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Desulfurization of Coal in a Fluidized-Bed Reactor

Abstract
The pioneering investigation of Jacobs and Mirkus (1) 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 2-10% or steam concentrations in the range of 0-85%. The sulfur content of the char declined as the treatment temperature.

Disciplines
Catalysis and Reaction Engineering | Nuclear Engineering | Petroleum Engineering | Process Control and Systems

Comments
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Desulfurization of Coal in a Fluidized-Bed Reactor

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The pioneering investigation of Jacobs and Mirkus (1) 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 2-10% or steam concentrations in the range of 0-85%. The sulfur content of the char declined as the treatment temperature was increased 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 (2) 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 10-17% weight loss. However, the results of a similar series of experiments by Block et al. (3) 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 \((3,4,5,6)\). 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 evolution rate of hydrogen sulfide. Yergey et al. \((7)\) attributed the first peak, which occurred in the range of 390°–470°C for different coals, 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 hydrogen sulfide in the gas phase which severely limits the concentration build-up of hydrogen sulfide \((5,8,9,10)\).

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 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 was passed through a fluidized bed reactor containing the coal being treated and then 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 periodical-ly 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
Figure 1. Experimental apparatus flowsheet
effective pore size of 20μm. It was also equipped with a thermo­
well and a device for injecting coal at a point just above the
gas distributor. The reactor was placed in an electrically heat­
ed, 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 were analyzed with the mass
spectrometer. After a run was completed, the reactor was un­
coupled 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. This method of analysis did not distinguish
between sulfur present as ferrous sulfide (FeS) and organic
sulfur.

**Materials.** Two run-of-mine (ROM) 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 screen­
ed to provide material in the -20+40 mesh size range. After
siev­ing, each sample was split into two fractions. One fraction
was used 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 con­
tent as well as the pyritic sulfur content of the coal, the
beneficiated fraction is referred to as deashed coal. The com­
position and heating value of the two run-of-mine samples and
corresponding deashed fractions are shown in Table I.

**Results and Discussion**

**First Series of Runs.** The first series of runs was carried
out to determine the effects of four different treatment gas com­
positions 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
Table I. Composition of Jude Mine Coal on an As-Received Basis

<table>
<thead>
<tr>
<th>Type of Analysis</th>
<th>Sample I</th>
<th>Sample II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM</td>
<td>Deashed</td>
</tr>
<tr>
<td>Proximate (wt %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>moisture</td>
<td>6.35</td>
<td>2.24</td>
</tr>
<tr>
<td>volatile matter</td>
<td>41.14</td>
<td>46.03</td>
</tr>
<tr>
<td>fixed carbon</td>
<td>38.68</td>
<td>48.84</td>
</tr>
<tr>
<td>ash</td>
<td>13.83</td>
<td>2.90</td>
</tr>
<tr>
<td>Sulfur (wt %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfate</td>
<td>0.49</td>
<td>0.39</td>
</tr>
<tr>
<td>pyritic</td>
<td>2.40</td>
<td>0.60</td>
</tr>
<tr>
<td>organic</td>
<td>3.54</td>
<td>3.97</td>
</tr>
<tr>
<td>total</td>
<td>6.43</td>
<td>4.96</td>
</tr>
<tr>
<td>Heating value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Btu/lb)</td>
<td>10,980</td>
<td>13,430</td>
</tr>
<tr>
<td>Specific sulfur content</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(lb. S/10^6 Btu)</td>
<td>5.86</td>
<td>3.69</td>
</tr>
</tbody>
</table>

as Sample I in Table I 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 30-40 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 5-10 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 II. Since duplicate runs were made at the lowest and highest temperatures, each listed value represents an average for two runs at these temperatures. 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 because of the escape of volatile matter. This loss increased directly with temperature but was
Table II. Results of the First Series of Runs with Run-of-Mine Coal

<table>
<thead>
<tr>
<th>Trt. Gas</th>
<th>Temp. (°C)</th>
<th>Wt. Loss (%)</th>
<th>Sulfur Removed (%)</th>
<th>lb. S (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pyritic</td>
<td>Organic</td>
</tr>
<tr>
<td>100% N(_2)</td>
<td>235</td>
<td>11.6</td>
<td>9.2</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>14.0</td>
<td>7.8</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>31.6</td>
<td>7.4</td>
<td>49.1</td>
</tr>
<tr>
<td>85% H(_2)</td>
<td>235</td>
<td>11.8</td>
<td>7.1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>15.0</td>
<td>7.7</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>33.6</td>
<td>29.2</td>
<td>35.4</td>
</tr>
<tr>
<td>4% O(_2)</td>
<td>235</td>
<td>11.7</td>
<td>8.2</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>16.0</td>
<td>12.9</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>410</td>
<td>30.7</td>
<td>41.2</td>
<td>46.4</td>
</tr>
<tr>
<td>10% O(_2)</td>
<td>240</td>
<td>10.0</td>
<td>7.9</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>330</td>
<td>18.5</td>
<td>8.6</td>
<td>22.7</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>63.0</td>
<td>73.3</td>
<td>79.8</td>
</tr>
</tbody>
</table>

\(^a\)Specific sulfur content of char product.

not much different for different treatment gases except for the case when a gas containing 10% oxygen was used at the highest temperature, and over 60% of the coal was consumed. With this one exception the weight loss seemed caused primarily by pyrolysis rather than by 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 was used, and only a small amount of light oil and water was condensed when either of the oxygen bearing gases was used.

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

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

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 II). However, when either hydrogen- or oxygen-bearing gases were used, a significant percentage of the pyritic sulfur was removed at the highest temperature 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 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 caused mainly by 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 using the relation:

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

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 between forms of sulfur. 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 with an oxygen-bearing gas at 235°C. However, it does not 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 (4) 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 most of the treatments, the specific sulfur content of the treated run-of-mine coal (Table II) was actually slightly larger than that of the feed (5.86 lb. S/10^6 Btu). For run-of-mine coal the lowest
Figure 2. Sulfur distribution diagrams for coal char after oxygen treatments
specific sulfur content (4.9 lb. S/10^6 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/10^6 Btu) following most 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 I 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 25-50 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 10-15 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 using 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 III. 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 was used as the treatment gas, the off-gas contained small but significant 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 materials entering and leaving the system.

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
Table III. Results of Selected Runs in Second Series

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Coal Type</th>
<th>Trt. Gas</th>
<th>Temp. (°C)</th>
<th>Gas vel. (cm/sec)</th>
<th>Time (min)</th>
<th>Wt. loss (%)</th>
<th>Total S removed (%)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSN-1</td>
<td>ROM</td>
<td>100% N₂</td>
<td>375</td>
<td>44</td>
<td>60</td>
<td>32.8</td>
<td>39.1</td>
</tr>
<tr>
<td>MSN-4</td>
<td>deashed</td>
<td>100% N₂</td>
<td>395</td>
<td>26</td>
<td>60</td>
<td>23.5</td>
<td>41.8</td>
</tr>
<tr>
<td>MSH-1</td>
<td>ROM</td>
<td>87% H₂</td>
<td>395</td>
<td>48</td>
<td>60</td>
<td>29.8</td>
<td>44.1</td>
</tr>
<tr>
<td>MSH-3</td>
<td>deashed</td>
<td>84% H₂</td>
<td>400</td>
<td>32</td>
<td>90</td>
<td>22.4</td>
<td>32.3</td>
</tr>
<tr>
<td>MSO-7</td>
<td>ROM</td>
<td>10% O₂</td>
<td>375</td>
<td>34</td>
<td>90</td>
<td>37.4</td>
<td>48.7</td>
</tr>
<tr>
<td>MSO-8</td>
<td>deashed</td>
<td>10% O₂</td>
<td>370</td>
<td>26</td>
<td>90</td>
<td>30.1</td>
<td>41.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Liq. yield (lb./lb. coal)^b</th>
<th>Yield (SCF/lb. coal)</th>
<th>Heat. value (Btu/SCF)</th>
<th>Specific sulfur content (lb. S/10^6 Btu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Feed</td>
<td>Char</td>
<td>Char &amp; Gas</td>
</tr>
<tr>
<td>MSN-1</td>
<td>0.14</td>
<td>2.04</td>
<td>522</td>
<td>7.4</td>
</tr>
<tr>
<td>MSN-4</td>
<td>0.14</td>
<td>1.49</td>
<td>524</td>
<td>4.9</td>
</tr>
<tr>
<td>MSH-1</td>
<td>0.17</td>
<td>0.97</td>
<td>780</td>
<td>7.4</td>
</tr>
<tr>
<td>MSH-3</td>
<td>0.15</td>
<td>0.96</td>
<td>912</td>
<td>4.9</td>
</tr>
<tr>
<td>MSO-7</td>
<td>0.10</td>
<td>13.03</td>
<td>432</td>
<td>7.4</td>
</tr>
<tr>
<td>MSO-8</td>
<td>0.12</td>
<td>7.29</td>
<td>379</td>
<td>4.9</td>
</tr>
</tbody>
</table>

^a Determined by Equation 1.

^b Condensed tar and water.

^c Volume 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.
this quantity agreed reasonably well with the gas analysis made with the mass spectrometer. However, the quantity of sulfur appearing as noncondensible 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.

The specific sulfur content of both the product char and the char and fuel gas combined was estimated (Table III). 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.

Formation Rates 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 formation rate 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 noncondensible sulfur compound in the off-gas during these runs. For both treatment gases, the formation rate of hydrogen sulfide first increased, subsequently peaked, and then decreased monotonically with increasing conversion. The initial increase in the rate was probably caused by 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
Figure 3. Rate of \( \text{H}_2\text{S} \) formation during pyrolysis in nitrogen

Figure 4. Rate of \( \text{H}_2\text{S} \) formation during treatment with gas containing 85% hydrogen
sulfur species in coal, which is in agreement with Yergey et al. (7). 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 caused by the superposition of reactions involving the two sulfur species. Although the curves representing the formation rate 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 to treat coal, sulfur dioxide was usually the major noncondensible sulfur compound in the off-gas, but significant amounts of hydrogen sulfide were also present. The formation rate 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 caused by 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. 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
Figure 5. Rate of $SO_2$ formation during treatment with gas containing 10% oxygen.
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 would 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 would have a relatively high heating value. Hydrogen sulfide 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 used together with a 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 (1,2), 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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Literature Cited