inhibit HDS of coal/oil slurries, or possibly react with previously desulfurized components. Therefore, since reduced iron acts as an H₂S scavenger, instead of an H₂S producer as does pyrite, one possible reason for the differences in catalytic activities of reduced iron, reduced pyrite, and pyrite could be the different amounts of H₂S present during HDS as is shown in Table 4. In fact, the H₂S partial pressure was increased by a magnitude of two to three by the reduction of pyrite; whereas no traceable amount of H₂S product was present during the reduced iron run. Also, when different weight percentages of iron were charged with creosote oil (Table 5), no H₂S product was detected until less than one per cent by weight of iron was present. Interestingly enough, when iron was present in higher weight percentages (2.4 to 20%), the amount of sulfur removed during reaction was only slightly different, and when present in lower percentages (1.0 to 0.5%), it decreased in proportion to the amount of iron present, with trace amounts of iron being as effective as 0.5 weight percent. The retarding effect of H₂S on HDS is further evidenced in that when H₂S was added prior to reaction the amount of sulfur removed was less during hydrogenation/HDS of both a bituminous Kentucky No. 9/14 mixture coal and a sub-bituminous (Wyodak) coal (Table 10).

When iron gauze was used to scrub out any H₂S product formed during hydrodesulfurization of creosote oil, while being mounted in the top of the reactor above the oil, the amount of sulfur removal was about 20% higher than that obtained without any scavenger agents present; that is, the final sulfur content of the oil was 0.39% as opposed to 0.50%, a decrease equivalent to that obtained when one

weight percent of iron was present. Apparently then, H₂S does have a retarding effect on HDS as might be expected from thermodynamics.

When five weight percent iron and a sufficient amount of H₂S (to prevent its complete removal by reaction) were present during HDS of creosote oil, the amount of sulfur removal was only the same as that when either a trace amount or a half weight percent of iron was present (Table 5). Apparently H₂S retards the effectiveness of iron sulfide as a catalyst, with trace amounts of iron sulfide having about the same catalytic effect on HDS rates as larger amounts when an appreciable H₂S atmosphere exists. Since H₂S does have a thermodynamic effect on the HDS reactions; however, the severity of its catalytic inhibition effect is not completely defined.

In summary then, reduced iron appears to favor HDS by scavenging H₂S product, preventing any reverse reactions and by catalyzing HDS reactions. Unfortunately, as shown in Table 6, reduced iron, like most HDS catalysts, also accelerates hydrogenation; as a result its use as a catalytic agent in the SRC process could contribute to excess hydrogenation. Because of its potential as an inexpensive HDS catalyst, however, further experiments are now in progress to better evaluate its role in accelerating HDS reactions and its selectivity for HDS versus hydrogenation.

Hydrodesulfurization Kinetics in the SRC Process

As shown in Figure 5, the variation of organic sulfur content of a coal/creosote-oil reaction mixture with time follows a path close to that expected for an overdamped second order dependence of rate on organic sulfur content. This kinetic behavior is consistent with the basic nature of HDS reactions as described in the foregoing discussion, in that it can be modelled by considering the reaction mixture to contain only two hypothetical sulfur-containing compounds with significantly different rate constants. The desulfurization reaction of each of the two hypothetical components is assumed to follow first-order kinetics. A test as to whether this assumed kinetic model is representative is the difference in magnitude of the experimental rate constants, for the actual two groups of lumped sulfur components are known to react at two widely differing rates. The large difference in slope of the two lines in Figure 6 indicates that the experimental rate constants are indeed significantly different, attesting that the model is representative.

The high sensitivity of HDS rate to reaction temperature and its low sensitivity to hydrogen concentration suggested that the HDS reactions were chemically controlled and pseudo-homogeneous kinetics were thus used in modeling. Furthermore, since the retarding effect of H₂S and the catalytic effect of pyrite coal minerals apparently either offset each other or exist to such an extent that the effect on HDS rate is insignificant - as a first-hand approximation-no kinetic terms were used to represent the reverse reaction by H₂S product. The rate equation was thus written as:

$$r_{\text{HDS}} = -k_1 S_1 - k_2 S_2 \quad (1)$$

where: S₁, and S₂ are the organic sulfur concentration (g/cc) present in the form of the two hypothetical sulfur-containing components, respectively. For a batch reactor,

$$S = S_{10} e^{-k_1 t} + S_{20} e^{-k_2 t} \quad (2)$$

The adjustable parameters S_{10} , S_{20} , K_1 and K_2 were determined empirically, using a nonlinear minimum sum-of-the-squares numerical search routine. The Arrhenius relationship was assumed, and rate data for three different reaction temperatures were used in determining empirical values for the four adjustable parameters. A list of these values is given in Table 7; and a comparison between predicted HDS paths and rate data is made in Figure 5, showing good agreement. Also, the Arrhenius plots of the empirical rate coefficients are given in Figure 6. The rate coefficients for the two hypothetical components differ by two orders of magnitude (Table 8), in consistency with the large difference in slopes of the two straight lines in Figure 6. In addition, the high activation energy (Table 8) for the reactive sulfur-containing component provides further evidence that the desulfurization reactions are chemically, rather than mass transfer controlled. Note that there is no catalyst present, except for the indigenous coal mineral matter. Finally, as shown in Table 9, the energies and enthalpies of activation are indicative of chemical rate processes, rather than transport processes. The high activation energy and low entropy of activation for the fast reaction are indicative of a homogeneous reaction; the lower values for the slow reaction indicate a possible catalytic effect, perhaps due to coal mineral matter. Here again, however, since the exact reaction mechanism is unknown, one must exercise caution when attaching significance to these numerical values.

Conclusions

Hydrodesulfurization reactions occur, under reaction conditions used in the SRC process, at a rate that is practically independent of hydrogen concentration. Reduced iron has a catalytic effect on HDS reactions; in fact, it exhibits a significant memory effect. Because of additional H_2S product, pyrite has only a slight catalytic effect on HDS reactions. The retardation of HDS reactions by H_2S product is due to catalytic inhibition as well as thermodynamic effects. HDS reactions can be modeled as two first-order reactions occurring in parallel, with two widely different rate constants.

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Table 1
 NETS AND ORGANIC SULFUR
 IN REACTOR MIXTURE

Reacting Temp., °C.	Reaction Time Min.	2600 PSI		7000 PSI		1000 PSI		Average Total Organic
		Total Organic						
385	15	.85	.82	.94	.81	.95	.82	.95
410	15	.88	.75	.89	.76	.81	.73	.82
435	15	.81	.68	.81	.69	.84	.71	.82
385	30	.89	.76	.90	.77	.89	.76	.89
410	30	.81	.68	.83	.70	.86	.73	.89
435	30	.73	.63	.73	.68	.89	.67	.89
385	60	.81	.70	.87	.74	.89	.76	.86
410	60	.75	.68	.81	.72	.86	.73	.86
435	60	.73	.60	.74	.61	.73	.60	.73
385	120	.81	.68	.87	.74	.89	.76	.89
410	120	.75	.61	.75	.63	.86	.73	.86
435	120	.65	.53	.66	.53	.69	.56	.67

Table 2. Effect on Gaseous Hydrogen and Solvent Type on Liquefaction and Hydrodesulfurization of Coal

Solvent Type	Atmosphere (atm)	Conversion (Based on Cresol Solubles) %	Total Sulfur in Reaction Mixture	Total Sulfur in Solvent (±)	Total Sulfur in Total Solvent (±)
Cresote Oil	2000 psi H ₂	42.1	.90 ± .02	.5	2.0
Hydrogenated Cresote Oil	2000 psi H ₂	83.1	.49 ± .03	trace	2.0
Psycyle Oil (Sample No. 16171)	2600 psi H ₂	70.9	.73 ± .01	.25	2.1
Cresote Oil	2000 psi H ₂	61.0	.91 ± .05	.5	2.1
Hydrogenated Cresote Oil	2000 psi H ₂	90.7	.51 ± .03	trace	2.0
Psycyle Oil (Sample No. 16171)	2000 psi H ₂	85.8	.75 ± .02	.26	2.2

NOTE: Reaction Time = 15 min.
 Solvent-to-Coal Ratio = 3/1
 Reaction Temperature = 410°C

Table 3
Effect of Solvent/Coal Ratio on Hydrosulfurization and Liquefaction

Solvent-to-Coal Ratio	Temperature (°C)	Conversion based on Cresol Solubles	Residual Organic Sulfur
1.5/1	410	84.5	1.45
2/1	410	85.3	1.39
3/1	410	90.7	1.55
3/1	385	80.4	1.66
4/1	385	83.6	1.81

Operating Conditions: 2,000 rpm
2,000 psig H₂

Reaction Time = 15 min.

Initial organic Sulfur = 1.63

Table 4
CATALYST SCREENING RUNS:
LIQUID S SULFUR, TOTAL PRESSURE, AND FINAL GAS COMPOSITION

MINERAL	% S	TOTAL PRESSURE (10 ⁻³ PSI)	H ₂ (10 ⁻³)	PARTIAL PRESSURES (PSI)			
				H ₂ S	CO ₂	CH ₄	C ₂ -C ₅
NONE	0.52	2.40	2.13	10.	2.5	64.	18.
NONE	0.46	2.42	2.23	7.1	2.0	62.	24.
MUSCOVITE (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.
PYRITE (-80, + 150)	0.41	1.99	1.54	230.	1.1	99.	36.
IRON (-325)	0.27	1.98	1.75	<1.	12.	16.	20.
REDUCED PYRITE	0.36	1.96	1.85	17.	0.4	61.	18.
COAL ASH	0.23	1.92	1.72	<1.	1.4	57.	15.3
SIDERITE	0.34	1.81	1.61	<1.	67.	93.	29.
SRC SOLIDS (-325)	0.32	1.73	1.48	13.	24.	85.	30.
PYRITE (-325)	0.55	1.63	1.22	196.	7.3	133.	71.
Co-Mo-AL (-80, + 150)	0.02	1.12	0.92	<1.	1.9	128.	74.
Co-Mo-AL (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.

Table 5. Effect of Iron Concentration On Hydrodesulfurization of Cresote Oil

Iron Concentration (weight percent)	Final H ₂ S Partial Pressure (Pst)	Residual Sulfur (percent)
20.	0.	.34
20.	0.	.34
13.	0.	.35
13.	0.	.36
13.	0.	.35
4.7	0.	.35
2.4	0.	.38
0.99	8.	.40
0.49	66.	.43
trace (memory effect)	63.	.42
trace (memory effect)	--	.45
0	36.	.50
0	67.	.50

Reaction Conditions:

Temperature = 425°C
H₂ Pressure = 3000 psig @ 425°C
Agitation Rate = 1000 rpm
Initial Sulfur Concentration = 0.64 percent
Reaction Time = 2 hours

Table 7

Hydrodesulfurization Model Parameters

S ₁₀	1.53 x 10 ⁻³ g/cc
S ₂₀	6.51 x 10 ⁻³ g/cc
K ₁ (385°C)	1.69 x 10 ⁻² min ⁻¹
K ₁ (410°C)	5.30 x 10 ⁻² min ⁻¹
K ₁ (435°C)	15.32 x 10 ⁻² min ⁻¹
K ₂ (385°C)	8.15 x 10 ⁻⁴ min ⁻¹
K ₂ (410°C)	13.89 x 10 ⁻⁴ min ⁻¹
K ₂ (435°C)	22.74 x 10 ⁻⁴ min ⁻¹

Table 8

Arrhenius Constants

ln K ₁₀	27.11	min ⁻¹
ln K ₂₀	7.417	min ⁻¹
ΔE ₁	40.78	kcal
ΔE ₂	18.99	kcal

Table 9

Comparison of Energies, Enthalpies, and Entropies of Activation of Hydrodesulfurization with Data for Hydrodesulfurization of Coal Tar over WS₂ Catalyst.*

	HDS Model		Coal Tar*	kcal/mole
	Reaction 1	Reaction 2		
ΔE	40.7	38.9	11	kcal/mole
ΔH	39.2	15.8	9	kcal/mole
ΔS	-16.8	-58.2	-50	C.U.

*S. A. Quader, W. H. Wiser, G. R. Hill

I. & E.C. Process Design and Development

Vol. 7, No. 3, 395, July, 1968

Table 6: Comparison of Hydrogenation and Hydrodesulfurization of Cresote Oil in the Presence of Iron Catalyst

Wt. % Fe	(H/H ₀)AVG	(S _F /S ₀)AVG
0	0.80	0.78
0.5	0.71	0.63
1.0	0.74	0.62
2.4	0.74	0.58
4.7	----	0.55
13.0	0.69	0.56
20.0	0.64	0.52

Table 10: Effect of H₂S on Rate of Hydrodesulfurization of Kentucky and Wyodak Coals

Atmosphere	Coal Type	Solvent Type	Solvent-to-Coal Ratio	Cresol Soluble Yield (%)	Total % Sulfur Before	Total % Sulfur After	% Sulfur Liquid Fraction	% Sulfur Solid Fraction
H ₂	Wyodak	Recycle	3:1	76.0	0.52	0.41	0.35	1.15
H ₂ + H ₂ S	Wyodak	Recycle	3:1	76.6	0.52	0.72	0.62	2.04
H ₂	Kentucky 9/14	Recycle	2:1	86.4	1.10	0.80	0.52	2.86
H ₂ + H ₂ S	Kentucky 9/14	Recycle	2:1	88.9	1.10	0.98	0.60	3.58

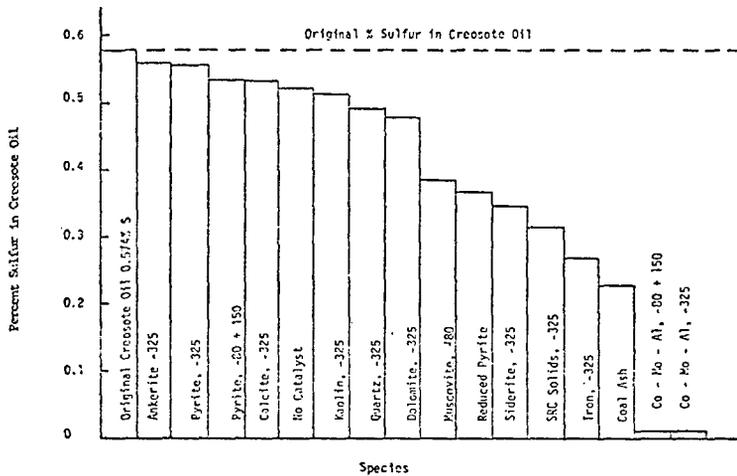


Figure 1. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST

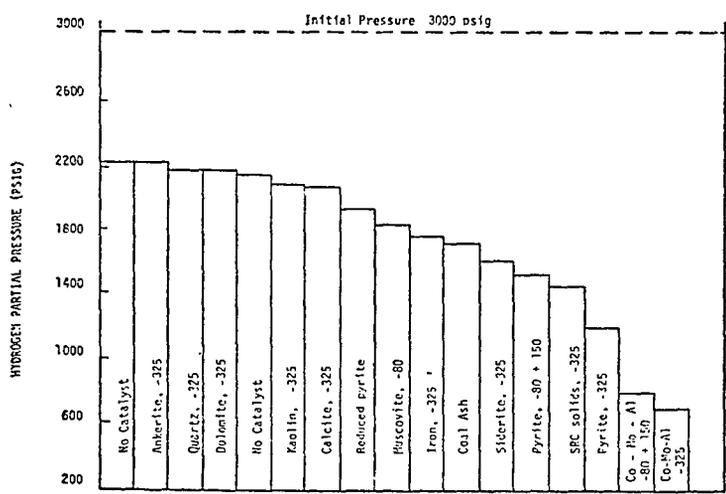
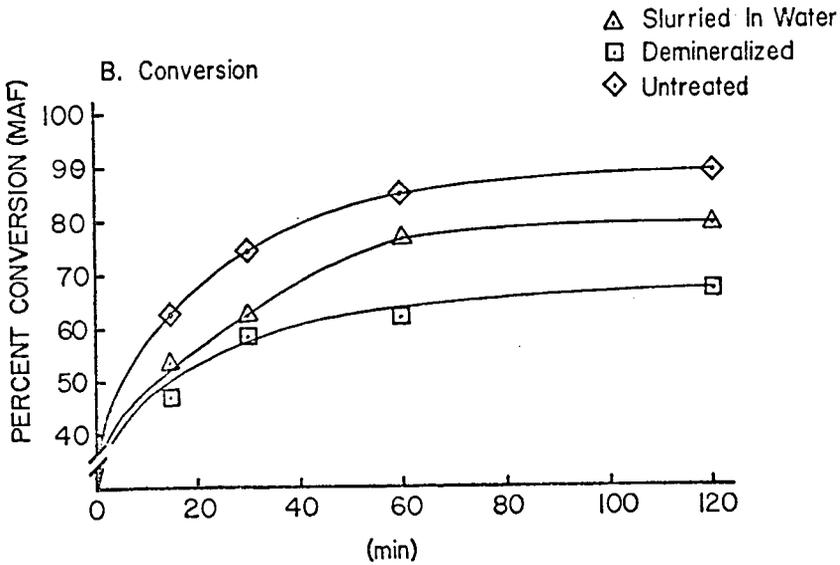
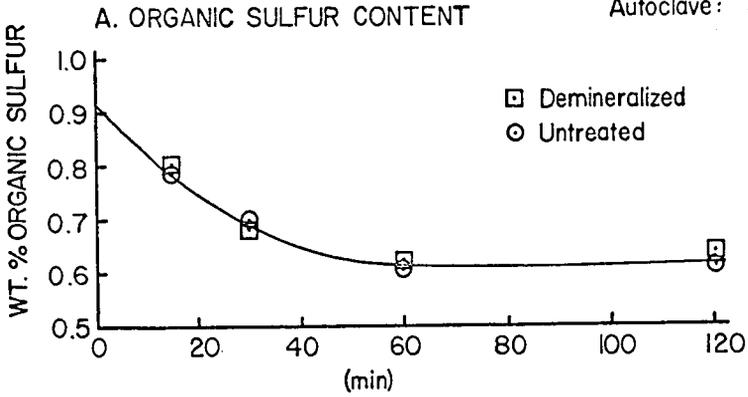


Figure 2. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST

Figure 3. Effect of Demineralizing Coal Feed and Slurrying Coal Feed with Water on Conversion

Temperature: 410° C
 H₂ Pressure: 2000psig @ 410°C
 Agitation Rate: 1000 rpm
 Autoclave: 300 cc



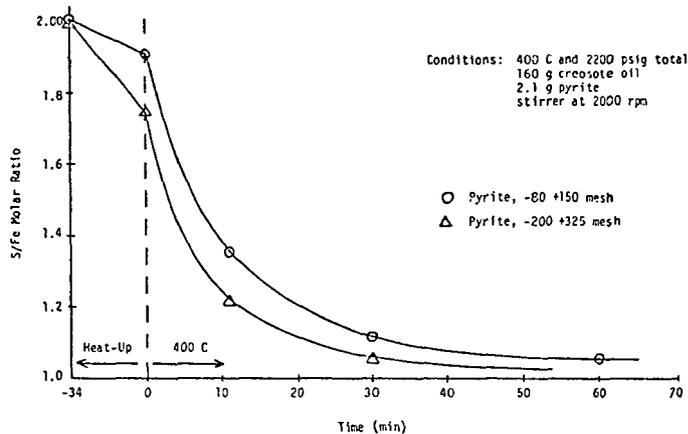


FIG. 4. PYRITE REDUCTION AS A FUNCTION OF TIME

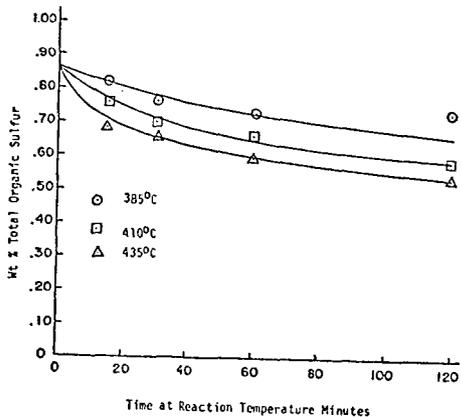


Figure 5. Effect of Reaction Temperature on Organic Sulfur Concentration

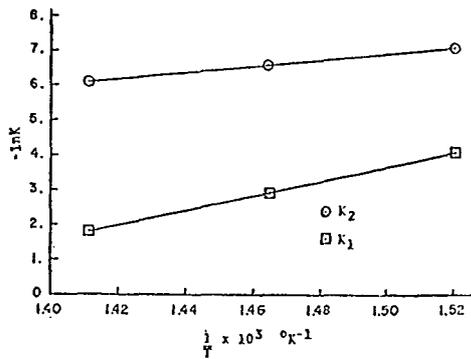


Figure 6. Arrhenius plot for hydrodesulfurization

PREPARATIVE GPC SEPARATIONS OF SOLVENT REFINED COALS. W. M. Coleman, D. L. Wooton, H. C. Dorn and L. T. Taylor, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

A preparative quantitative separation of the THF soluble portion of several solvent refined coals (Pittsburg #8, Amax, etc.) has been demonstrated employing gel permeation chromatographic techniques utilizing three column packings: (1) a styrene-divinyl benzene packing (BioBeads S-X4), (2) a cross linked poly(N-acryloylmorpholine) polymer (Enzacryl Gel K1), and (3) a modified alkylated dextran (Sephadex LH-20). Each packing material will be evaluated based on the extent and time of separation as well as the cost of materials. Fractional weight distributions within each SRC separation are determined and their average molecular weights compared. Weight distributions for common fractions of different SRC solid products derived from various feed coals will also be discussed.

MINOR AND TRACE METAL ANALYSIS OF SOLVENT REFINED COALS BY FLAMELESS ATOMIC ABSORPTION. W. M. Coleman, P. Szabo, D. L. Wooton, H. C. Dorn, L. T. Taylor, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA. 24061.

Several solvent refined coals differing in the raw feed coal used, their THF insoluble fraction, their THF soluble fraction and their sized separated fractions have been analyzed for twelve metallic elements (Mg, Al, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cl, Pb) via flameless atomic absorption spectroscopy. Prior to analysis each sample was wet ashed with equal quantities of concentrated H_2SO_4 and 30% H_2O_2 . Matrix effects were compensated for by the method of standard additions and deuterium arc background correction. Metal analysis on a National Bureau of Standards Coal employing the same ashing and analysis scheme were determined and compared with certified values.

AGING CHARACTERISTICS OF COAL LIQUIDS

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INTRODUCTION

Materials handling and storage is an important part of any chemical process. The SYNTHOIL process (1), which converts coal to a low-ash, low-sulfur fuel oil, requires careful storage to control the viscosity of the product. The economics of this process requires a light hydrogenation of coal, and therefore any chemical changes during storage that may increase the viscosity of the product to a level at which it becomes a handling problem must be avoided. Recommended handling procedures can be determined by laboratory studies. Previous studies (2,3) give a brief resume of the changes in viscosity of SYNTHOIL samples during ambient storage for times up to 120 days. The present report, also based on viscosity measurements, covers a variety of storage conditions which include storage temperatures of 30°-61°C, atmospheres of nitrogen, air and oxygen, both stirred and unstirred samples and ambient light versus darkness. Further studies of these samples based on chemical and instrumental analyses will be reported.

EXPERIMENTAL

Aging tests were made on three coal liquids from SYNTHOIL run FB-53. Run FB-53 was made with a West Virginia coal, (Pittsburgh Seam, hvAb) and operated at 4000 psig H₂ and 450°C. Pelleted CoO-MoO₃-SiO₂-Al₂O₃ catalyst was used in the reactor. The samples investigated were from Batches 1, 21, and 50 which were obtained after 4, 84, and 200 hours, respectively, of operation of the coal liquefaction reactor.

The most comprehensive aging tests were made on the Batch 1 sample. After an initial viscosity measurement, a 200 ml sample of this batch was transferred to each of fifteen one-liter containers. Each sample was simultaneously connected to the aging apparatus and there subjected to a particular combination of the aging factors. Periodically ~10 g samples were removed from the aging containers and viscosity measurements made. All viscosity measurements were made with a Brookfield viscometer which permitted measurements at various temperatures. Thus, viscosity measurements were made at two temperatures, 30°C and 61°C, by circulating water from the aging baths through the heating jacket of the viscometer.

Similar, though less extensive, aging tests were performed on samples from Batches 21 and 50 from run FB-53. Data accumulation was limited because of the high initial viscosities of these samples and their rapid rate of change.

RESULTS AND DISCUSSION

The results of the aging tests are presented in Figures 1-3. The graphs represent the change in viscosity that occurs with aging time; infrared spectra in the figures were obtained on thin films of representative samples.

Figure 1 shows the changes in viscosity that occur when Batch 1 samples are stored at 61°C, stirred, exposed to light and subjected to one of the three

test gases, oxygen, air or nitrogen. In this and all subsequent figures, exposure to oxygen had the most pronounced impact upon the increase in viscosity; exposure to air had the next strongest impact. A small change was noted for the samples exposed to nitrogen. Also included in Figure 1 are the results for Batch 50 samples aged at the same conditions, i.e., 61°C, exposed to light and exposed to oxygen, air or nitrogen. As the figure shows, the initial viscosity of these samples is much greater than that for Batch 1 which was obtained early in the run. The much more rapid increase in viscosity of these Batch 50 samples confirms previous work (2).

The most significant viscosity increases occurred in samples exposed to oxygen. Hydrocarbon oxidation is confirmed by the infrared spectra shown in Figure 2. The spectrum obtained from the fresh reactor oil and spectra from oils exposed to different gases differ at 1690 cm^{-1} which has been assigned to carbonyls that have been formed during aging. That the formation of this band is progressive (continues throughout the aging process) can be shown by the gradual increase of the carbonyl absorption. There are many ways in which this light oxidation of SYNTHOIL may cause the observed viscosity increase. The formation of carbonyls represents a small increase in molecular weight. Carbonyls might combine with phenols as hydrogen bonded molecules or as polymers, or oxidation may proceed by way of peroxide formation and a free-radical mechanism. The ultimate objective of this work is the identification of an appropriate mechanism and the development of an inhibitor. Lin (4) has made some helpful observations.

The observed increase in viscosity for a sample stored under nitrogen may be explained in several ways. There may be a physical agglomeration similar to the crystallization of a solid from a supernatant liquid. There may be a chemical interaction between the acidic and basic components which are known to be present in SYNTHOIL (5). Further, there may be a volatilization of the lighter components under the influence of heat and stirring. Volatility effects were minimized by using a slow gas input and covered containers.

Figure 3 shows the results for samples exposed to the same gases, but aged at 45°C. The same ordering of increased viscosity of samples relative to the exposure gas as noted for the samples stored at 61°C is found; i.e., oxygen > air > nitrogen. Figure 3 also contains data for Batch 21 stored at 45°C. As noted previously, these results show that faster rates of increase in viscosity occur for samples with higher initial viscosities.

Viscosity data were obtained at 30°C for the nine samples aged in the three gases and at three temperatures. Similar relationships to those found for the viscosity measurements at 61°C are apparent. One distinction is that the changes noted for the samples exposed to nitrogen and air appear more severe. This is undoubtedly due to the substantially higher initial viscosity occasioned by the lowering of the temperature at which the viscosities were measured. An examination of the melting points of typical benzenoid molecules makes it apparent that there will be wide variations of viscosity with temperature.

The effects of not stirring the sample and not exposing the samples to ambient light were observed. A significant reduction in the aging of the samples exposed to either oxygen or air occurs when the particular sample is not stirred; the sample exposed to nitrogen shows no change. This obviously indicates that stirring merely exposes new sample constantly to the oxygen in the gaseous environment; i.e., there is no intrinsic effect due to mechanical agitation of

the sample. In addition, these results also indicate that the ambient light of the laboratory has essentially no impact on the aging properties of these samples. Further study of sunlight or other UV sources would be necessary.

Solvent separations made using the original sample, a sample after 35 days storage at 61°C under nitrogen, and a sample after 28 days storage at 61°C under oxygen gave the following data:

	Oil	Yield, Percent by Weight		Ash
		Asphaltene	Benzene Insol.	
Original	73	20	7	3
N ₂ Storage	75	18	7	3
O ₂ Storage	62	20	18	3

For this table Oil is defined as benzene soluble, pentane soluble materials and Asphaltene as benzene soluble, pentane insoluble materials. As the data indicate, no changes in component distribution occurred for the sample stored under N₂, while the sample stored under O₂ showed a decrease in oil and a corresponding increase in benzene insoluble materials. This increase in benzene insoluble material may indicate polymer formation.

CONCLUSION

These data provide some insight into the effects of time, heat, light, mechanical agitation, and gaseous environment on SYNTHOIL aging. Further analyses underway include solvent and chromatographic separations and spectral identification of the aging products. These should help to establish a mechanism for aging and perhaps suggest inhibitors which will improve the storage characteristics of SYNTHOIL.

ACKNOWLEDGMENT

SYNTHOIL samples were provided by Exploratory Engineering, PERC, Dr. Paul M. Yavorsky, Supervisor. Solvent extraction data were provided by Dr. Frank K. Schweighardt, Spectro-Physics, PERC.

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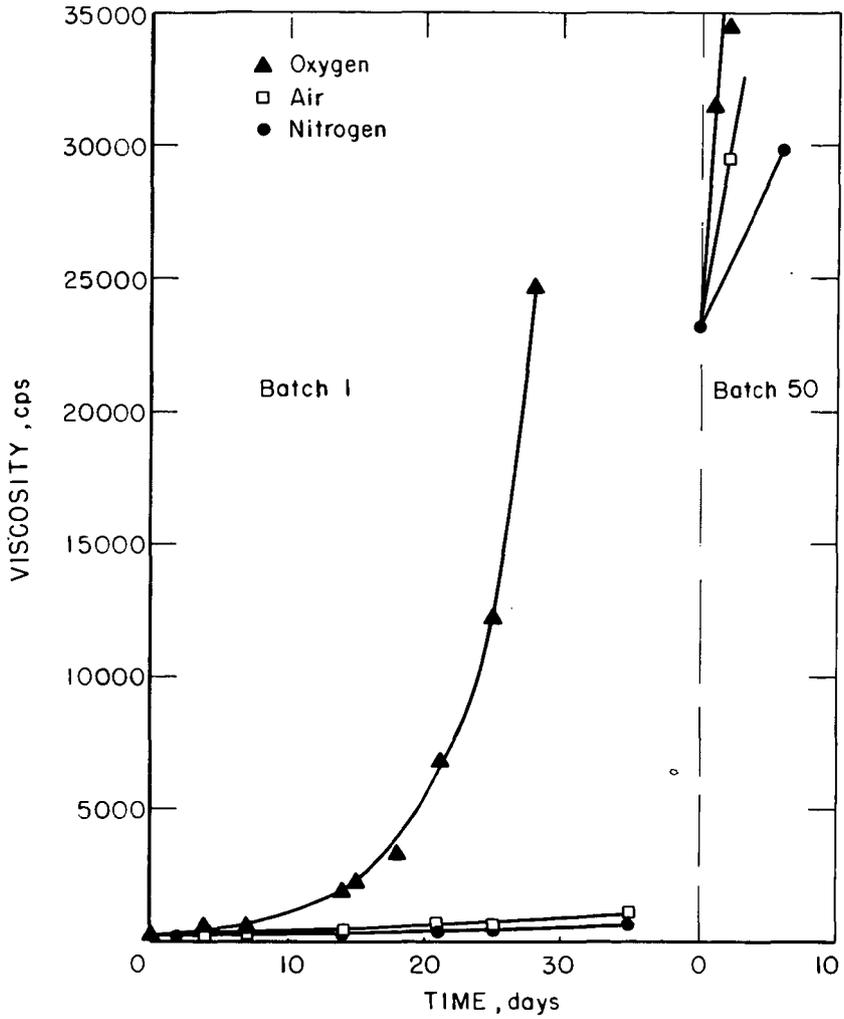


Figure 1 -Viscosity change with storage time Storage at 61°C, viscosity at 61°C .

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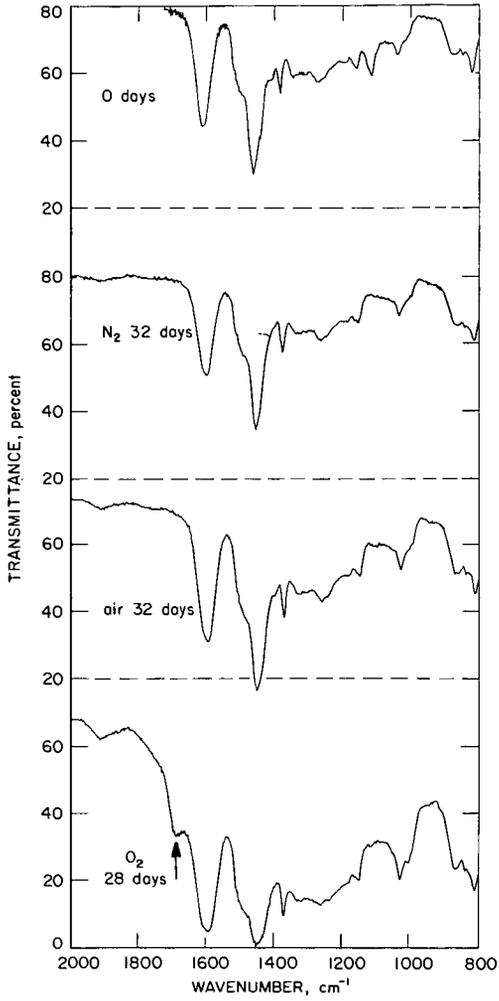


Figure 2 - Infrared spectra showing the increase of C=O during SYNTHOIL storage in various gases.

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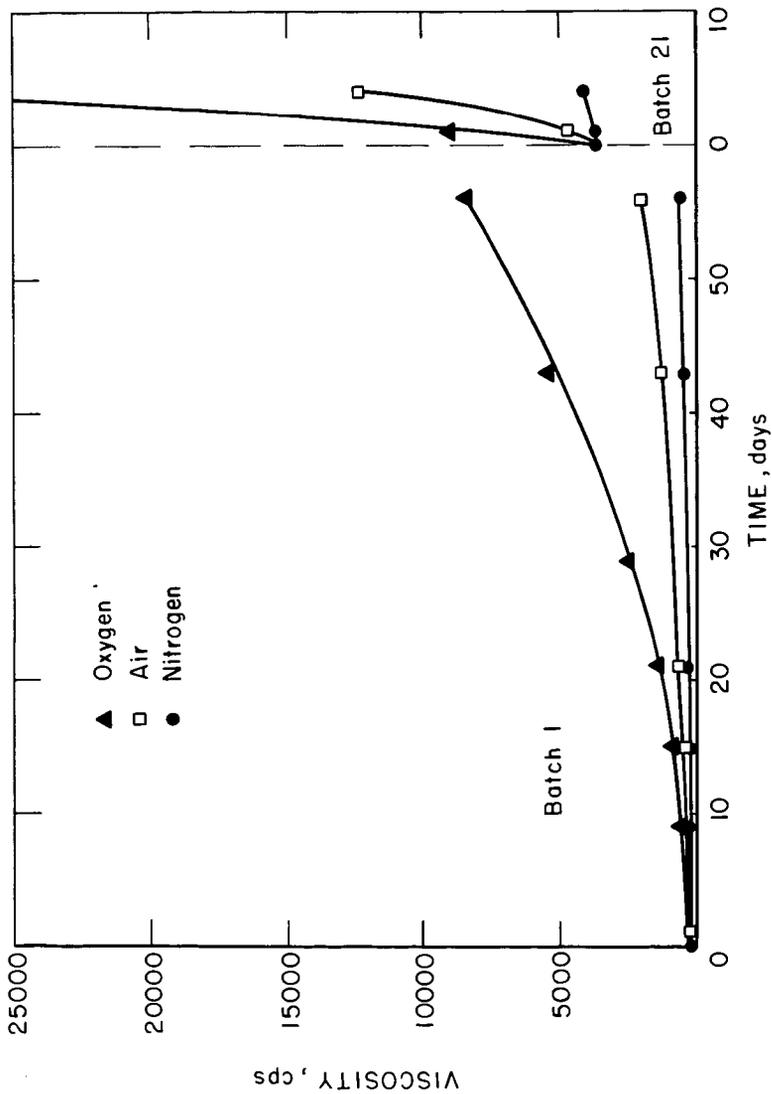


Figure 3 - Viscosity change with storage time Storage at 45°C, viscosity at 61°C

6-23-76 L-14935

THE TOSCOAL PROCESS - PYROLYSIS OF WESTERN COALS AND LIGNITES FOR CHAR AND OIL PRODUCTION

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INTRODUCTION

Western coals and lignites generally have high moisture and organic-bound oxygen contents compared to Eastern coals. Arkansas lignites contain as much as 52% moisture (1), and Powder River subbituminous coals contain from 21 to 30% moisture (2). Pennsylvania bituminous and anthracitic coals contain only 3-6% moisture (3). To the extent that coal contains organically-bound oxygen, it has already been "burned" and its heating value has suffered accordingly. The oxygen values of coals vary inversely with coal ranking. Anthracites contain about 3% oxygen, on a moisture and ash free basis. Corresponding values for lignites are 20-30% (4).

The disadvantage of high oxygen and moisture contents in Western coals is offset by their low sulfur contents, and large volumes of Western coals are being shipped to the East despite freight rates which are very high when calculated on a heating value basis.

Any technique which effects selective removal of moisture and combined oxygen, primarily as carbon dioxide and water, will be of interest unless the cost is too high or an offsetting quality disadvantage results.

Removal of moisture has been widely discussed and examined (5,6,7). Lignites and subbituminous coals have been dried on a very large scale (5). Shipment, handling and storage problems were circumvented, and successful utility burning tests were run. While drying reduces shipping weight and increases the heating value of the solid fuel, it does not produce oil and high Btu gas coproducts.

Low temperature pyrolysis, i.e., to 800-900°F, removes any moisture remaining after the usual preheating steps and, more significantly, produces valuable oil and gas products while eliminating much of the organically-bound carbon dioxide and water. Both carbon dioxide and water are easily removed, if desired, from the gaseous and liquid hydrocarbon products.

The char product produced from low temperature carbonization can be used as a utility boiler fuel, potentially as the major component in the manufacture of formcoke and as a feedstock to gasification which would make a synthesis gas free of hydrocarbons and tars.

The oil product may be used as a fuel oil and as a source of chemicals. It may be converted to pitch binders for carbon and to metallurgical coke.

Previous reports have been given on the TOSCOAL process (8,9,10). Since these initial reports, we have continued our development efforts and have successfully

extended our pilot plant test work to coals having caking properties and have found the char to be an attractive feed to gasification.

DESCRIPTION OF THE TOSCOAL PROCESS

Tosco Corporation has investigated oil shale retorting by the TOSCO II process at the pilot plant and semi-works scale since the late 1950's. Operations at our 1,000 ton/day Parachute Creek semi-works were terminated by Tosco Corporation and its partners in 1972, after total expenditures of more than 50 million dollars. In 1969 and 1970 we were successful in retorting subbituminous coal in our 25-ton per day oil shale pilot plant located near Denver, without significant changes in process conditions normally designed for oil shale. We have chosen the name TOSCOAL to designate the process which involves the application of our oil shale retorting technology to the low temperature pyrolysis of coal.

A diagram of the TOSCOAL process is shown in Figure 1. Coal is fed to a surge hopper and dried and preheated by dilute phase fluid bed techniques. This step may be modified, as required, to effect deagglomeration (decaking). The preheated feed is then transported to a pyrolysis drum where it is contacted with heated ceramic balls. The char product leaves the pyrolysis drum at 800-1000°F, passes through the trommel screen and is subsequently cooled and sent to storage. The cooled ceramic balls, being larger than the coal, pass over the trommel screen into a separate compartment and are returned to the ball heater by means of an elevator. Pyrolysis vapors are condensed and fractionated. Uncondensed gas, having a heating value of 500-1000 Btu/lb, may be utilized as a ball heater fuel or processed and sold after sulfur removal. Removal of contained carbon dioxide would raise the heating value of the gas to even higher levels.

The TOSCO II oil shale process produces essentially 100% of the oil yield measured by Fischer assay or about 0.8 barrel barrel of oil from a ton of oil shale having a Fischer assay of 35 gal/ton. TOSCOAL processing of coal also produces about 100% of the oil predicted by Fischer assay. Subbituminous coals yield 0.3 to 0.6 barrels of oil per ton of raw coal. Oil yields from bituminous coals are greater.

TOSCOAL processing offers several advantages:

1. The use of an indirect heat source results in the production of gas having a high heating value.
2. The process is continuous.
3. The process operates with a high throughput of solid product per unit volume of retort and with good heat transfer and moderate mixing.
4. Pollution control is much better than for conventional coke ovens used in high temperature carbonization.

Previously reported pilot plant runs with a non-caking Wyoming subbituminous coal have now been augmented by successful operations with coals having Free Swelling Indices (FSI) of 1 and 3.5. Prior deagglomeration, by fluid bed treatment with steam and air, was needed before processing the coal having the FSI of 3.5.

We have used the Tosco Material Balance Assay (TMBA) technique (11) to determine a product slate and to provide sufficient product for property determinations. Data obtained provide a useful benchmark with which to compare pilot plant retorting results. The TMBA procedure requires only 100 grams of representative coal. The apparatus used for TMBA is illustrated in Figure 2. The method is basically the well known Fischer assay procedure with provision for collecting all of the product gas for later analysis by gas chromatography. Coal is placed in the steel retort and the head is bolted on to assure no loss of vapors. The contents of the retort are heated to a terminal temperature of 930-950^oF using a prescribed temperature-time profile. Oil and water are collected in the centrifuge tube which is immersed in ice water. The gas product passes through a pressure activated solenoid valve and is collected in the glass container shown. Good material balances are obtained on a routine basis.

PILOT PLANT RESULTS WITH COAL

1. Subbituminous Coal

Our initial pilot plant work was carried out on several hundred tons of subbituminous coal obtained from the Wyodak mine located near Gillette, Wyoming. A typical analysis of this coal, as received, is shown in Table 1.

It is our observation, in the pilot plant retorting of this coal, that the mechanical handling of the solid and liquid products was very similar to that experienced in extensive prior operations with oil shale.

Pilot plant retorting was conducted at three retorting temperatures with the results given in Table 2. TMBA data are included for comparison. The char yield decreased with increased retorting temperature, and the oil yield increased. The water yield was not defined accurately in the pilot plant since some steam was used in the process. Accordingly, the water yield was calculated from the moisture of the coal and from Fischer assay data. The compositions of the coal feeds to these four test runs were not identical, although each coal was from the Wyodak mine.

Product char properties are listed in Table 3 and plotted in Figure 3. The char volatile matter values decreased, and the heating values increased as the retort temperature was raised. The general range of heating values obtained is excellent for boiler fuel application and represents about a 50% increase over the heating value of the corresponding raw coal.

The properties of the oil products are given in Table 4. The oil properties change only slightly with increased retort temperature. The low sulfur values are to be noted. The oils are rich in potential chemical values. In particular, the IBP to 446^oF portion of the tar produced in Run C-3 contained 65 weight percent of phenols, cresols, and cresylic acids.

The retort gas yields are given in Table 2. The product gases gave the analyses shown in Table 5. It is to be noted that the mixture obtained has a high heating value, and the heating value obtained after removal of acid gases is in the natural gas range. Removal of the butane and heavier components for other use would tend to slightly reduce the reported heating values.

FIGURE 1. TOSCOAL Process

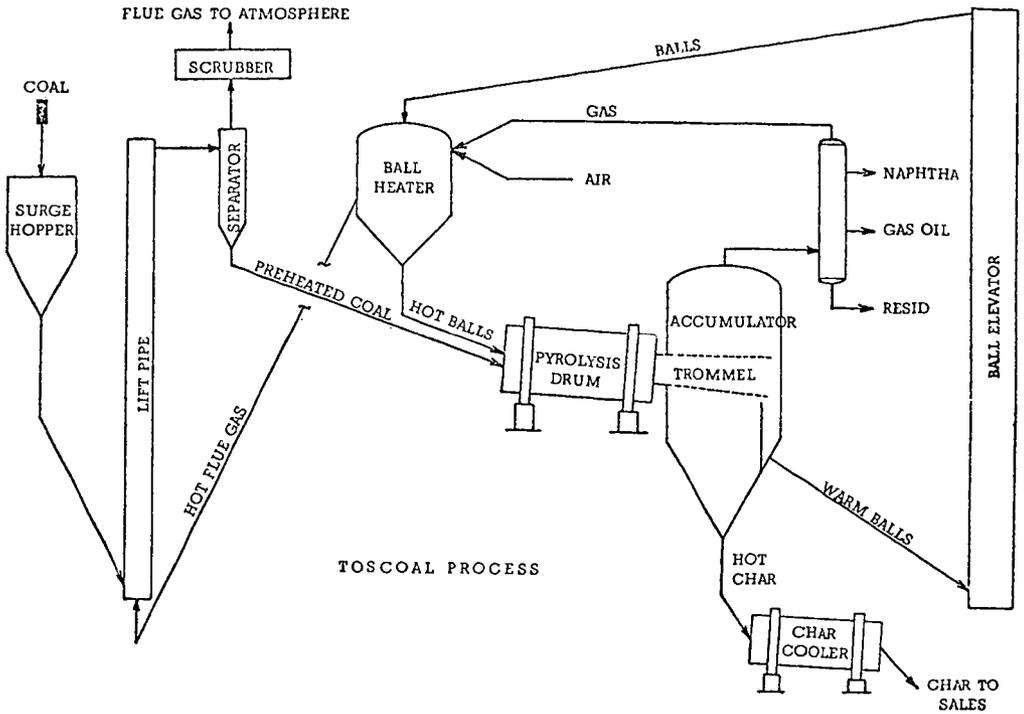


FIGURE 2. Product Collection Assembly - Tosco Material Balance Assay

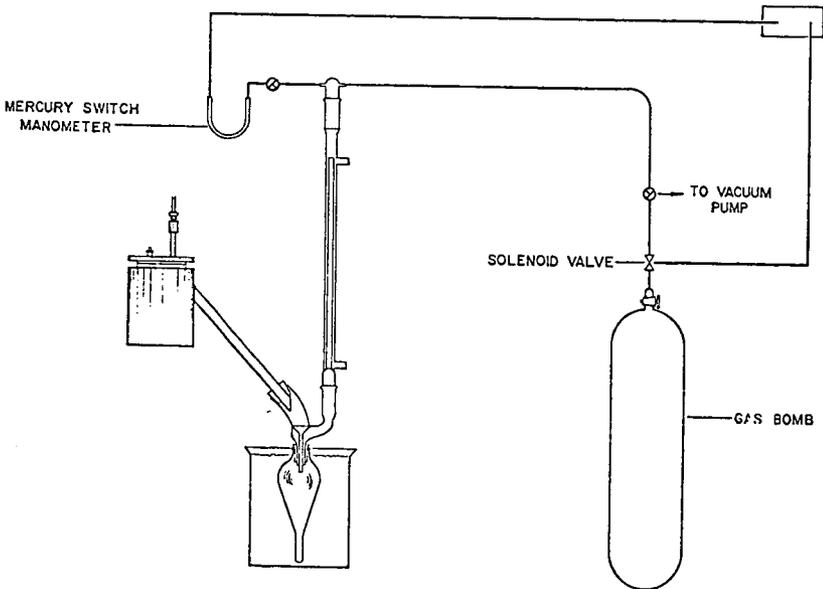


TABLE 1
WYODAK COAL ASSAY
(Samples 120-8, 120-10)

<u>Proximate (wt %)</u>		<u>Ultimate (wt %)</u>	
Moisture	30.0	Carbon	46.4
Ash	5.3	Hydrogen	2.8
Volatile Matter	30.7	Oxygen	14.7
Fixed Carbon	<u>34.0</u>	Nitrogen	0.7
Total	100.0	Sulfur	0.3
Heating Values,		Moisture	30.0
Gross, Btu/lb	8,139	Ash	<u>5.3</u>
Net, Btu/lb	7,570	Total	100.2

Other Data

Free Swelling Index	0
Hardgrove Grindability	56
Lb SO ₂ /MM Btu	0.74

TABLE 2
TOSCOAL RETORTING OF WYODAK COAL
Product Yields (lb/ton of as-mined coal)

Retort Temperature	<u>Pilot Plant</u>			<u>TMBA</u>
	<u>800°F</u>	<u>900°F</u>	<u>970°F</u>	<u>935°F</u>
Run No.	C-8	C-2	C-3	3383
Char	1049.0	1011.7	968.7	989.7
Gas (C ₃ and lighter)	119.0	156.7	126.0	156.5
(SCF/ton)	(1250.0)	(1777.0)	(1624.9)	(1876)
Oil (C ₄ and heavier)	114.0	143.0	186.2	157.8
(gal/ton)	(13.2)	(17.4)	(21.7)	(19.8)
Water	<u>702.0*</u>	<u>702.0*</u>	<u>702.0*</u>	<u>702.0</u>
Totals (lb)	1984.0	2013.4	1982.9	2006
Recovery (%)	99.2	100.7	99.1	100.3

* Value assumed from Fischer assay and moisture content. The addition of steam to the process prevented accurate measurement of water produced in retorting.

TMBA Tosco Material Balance Assay, No. 3383

TABLE 3
TOSCOAL CHAR PROPERTIES

<u>Retort Temperature</u>	<u>Pilot Plant</u>			<u>TMBA</u>
	<u>800°F</u>	<u>900°F</u>	<u>970°F</u>	<u>935°F</u>
Run No.	C-8*	C-2	C-3	3383
<u>Proximate (wt %)</u>				
Moisture	0.0	0.0	0.0	0.0
Ash	12.4	10.0	9.8	8.9
Volatile Matter	25.3	19.7	15.9	15.8
Fixed Carbon	<u>62.3</u>	<u>70.3</u>	<u>74.3</u>	<u>75.3</u>
Total	100.0	100.0	100.0	100.0
<u>Ultimate (wt %)</u>				
Carbon	68.8	74.7	77.5	76.5
Hydrogen	3.4	3.0	2.9	3.0
Oxygen	13.3	11.8	8.3	7.8
Sulfur	0.5	0.2	0.3	0.4
<u>Other Data</u>	1.0	1.2	1.3	
Equilibrium Moisture (wt %)	10.0	10.8	9.9	ND
Hardgrove Grindability	59.5	49.1	45.6	ND
<u>Heating Values</u>				
Gross, Btu/lb	11,826	12,560	12,963	13,155
Lb SO ₂ /MM Btu	0.85	0.32	0.46	0.61

* Feed Wyodak coal was different from that used in runs C-2 and C-3.

ND Not determined

TMBA Tosco Material Balance Assay, No. 3383

TABLE 4
TOSCOAL OIL PROPERTIES

<u>Retort Temperature</u>	<u>Pilot Plant</u>			<u>TMBA</u>
	<u>800°F</u>	<u>900°F</u>	<u>970°F</u>	<u>935°F</u>
Run No.	C-8*	C-2	C-3	3383
<u>Ultimate (wt%)</u>				
Carbon	81.4	80.7	80.9	81.4
Hydrogen	9.3	9.1	8.7	9.4
Oxygen	8.3	9.4	9.3	7.0
Nitrogen	0.5	0.7	0.7	0.6
Sulfur	<u>0.4</u>	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>
Total	99.9	100.1	99.8	98.6
Heating Value (Gross, Btu/lb)	16,590	16,217	15,964	16,465
API Gravity	7.9	4.5	1.9	12.8
Pour Point (°F)	90	100	95	ND
Conradson Carbon (wt%)	7.6	9.9	11.4	ND
<u>Distillation** (vol%)</u>				
2.5	413°F	420°F	390°F	ND
10	490	475	405	
20	575	550	455	
30	645	625	545	
40	710	700	640	
50	765	775	725	
<u>Viscosity (SUS)</u>				
180°F	122	123	128	ND
210°F	63	66	69	ND

* Feed Wyodak coal was different from that used in Runs C-2 and C-3.

** Combination of TBP and D-1160 distillations.

TMBA Tosco Material Balance Assay, No. 3383 ND Not Determined

TABLE 5

TOSCOAL GAS ANALYSES

Retort Temperature	Pilot Plant			TMBA
	800°F	900°F	970°F	935°F
Run No.	C-8*	C-2	C-3	3383
<u>Component (mole %)</u>				
H ₂	0.8	1.0	7.8	5.6
CO	18.0	17.3	18.4	15.1
CO ₂	51.1	42.3	36.4	44.7
H ₂ S	1.7	1.3	0.3	0.8
CH ₄	16.9	22.0	24.9	22.4
C ₂ H ₆	3.6	4.7	4.4	4.6
C ₂ H ₄	1.9	1.9	2.4	2.3
C ₃ H ₈	1.3	2.2	1.2	1.2
C ₃ H ₆	1.6	3.7	1.6	1.4
iC ₄ H ₁₀	0.1	0.1	0.0	0.1
C ₄ 's (other)	0.3	2.0	1.1	1.0
C ₅ 's	1.0	1.8	0.7	0.5
C ₆ 's	0.7	0.6	0.4	0.5
C ₇ 's	0.5	0.1	0.3	0.0
C ₈ ⁺	<u>0.2</u>	<u>0.0</u>	<u>0.1</u>	<u>0.0</u>
Total	99.7	101.0	100.0	100.2
Average Molecular Weight	35.9	35.0	30.6	32.3
Weight Percent Carbon	40.5	45.9	44.7	42.0
<u>Heating Values (Calculated)</u>				
Gross, Btu/SCF	534	717	630	552
Net, Btu/SCF	494	663	580	508
Calculated with CO ₂ and H ₂ S removed				
Gross, Btu/SCF	1,113	1,234	995	998
Net, Btu/SCF	1,029	1,138	920	919

* Feed Wyodak coal was different from that used in Runs C-2 and C-3.

2. Higher Rank Coals

The successful operation of the TOSCOAL pilot plant with sub-bituminous coal was encouraging and suggested access to most of the Western coals and lignites. However, some Western coals and most of the Eastern coals are of higher rank and have an FSI ranging from 1 to 9. The feasibility of retorting with heated ceramic balls was in question since caking coals fuse below the retorting temperature range of 800-1100°F. Some short process tests with Illinois No. 5 coal (FSI-4) confirmed that the retort mix became "sticky" and resistant to flow.

We first processed six tons of coal from the Plateau Mine (Price, Utah) which had an FSI of 1, i.e., only a slight tendency to swell on heating. Coal assays are listed in Table 6 and pilot plant product yields and properties are given in Table 7, along with comparative TMBA results. No problems were encountered with this coal and no pretreatments, other than the usual drying and preheating, proved to be necessary.

Processing of Illinois No. 6 coal, having an FSI of 3.5, required pre-treatment with steam and air at 570°F in a fluid bed before retorting. Pilot plant operability was good after this deagglomeration.

Assay data for the raw and pretreated coal are given in Table 6. The effect of deagglomeration was to decrease the TMBA oil yield and to increase the char yield. Deagglomeration presumably involves uptake of oxygen by the coal since subsequent pyrolysis (TMBA) shows an increase in product carbon dioxide in the gas. The raw coal yielded 11 pounds of CO₂ per ton of coal, and the corresponding value for coal treated with steam and air was 31 pounds.

Pilot plant processing of three tons of the deagglomerated coal was carried out to produce the results given in Table 7. Due to the short run length, material balances were not attempted at each of the two conditions.

LABORATORY RETORTING

It is not always possible to obtain sufficient test coal for pilot plant operations. As described above, we have used the TMBA procedure to investigate retorting of small quantities of coal. Although TMBA is a batch operation and TOSCOAL processing is continuous, we have found the product yields and product properties to be sufficiently similar to encourage wider use of this relatively simple laboratory procedure.

An excellent application of the use of low temperature carbonization as an assay technique for coal was reported by Landers in 1961 (12). Data, similar to those produced using TMBA, were reported on 220 domestic and foreign coals.

The Tosco Fischer assay procedure has been applied to a number of Western coals and lignites. Five examples, other than those discussed above, are described in Table 8. The assays of the coals and product chars are shown. The increase in the heating value of the char, as compared to the raw coal, is to be noted. In examination of product yields, it is apparent that low temperature carbonization of the materials shown produces about a 50% yield of char, based on the as-mined raw coal or lignite. Gas, oil and water yields vary with the source of the coal and with the retorting conditions.

TABLE 6
ASSAYS OF PLATEAU COAL, ILLINOIS NO. 6 COAL
AND DEAGGLOMERATED ILLINOIS NO. 6 COAL

	<u>Plateau Coal</u>	<u>Illinois No. 6 Coal</u>	
		<u>As Received</u>	<u>Deagglomerated</u>
Proximate (wt%)			
Moisture	10.0	8.8	0.7
Ash	13.0	6.7	8.3
Volatile Matter	34.1	32.0	31.6
Fixed Carbon	<u>42.9</u>	<u>52.5</u>	<u>59.4</u>
Total	100.0	100.0	100.0
Sulfur	0.9	0.7	0.7
Free Swelling Index (FSI)	1.0	3.5	1.5
Heating Value (Gross, Btu/lb) (Dry Basis)	11,906	13,293	13,071
TMBA Results (Dry Coal Basis)			
TMBA No.	1252	1340	1341
TMBA Temp. (°F)	970	932	932
Oil, lb/ton	358.3	245.9	166.6
(gal/ton)	(45.6)	(27.9)	(19.0)
(API)	(18.6)	(2.2)	(2.7)
Char, lb/ton	1,417.9	1,603.6	1,675.2
Gas, lb/ton	140.1	79.1	103.8
(SCF/ton)	(2,039)	(1,360.8)	(1,630.7)
(Btu/SCF)	(945)	(1025)	(857)
Water, lb/ton	<u>76.5</u>	<u>39.9</u>	<u>40.8</u>
Total lb/ton	1,992.8	1,968.5	1,986.4

TABLE 7

TOSCOAL PROCESSING OF HIGHER RANK COALS
 PLATEAU COAL AND DEAGGLOMERATED ILLINOIS NO. 6 COAL

	Plateau Mine, Price, Utah		Inland Mine No. 1 - Illinois No. 6 Coal		Tosco Material Balance Assay No 1341**
	Tosco Material Balance Assay		Sesser, Illinois - Pilot Plant**		
	Pilot Plant	No 1252	Pilot Plant	Total of Two Runs	
Retorting Temp (°F)	960	970	1075		932
Products (lb/ton, dry coal basis)					
Char	1399	1418	ND	1469	1675
Oil	308	358	ND	107	167
Gas	216	140	93	171	104
Water	77*	77	ND	41*	41
Total Material	2000	1993		1748***	1987
Total Hydrocarbon as Oil & Gas (includes CO & H ₂)	436	437			236
PRODUCT PROPERTIES					
Char, Volatile Matter (wt%)	14.0	ND	13.9	9.7	ND
Oil, API	14.3	18.6	ND	ND	2.7
Gas					
SCF/ton	2448	2039	1395	3088	1631
Btu/SCF	1173	945	944	852	857

* Value from TMBA was used

** Prior to retorting, the coal was deagglomerated by treatment with steam and air in a fluid bed.

*** Material balance closure was not good due to small amount of total feed to the pilot plant.

ND Not Determined

TABLE 8

FISHER ASSAY PRODUCT YIELDS AND PROPERTIES

Coal	(Fischer Assay Temperature - 950°F)				
	Big Horn (1)	Big Sky (2)	Savage (3)	Arkansas Lignite (4)	Elkol (5)
Proximate (wt %)					
Moisture	22.0	21.9	33.2	24.2	19.5
Ash	4.8	9.5	6.0	10.8	3.0
Volatile Matter	34.8	29.6	29.5	ND	30.6
Fixed Carbon	38.4	39.0	31.3	ND	46.9
Total	100.0	100.0	100.0		100.0
Heating Value, Btu/lb	9,578	8,948	7,230	ND	10,484
Product Yields (lb/ton of as-mined coal)					
Char (Volatile Matter, wt% (Heating Value, Btu/lb)	1,023.3 (13.2)	1,144.6 (15.0)	879.1 (13.0)	899.6 (ND)	1,143.0 (15.4)
Gas (C ₃ & lighter) (SCF/ton) (Btu/SCF)	136.6 (1,940.4) (617)	118.9 (1,674.9) (613)	155.7 (1,886.7) (451)	155.2 (1,875.1) (500)	131.8 (1,933) (693)
Oil (C ₄ & heavier) (gal/ton)	222.2 (27.5)	162.7 (20.5)	126.9 (15.8)	295.9 (37.8)	187.0 (22.9)
Water	617.2	568.5	807.3	650.2	535
Total (lb)	1,999.3	1,994.7	1,969.0	2,000.9	1,996.8
Recovery (%)	100.0	99.7	98.5	100.0	99.8

(1) Big Horn Coal Company, Sheridan, Wyoming
 (2) Peabody Coal Company, Big Sky Mine, Colstrip, Montana
 (3) Knife River Coal Mining Company, Savage, Montana
 (4) Fischer Assay No 1258
 (5) Kemmerer Coal Company, Elkol Mine, Frontier, Wyoming
 ND - Not Determined

Using the type of data given in Table 8 it is feasible to estimate the yields and product properties to be obtained from commercial operations at any desired scale.

UTILIZATION OF PRODUCT CHAR

Utility Boiler Fuel

Important characteristics of solid fuels include the temperature of ignition, the temperature at the maximum rate of ignition, and the temperature at which complete burnout occurs. In most cases higher volatile matter and higher surface area are reflected in improved ignition characteristics. Chars from lower rank coals, such as lignite and subbituminous, generally ignite and burn rapidly due to the large surface area.

Laboratory tests have been conducted on TOSCOAL chars by three major boiler manufacturers. One found that the ignition characteristics were satisfactory and concluded that the char could be burned readily in a conventional, horizontally-fired boiler. Babcock and Wilcox personnel conducted burning profile tests on char in comparison to other solid fuels using the procedure published by Wagoner and Duzy (13). The results are illustrated in Figure 4. The "C-4 TOSCO" char was produced in our pilot plant from Wyodak coal by retorting at 800°F. The Tosco char ignited more readily and burned out completely at a lower temperature than did bituminous coals.

Another boiler firm conducted small scale firing tests with char from the C-3 pilot plant run. They concluded that this low VM char (16%) burned in a similar fashion to Pennsylvania low volatile bituminous coal.

Commonwealth Edison (Chicago) and others have extensively investigated the utility boiler firing of partially dried lignite (5). Improvements over firing raw lignite were observed.

Texas lignite has been used as a boiler fuel after both charring and drying (14). The current practice of Texas Utilities is to burn dried lignite at their Rockdale mine facility.

Formcoke

There is currently great interest in finding a substitute for the conventional blast furnace coke used in making iron for subsequent conversion to steel. The coke is made from expensive coking coals, and the manufacturing process involves substantial air pollution. The use of non-coking coals, such as those found in the Western United States would be attractive since they are cheap and the supply is virtually limitless. Much of the technology currently being investigated for manufacturing synthetic coke (formcoke) involves pyrolysis of non-coking coals and subsequent production of calcined briquettes or pellets from the char (15, 16, 17, 18). The addition of a pitch binder and sometimes some coking coal and other solids is required. Our judgment is that the TOSCOAL process can produce a satisfactory char and, after further oil processing, the pitch binder in an efficient and environmentally clean manner.

Feed to Gasification

One of the major problems encountered in coal gasification is handling the tars produced along with the primary gas product. These tars may cause

FIGURE 3

EFFECT OF TOSCOAL PROCESSING TEMPERATURE
ON CHAR VOLATILE MATTER AND GROSS HEATING VALUE
(Pilot Plant Results)

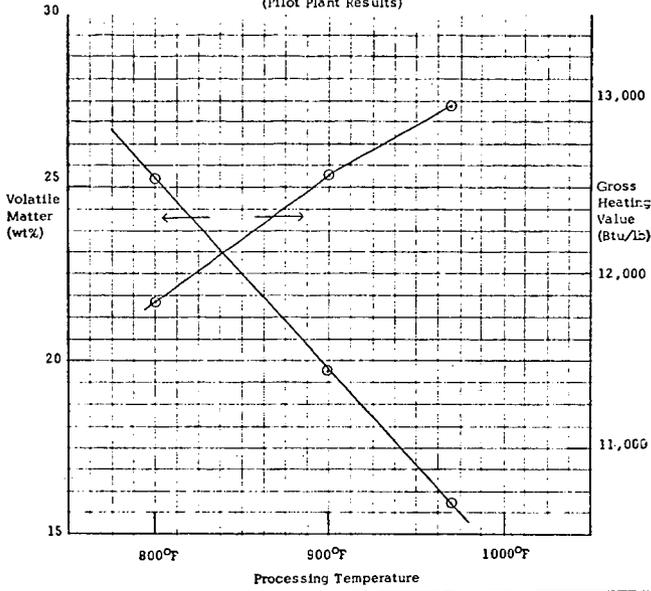
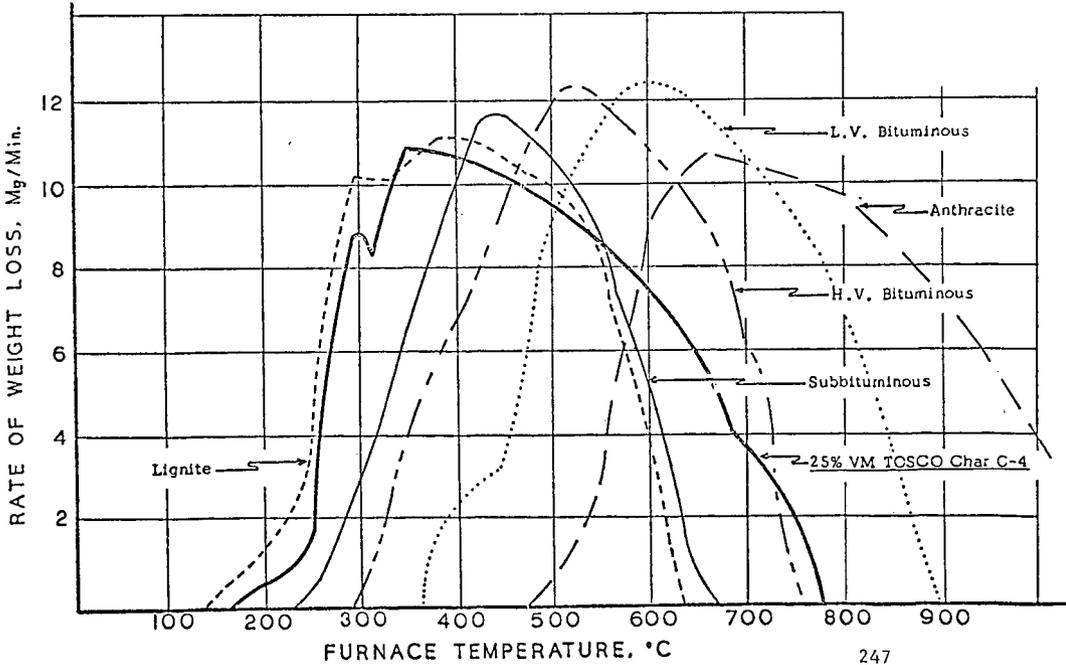


FIGURE 4

DTGA BURNING PROFILE



problems in heat recovery, in recovery of particulate solids and in water purification. Gasification of TOSCOAL char produces a synthesis gas free of tars and very low in methane, as illustrated in Table 9. Such a gas can be converted to high purity hydrogen or used as synthesis gas feed for methanol production.

Gasification of char has been investigated previously by FMC and others in the consortium called COGAS Development Company (19,20,21).

TABLE 9

GASIFICATION OF TOSCOAL CHAR
FROM ILLINOIS NO. 6 COAL

Conditions

Reactor Temperature (°F)	1525
Fluidizing Gas	Steam (no air or O ₂)

Product Gas Composition (Mole %)

H ₂	59.5
CO	18.3
CO ₂	19.9
H ₂ S	0.1
CH ₄	<u>2.3</u>
Total	100.1

UTILIZATION OF OIL

Oil from low temperature carbonization, 800-1000°F, of coal differs from that produced in a coke oven (1600°F) in that it contains a larger amount of oxygen and hydrogen and lower levels of pure compounds such as benzene and naphthalene.

Use of oil from TOSCOAL processing as a fuel oil is reasonable. Oils from Western coals and lignites generally have low-sulfur contents.

The oil from Run C-3, 970°F retorting of Wyodak coal (Table 4) yielded, by distillation, an IBP to 446°F fraction having a cresylic acid content of 65 volume percent. These acids are used in the manufacture of phenolic resins and phosphate ester plasticizers.

Oils from low temperature carbonization have been hydrogenated to a synthetic crude oil which has then been evaluated as a refinery charge stock (22), and as a carbon black feedstock (23).

After thermal treatment, oil from low temperature carbonization of lignite can be used as electrode pitch (24) and for the manufacture of coke (25).

Pitch, to be used in formcoke manufacture, can be made by air blowing the liquid product from low temperature carbonization (26).

ECONOMICS

The cost of a potential commercial TOSCOAL processing plant, using a subbituminous coal of the Big Horn type has been estimated. The design plant capacity yields are:

1) Feed rate, ton/day of "as mined" coal	7,230
2) Dry char product, ton/day	3,910
3) Oil product, bbl/day	4,130
4) Net product gas, MM Btu/day	2,261
5) Net gas, oil and dry char HHV values as a percent of wet feed HHV	94.7

Part of the hydrocarbon product mix is used internally as process fuel.

The plant envisioned is based on a maximum size single pyrolysis train operating at a retort temperature of 900^oF. Operation at 800^oF would increase plant capacity, but would produce somewhat less liquid product per ton of feed coal.

The investment, in June 1976 dollars, would be \$73 million for the pyrolysis battery limits. The investment cost does not include the mine, feed preparation, product storage, land, buildings, rail siding and loading facilities and offsite utilities. Equipment for sulfur dioxide removal is also not included but may not be necessary.

Components of the operating cost are:

- 1) A total of 28 shift workers
- 2) Maintenance cost of \$2.8 MM/year
- 3) Operating supplies of \$0.5 MM/year
- 4) Power requirement of 37 MM KWH/year

Expenditure of these estimated investment and operating costs would produce a superior solid fuel which would offer cost savings in utility power generation. A recent study (27) compared investment costs and operating parameters for a 500 megawatt P.C. (pulverized coal) fired boiler to be fired, on the one hand, with Gillette, Wyoming coal and North Dakota lignite and, on the other hand, with chars from these coals. In the Gillette coal case an investment savings of nine dollars per installed KW can be realized, for the boiler island, in changing fuels from raw coal to char. These savings are mainly in reduced requirements for pulverizers and for boiler furnace size. Further, boiler efficiency would improve by 5.3% and internal power consumption, mainly for fans and pulverizers, would decrease by 2,500 KW.

Corresponding savings in the North Dakota lignite case were higher. The investment would be reduced by \$17.5 per installed KW. Boiler efficiency would improve by 6.8%, and internal power consumption would decrease by 6,300 KW.

In addition to savings in power generation, an advantage of char over moist, "as mined" coal and lignite would be in lowered freight costs. Assuming a freight cost of 12 mills/ton mile, the cost of shipping a ton of Wyodak coal (Table 1) 1,000 miles would be \$12.00 or \$.74/MM Btu. On the same basis, the cost of shipping one ton of Wyodak char (C-8 run, Table 3) would be only \$.51/MM Btu. This saving assumes there would be no offsetting cost in handling the more pyrophoric and dusty char.

Covered hopper cars have been manufactured by Thrall Car Manufacturing Company (Chicago Heights, Illinois) and perhaps could be used to haul char produced from low temperature carbonization. Currently, the "flip top" cars are being used to ship "as mined" lignite across North Dakota to the Big Stone Power project at Big Stone City, South Dakota. The covered car was needed to reduce dust loss and to prevent freezing during the winter.

SUMMATION

TOSCOAL processing of coal is based on technology acquired in twenty years of continuous work on the TOSCO II oil shale retorting process. Coals of low rank can be used directly. Those of higher rank may be retorted after treatment with air and steam to effect decaking.

Processing of Western coals and lignites is of interest in reducing the large freight costs currently involved in transporting moisture and non-combustible components. Use of chars rather than coal as utility boiler fuels offers investment and operating cost advantages. Chars produced may also be used in the manufacture of formcoke and as an improved feedstock in gasification.

Liquid products may be used as a fuel, and as a source of chemicals, coke and pitch binders.

High heating value gas is produced as a coproduct.

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