LOW-SULFUR LIQUID FUELS FROM COAL

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INTRODUCTION

Coal combustion is a major source of sulfur dioxide, and since electric utilities are the major consumers of coal, power generating stations are the principal points of origin for this pollutant.[1] Consequently, the air pollution regulations designed to check the emission of sulfur dioxide concern the electric utilities. The sulfur dioxide abatement regulations of many communities translate to a permissible concentration of 0.3 - 1.0 percent sulfur in fuels,[2] with 0.7 a common limit. This level of sulfur is too low for most of the coal that has been consumed by power generating stations to be permissible fuels.[3] The present work describes a method for producing an acceptable low-sulfur utility fuel by hydrodesulfurizing coal catalytically in a continuous fixed-bed reactor.

The reaction of coal with hydrogen has been studied extensively in the past with the objective of producing gasoline and special fuel oils.[4,5,6] At elevated temperatures and pressures and in the presence of suitable catalysts, coal reacts with hydrogen to give a mixture of liquid and gaseous hydrocarbons and the heteroatoms in coal are eliminated as hydrides. The initial liquid hydrocarbon products may then be upgraded to gasoline or other high grade fuels but an item of major cost in the process is hydrogen. Coals contain about 5 percent hydrogen, gasoline about 14 percent, and many fuel oils about 9-11 percent. Thus, large quantities of hydrogen, an expensive gas, are required to produce gasoline or such oils from coal. However, detailed considerations of past data reveal that the consumption of hydrogen in the primary liquefaction of coal is small; the bulk of the hydrogen is consumed in upgrading the products of primary liquefaction. A solution to the fuel problem of the electric utilities may, therefore, be found by limiting the hydrogenation of the coal to the primary liquefaction step only, making desulfurization with minimal hydrogen consumption the exclusive objective. The expenditure of hydrogen on the primary liquefaction of coal is of course unavoidable because of the molecular alterations associated with removal of bound sulfur; however the far larger expenditure of hydrogen in upgrading the products of primary liquefaction to even lower molecular weights may be eliminated.

The work of this report shows that the reaction of coal with hydrogen may be conducted under select conditions that promote desulfurization but minimize additional hydrogenation of the products from the primary liquefaction. The relatively viscous liquid product may then be used as a low-sulfur utility fuel either directly or after further physical refinement by removal of the ash and unreacted coal, depending on the design of the furnace to be fired with it. An ash-free fuel is of considerable benefit to some furnace-boiler or even turbo-engine installations.

Hydrodesulfurization of a tar slurry of coal containing 3.4 percent sulfur to yield a fuel having 0.3 percent sulfur at 4,000 psig was described in our earlier publication.[9] It has now been found that fuel oils containing an equally low level of sulfur are obtained at the more economical conditions of reduced pressure of 2,000 psig and shorter residence time when the product is centrifuged and recycle oil is used instead of tar as feed vehicle. Complete solids removal would yield oils of only 0.18 percent sulfur from this coal at these conditions. The yields and chemical and physical properties of desulfurized synthetic fuel oils from three different coals are detailed in this report.

EXPERIMENTAL

Basically, to effect hydrodesulfurization without unnecessary hydrogenation, a short residence time in a packed-catalyst-bed reactor is used. Conditions are highly turbulent to prevent plugging and to assist catalysis. Extensive engineering details concerning plant operations and selection of conditions have been presented elsewhere;[10] thus a brief description of the experimental approach suffices here.

Plant and Procedure. Figure 1 is a simplified diagram of the hydrodesulfurization plant. The reactor was a 68-foot long tube of 5/16-inch id, folded into 3-1/2 hairpin loops to fit inside a vertically placed, 10-foot long, cylindrical furnace of 10-inch id. The reactor was charged with about 2 lb of a commercial Co-Mo/SiO_2-Al_2O_3 catalyst. The feed stream of coal slurry in high-temperature tar and hydrogen passed through a preheater before entering the reactor from the bottom end. The product stream leaving the reactor at the top end was led through a water-cooled condenser to a high-pressure receiver for liquid products. The liquids and unreacted solids were collected in this receiver from where they were intermittently discharged into a vessel at atmospheric pressure. The gases leaving the receiver were passed through a second condenser and a second high-pressure receiver to ensure condensation and collection of any low-boiling product not retained in the first receiver. It may be mentioned, inter alia, that in the series of runs described in this paper, no liquid was collected in the second high-pressure receiver. The gas stream was scrubbed with alkali solution to remove H_2S and NH_3, then finally reduced to atmospheric pressure, metered, sampled, and flared. In multiple-pass experiments, the products were reintroduced into the reactor for as many repeated hydrotreatments as desired.

Since a commercial operation will almost certainly be conducted with slurries of coal in a portion of the steady state liquid generated in the process itself, the hydrodesulfurization of coal in a vehicle of coal-derived liquid was also studied. The coal-derived liquid was prepared by conducting a 4-cycle hydrodesulfurization experiment in which the feed for the first cycle was a slurry of 30 wt pct coal in tar while the feeds for the second, third, and fourth cycles were slurries of 30 wt pct coal in the centrifuged liquid products from the preceding cycle. It is estimated that the centrifuged liquid products from the fourth cycle contained at least 80 percent coal-derived liquids.

For secondary reasons, continuous operation of the plant was limited to a maximum of 12 days after which the plant was shut down for 2 days. Each run was started with a newly made reactor charged with fresh catalyst.

Sampling of the Products and Analysis. The liquid products from 25 lb of slurry feed were collected in a batch and sampled for analysis. Benzene insolubles, asphaltenes, and oils were determined by conventional solvent analysis: asphaltenes are soluble in benzene but insoluble in pentane, whereas oils are soluble both in benzene and pentane. Ash was determined by igniting the benzene insolubles. The concentrations of sulfur in the total liquid products and in the benzene insolubles, asphaltenes, and oils separately were determined by the Bomb-Washing Method.[7] The distribution of pyritic, organic, and sulfate sulfurs in the benzene insolubles was determined by the method recommended for the determination of forms of sulfur in coal.[8] The sulfur in asphaltenes and oils was assumed to be all organic.

Samples of the tail gas were analyzed periodically by gas chromatography to determine the formation of gaseous hydrocarbons. A small amount of methane is made.

Materials. Analyses for the three different feed coals and the high-temperature tar used in this work are presented in table 1. The coals were ground to pass 100 percent through a 14-mesh U.S. Standard sieve and 70 percent through a 200-mesh sieve. The high-temperature tar was derived from the coking of metallurgical grade bituminous coal and had been topped to 400° C by the suppliers, Koppers Co., Inc.* The Co-Mo/SiO_2-Al_2O_3 catalyst was purchased from Harshaw Chemical Co. (Manufacturer's identification number: 0402T).

RESULTS AND DISCUSSION

Hydrodesulfurization of Coal Using High-Temperature Tar as Vehicle. The results from the hydrodesulfurization of three different coals in a vehicle of high-temperature tar at 2,000 psi and 450° C are presented in tables 2 and 3. The tar was a useful facsimile of recycle product oil until it became available. In tar, Pittsburgh seam coal containing 1.3 percent sulfur was desulfurized to a fuel containing 0.3 percent sulfur, an Indiana #5 seam coal containing 3.4 percent sulfur was desulfurized to a fuel containing 0.42 percent sulfur, and a Middle Kittanning #6 seam coal containing 3.0 percent sulfur was desulfurized to a fuel containing 0.36 percent sulfur. In each case, the ash in the feed remained quantitatively in the products. The calorific value of the products from the three coals were about the same, 16,400 Btu/lb. About 284 scf of H_2 was consumed in processing 100 lb of the feed prepared from Pittsburgh seam coal, 304 scf of H_2 in processing 100 lb of feed prepared from the Indiana #5 seam coal, and 330 scf of H_2 in processing 100 lb of feed prepared from Middle Kittanning #6 coal. These figures for the consumption of hydrogen were calculated from the analyses of the feeds and the products and the yields of the liquid and gaseous products. The eliminated sulfur was assumed to be in the form of H_2S and nitrogen as NH_3. The consumption of hydrogen for reaction with oxygen was calculated by assuming total elimination of oxygen from the product. Determinations of oxygen by difference supports this assumption. In view of expected inaccuracies, these indirect figures should be considered only approximately indicative of the hydrogen requirement for the process. The plant is being modified to measure the consumption of hydrogen directly.

From the additional properties of the products listed in table 3, it is seen that the viscosities of the products from the two high-sulfur coals are lower than the viscosity of the products from Pittsburgh seam coal. It appears that the lower grade coals hydrogenate more extensively.

None of the products in table 3 contained components distillable below 200° C and the fraction distillable below 355° C was about the same, 20 percent by weight for each of the products.

Hydrodesulfurization of Coal in a Vehicle of Coal-Derived Liquid and the Properties of the Products Before and After Centrifugation. Tables 2 and 3 also contain the results from the hydrodesulfurization of Middle Kittanning #6 coal in a vehicle of coal-derived liquid (recycle oil). It may be noted that these results refer to a one-pass hydrotreatment of the feed compared to three-pass hydrotreatments of the feeds prepared in high-temperature tar. Thus the residence time is only one-third of that used for the tar slurry feeds. The concentration of sulfur in the products was 0.48 percent before centrifugation and 0.31 percent after centrifugation. The centrifugation residues amounted to about 9.5 percent by weight of the whole liquid products, and consisted of 33 percent organic benzene

* References to specific brands of materials are made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1.- Analyses of the feed coals and feed tar, as received

	hvab Pittsburgh seam coal	hvbb Indiana #5 seam coal	hvbb Middle Kittanning #6 seam coal	High-temperature tar
Proximate analysis, wt pct				
Moisture	1.0	6.1	2.4	-
Ash	11.1	8.9	9.4	-
Volatile matter	33.7	38.6	39.2	-
Fixed carbon	54.2	46.4	48.6	-
Ultimate analysis, wt pct				
Moisture	1.0	6.1	2.4	-
Ash	11.1	8.9	9.8	0.7
Carbon	73.5	67.0	71.0	92.3
Hydrogen	4.9	5.3	5.2	4.9
Nitrogen	1.4	1.4	1.3	1.2
Oxygen, by difference	6.8	7.9	7.3	0.3
Sulfur	1.3	3.4	3.0	0.6
as sulfate	0.07	0.37	0.01	-
as pyrite	0.60	0.98	1.28	-
as organic	0.63	2.07	1.71	0.6
Solvent analysis, wt pct				
Benzene insolubles	-	-	-	14.0
Asphaltenes	-	-	-	39.6
Oil	-	-	-	46.4
Heat content, Btu/lb	13,320	11,750	12,540	16,260

TABLE 2.- Hydrodesulfurization of coal slurries at 450° C and 2,000 psi
Slurry feed rate: 5 lb/hr
Hydrogen feed rate: 500 scfh

Feed	Gross Oil Product Analysis			
	S, wt pct	Ash, wt pct	Calorific value, Btu/lb	H_2 consumed, scf/100 lb of feed
30 wt pct Pittsburgh seam coal in tar[1]	0.3	1.5	16,450	284
30 wt pct Indiana #5 seam coal in tar[1]	0.42	2.7	16,415	304
30 wt pct Middle Kittanning #6 seam coal in tar[1]	0.36	2.5	16,310	330
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquid,[2]				
before centrifugation	0.48	3.5	16,200	139
after centrifugation[3]	0.31	1.3	16,840	-

[1] 3-pass hydrotreatment.
[2] 1-pass hydrotreatment.
[3] Centrifuge cake = 9.5 percent of gross product.

TABLE 3.- Some additional properties of the products from hydrodesulfurization of coal slurries at 450° C and 2,000 psi

Slurry feed rate: 5 lb/hr

Hydrogen feed rate: 500 scfh

Feed	Products					Distillable fraction, wt pct	
	Sp. gr., 60°/60° F	Viscosity, SSF at 180° F	C, wt pct	H, wt pct	N, wt pct	<200° C	<355° C
30 wt pct Pittsburgh seam coal in tar[1]	1.199	55	90.5	6.1	1.0	0.0	21.0
30 ey pct Indiana #5 seam coal in tar[1]	1.188	26	89.8	6.3	0.8	0.0	23.6
30 wt pct Middle Kittanning #6 seam coal in tar[1]	1.191	40	89.6	6.3	0.8	0.0	18.2
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquid,[2]							
before centrifugation	1.148	101	84.9	7.4	0.9	0.0	27.5
after centrifugation[3]	1.135	135	88.4	7.5	0.9	-	-

1 3-pass hydrotreatment.

2 1-pass hydrotreatment.

3 Centrifuge cake = 9.5 percent of gross product.

insolubles, 28 percent ash, 9 percent asphaltenes, and 30 percent oil. As may be expected, the specific gravity of the products was lower after centrifugation than before, but the viscosity of the products was surprisingly higher after centrifugation than before. This was probably due to atmospheric oxidation of the products during storage prior to centrifugation and during centrifugation. As is known, products of coal hydrogenation are sensitive to atmospheric oxidation.

It is interesting to note from table 2 that H_2 consumption drops remarkably when recycle oil is the vehicle instead of tar. As expected, the recycle oil is not as susceptible to further hydrogenation as tar is to initial hydrogenation.

Forms and Distribution of Sulfur in the Products. The forms and distribution of sulfur in the products from the hydrodesulfurization of Middle Kittanning #6 seam coal in high-temperature tar are presented in table 4. Similar data for products from the same coal processed in recycle oil have not been completed at this writing. The concentrations of sulfur in the benzene insoluble, asphaltene, and oil fractions of the products were determined separately. The bulk of the residual sulfur is always contained in the benzene insoluble fraction. This fraction, amounting to 13.2 percent of the products, contained 1.54 percent sulfur. The asphaltene and the oil fractions, which amounted to 21.7 and 65.1 percent of the products respectively, each contained 0.18 percent sulfur.

Thus it is clear that, if complete removal of the benzene insolubles could be obtained, theoretically 87 percent of the products may be recovered as an ash-free liquid containing only 0.18 percent sulfur. Aside from its premium quality as a fuel, such a liquid may be a valuable raw material for electrode carbon and to fuel turbine engine electric generators.

A determination of the forms of sulfur in the benzene-insoluble fraction revealed that 88 percent of the sulfur in it was organic, 7 percent pyritic, and 5 percent sulfate. The sulfur in the asphaltene and oil fractions may be assumed to be all organic. Thus, the total product contained 0.34 percent organic sulfur and only 0.01 percent each of pyritic and sulfate sulfurs. Since the feed contained 0.38 percent pyritic and 0.93 percent organic sulfur, the pyritic sulfur is evidently eliminated preferentially.

Data reported previously[9] showed that the fuel oil product from Pittsburgh seam coal could have a sulfur content as low as 0.09 percent if the benzene insolubles and ash are removed.

Yields. As is known, the concentrations of moisture, sulfur, and oxygen vary widely in coals. Removal of sulfur is of course the objective of the process, but the desulfurization is necessarily accompanied by removal of moisture and oxygen. Thus, yields of desulfurized fuels from coal may vary widely. If the desulfurized products are centrifuged, the yield of the centrifuged fuel will also vary with the concentration of mineral matter in coal. Evidently, a statement of yield will be meaningless unless accompanied by a statement of the maximum theoretical yield for each coal.

But even if the cumbersome practice of reporting yields together with the maximum theoretical yields is adopted, an important feature of the process will remain masked. The calorific values of the products are higher than the calorific values of the feeds, and despite mass losses in processing, the available heat from the products is frequently more than the available heat from the feeds. Thus, the heat content yields may be more than 100 percent even though the mass yields are less than 100 percent. Since for evaluating a fuel-making process

TABLE 4.- Forms and distribution of sulfur in the products from hydrodesulfurization of 30 wt pct Middle Kittanning #6 seam coal in tar

S, wt pct, in	
Benzene insolubles (13.2% of Prod.)	1.54
Asphaltenes (21.7% of Prod.)	0.18
Oil (65.1% of Prod.)	0.18
Forms of S, wt pct, in the benzene-insoluble fraction	
Sulfate	0.11
Pyritic	0.07
Organic	1.36
Forms of S, wt pct, in the total liquid products, assuming all S in asphaltenes and oil to be organic	
Sulfate	0.01
Pyritic	0.01
Organic	0.34
Total	0.36
S, wt pct, in the total liquid products by direct determination	0.38

the relevant yield is obviously the heat content yield, the following discussion will be in terms of Btu yields.

Generally, Btu yields in excess of 100 percent, when based on the liquid feed input, are explained thus: Hydrocracking reactions that produce lower molecular weights are slightly endothermic and absorb energy from the reactor system; more important, additional hydrogen is added to raise the calorific value.

From the figures presented in table 5, it will be seen that the Btu yields for the products from the hydrodesulfurization of coals in high-temperature tar are, in each case, in excess of 100 percent. The Btu yield for the hydrodesulfurization of Middle Kittanning #6 coal in coal-derived oil is 97 percent before centrifigation and 91 percent after centrifugation. It may be emphasized that the figures refer to the yields based on total feed, not coal alone. High-temperature tar also undergoes hydrotreatment and so does the recycle oil but not as extensively as tar. Therefore, the Btu yield appears lower for the recycle system.

SUMMARY AND CONCLUSIONS

It has been demonstrated that liquid fuels containing 0.3 percent sulfur may be prepared in entirety from coals containing 3.0 - 3.4 percent sulfur by catalytic hydrodesulfurization in a continuous fixed-bed operation at 450° C and 2,000 psi, followed by centrifugation of the products. The Btu yield of the centrifuged fuel is 91 percent. In areas where air pollution regulations are less stringent, the direct product of hydrodesulfurization may be used as a fuel without centrifugation. Such product contains 0.4 - 0.5 percent sulfur and its Btu yield is 97 - 102 percent. The desulfurized synthetic fuels are liquid at or near ambient temperature, suitable for direct use in oil-fired burners.

The residual sulfur in the products is essentially entirely of organic nature and the bulk of it is contained in the benzene-insoluble components. Because the product is liquid at low temperatures without significant volatility, solids separation should be relatively easy, to yield an ashless, very low-sulfur fuel oil.

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TABLE 5.- Yields of desulfurized fuels

Feed	Calorific value of feed, Btu/lb	Product		
		Exptal. Yield, wt pct	Calorific value, Btu/lb	Yield, Btu pct
30 wt pct Pittsburgh seam coal in high-temperature tar	15,378	94	16,450	100.6
30 wt pct Indiana #5 seam coal in high-temperature tar	14,907	93	16,415	102.4
30 wt pct Middle Kittanning #6 seam coal in high-temperature tar	15,144	94	16,310	101.2
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquids, ...	15,550			
before centrifugation		93	16,200	96.9
after centrifugation		84	16,840	91.0

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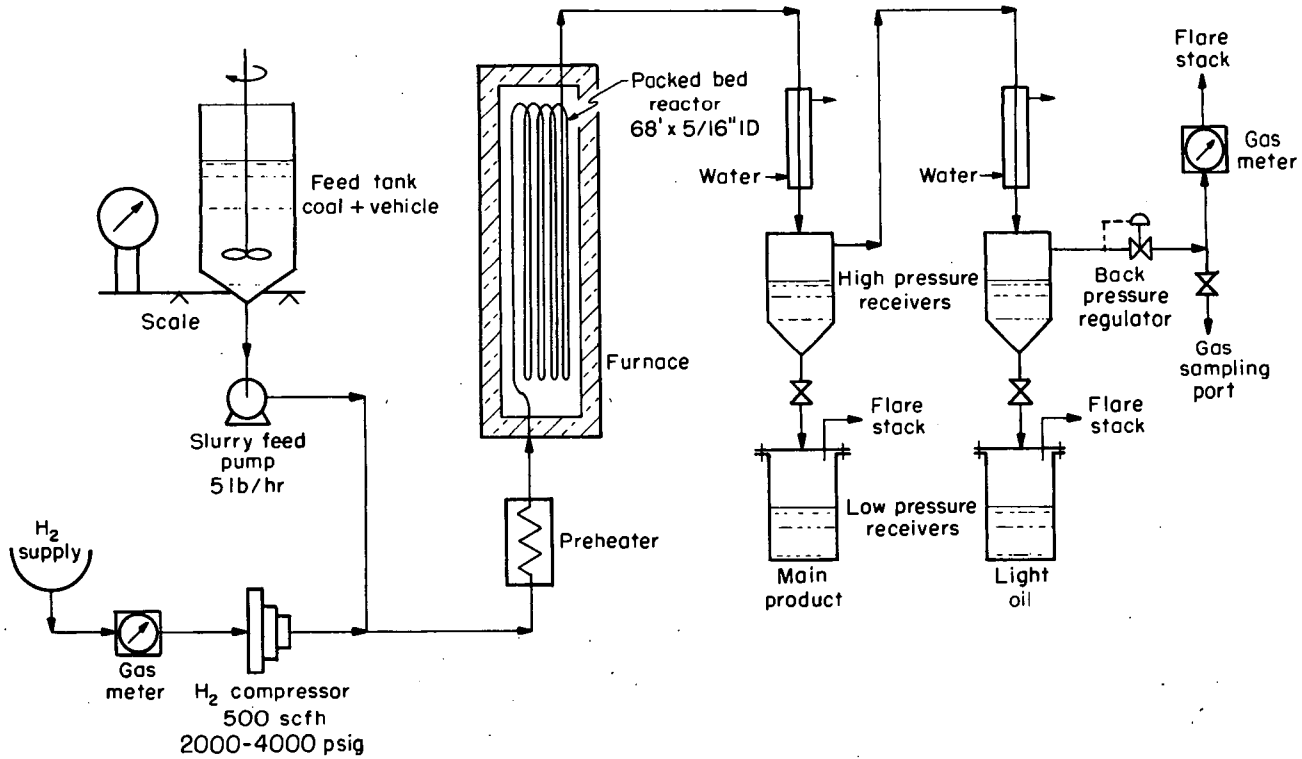

Figure 1—Simplified schematic diagram of hydrodesulfurization pilot plant.

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