

# The Selectivity of Coal Minerals as Catalysts in Coal Liquefaction and Hydrodesulfurization

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## Introduction

Certain coal minerals are well-known to catalyze liquefaction and hydrodesulfurization in coal conversion processes (1,2,3,4). It is generally understood in connection with liquefaction processes that heating coal to temperatures in the range of 350°C and higher produces free radicals by thermal bond rupture. These free radicals are then stabilized by abstracting a small entity such as a hydrogen atom from some source. The source may be hydrogen chemically interacted with the catalyst (coal minerals or other added catalysts), hydrogen on the hydroaromatic portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5,6,7). Some studies of catalytic hydrodesulfurization of coal-solvent slurry systems have been done with various commercial catalysts (8,9,10). Instead of voluminous work with good hydrogenation and hydrodesulfurization catalysts, little attention has been paid to coal mineral catalysis. Coal mineral catalysis might be important in the Solvent Refined Coal (SRC) process, in which solid boiler fuel is produced through mild or little hydrogenation of coal - probably mainly through dissolution of coal.

To better understand the importance of coal mineral catalysis in the SRC process, this work presents comparative results of the rates of hydrogenation and hydrodesulfurization of coal/oil slurries under different reaction conditions and in the presence of different coal minerals. The selectivity of coal minerals such as reduced iron and SRC residue (Wilsonville SRC pilot plant) for hydrodesulfurization as opposed to hydrogenation has been determined based on product distribution (oil, asphaltene and preasphaltene), sulfur content of each product and analyses of liquid products. The rate limiting steps, or the reaction step most affected by catalytic activity of coal minerals have also been examined.

## Experimental

### Equipment

All autoclave studies were performed in a commercial 300 cc magnedrive autoclave (Autoclave Engineers). The autoclave was equipped with a stirrer, thermowell, furnace, cooling coil, gas inlet and sampling lines. Coal-tetralin systems were studied in a small tubing-bomb reactor ( $\frac{1}{2}$ " O.D. stainless steel tube with 0.035" wall thickness). Under air atmosphere about 16 ml reactors were used with Swagelock caps on both ends. Hydrogen gas was introduced into a smaller tubing-bomb reactor (about 13 ml), sealed with Swagelock cap on one end, through 1/16" tube which was connected to the pressure indicator to read pressure change during reaction. Varian gaschromatographs (Model 1800) were used for analysis of oil fraction. A Leco sulfur determinator (Model 532) was used for analysis of sulfur in each product.

### Materials

Creosote oil (Allied Chemical Company) and light recycle oil (LRO) used in this study were obtained from Southern Services, Inc. The creosote oil has a carbon-to-hydrogen ratio of 1.25 (90.72% C and 6.05% H), a specific gravity of 1.10 at 25°C, and a boiling point range of 175 to 350°C. The creosote oil consists of 96.1% oil, 3.5% asphaltene, 0.2% preasphaltene and 0.3% pyridine insolubles. The light recycle oil (LRO) contains mainly oil (99.4%) and a little asphaltene (0.6%). The values

were obtained following the solvent extraction scheme, which will be described in the experimental procedure section. The sulfur content is 0.64% in the creosote oil and 0.26% in the light recycle oil (LRO).

Kentucky No. 9/14 mixture (-150+325 mesh, a high volatile bituminous coal) was used in all experiments (67.8% C, 4.9% H, 2.69% S and 12% mineral matter). All coal samples were dried overnight at 100°C and 25 inches Hg vacuum before use.

Co-Mo-Al and representative coal minerals (iron and SRC residue) were obtained and studied as catalysts for the reactions of hydrogenation and hydrodesulfurization. Co-Mo-Al is a commercial catalyst from Laporte Industries, Inc. (Comox 451). Iron is a reagent grade hydrogen reduced iron from Mallinckrodt, Inc. SRC residue was obtained from filter cake from Wilsonville SRC pilot plant (2.48% S). All catalysts were screened to -325 mesh before use. Presulfided Co-Mo-Al was prepared by collection of solid residue after reaction of creosote oil with Co-Mo-Al in the autoclave reactor. Sulfur content is about 2.76%.

Hydrogen and nitrogen gas cylinders (6000 psi grade) were supplied by Linde. The following chemicals were used: benzene (Mallinckrodt, nanograde or Fisher Certified A.C.S.), pentane (Mallinckrodt, nanograde), hexane (Fisher Certified), pyridine (Fisher Certified A.C.S.) and tetralin (J.T. Baker, practical grade).

### Procedures

A 2:1 solvent-to-coal weight ratio (40 grams of coal, 80 grams of solvent-LRO or creosote oil) was charged to the autoclave. In some cases, a 3:1 solvent-to-coal weight ratio was used. The reaction conditions used for most of runs were 410°C, a stirrer setting of 1000 rpm, and an initial hydrogen or nitrogen pressure of 2000 psig. A heat-up rate of about 12 to 20°C per minute was used, thus requiring a total heat-up time of about 30-35 minutes. After two hours of reaction, the autoclave contents were quenched to below 100°C within 15 minutes. Then all reaction products were collected in a container and cooled down to room temperature. Immediately, the products were subjected to analysis following the solvent extraction scheme. Each separated product was collected for sulfur analysis.

Usually 3 grams of coal and 6 grams of solvent (tetralin) were charged to the small tubing-bomb reactor (2.4 grams of coal and 4.8 grams of tetralin under hydrogen atmosphere). The reaction experimental procedures were similar to Neavel's (7). The vertical stirring rate was in the range of 100-500 times a minute. Immediately after reaction for 30 minutes in a fluidized sandbath and cooling down, all reaction products were collected by cleaning with benzene first and then with pyridine, then analyzed following the solvent extraction scheme. Each product was collected for sulfur analysis. The oil fraction was analyzed by gas chromatograph to see tetralin consumption during reaction.

About 9 grams of reaction products from the autoclave reactor or all products from the small tubing-bomb reactor were separated following a conventional solvent extraction scheme with pentane or hexane, benzene and pyridine, as shown in Figure 1. The actual weight of oil fraction was slightly higher than the difference between the original sample amount and the sum of asphaltene and benzene insolubles, indicating some solvent (benzene, hexane or pentane) remaining after rotaevaporation up to about 80-85°C under vacuum. To resolve this, the true value for oil or preasphaltene fraction was chosen as follows:

oil = sample - asphaltene - benzene insolubles

preasphaltene = benzene insolubles - pyridine insolubles

Good reproducibility was obtained with +1% deviation, based on percentage of each separated product (+3% deviation, based on dmmf coal).

## Results and Discussion

### Liquefaction

It is generally believed that coal liquefaction follows a coal→preasphaltene→asphaltene→oil route, by breaking C-O, C-S, C-C and possibly C-N bonds and stabilizing coal-derived free radicals by hydrogen transfer from hydrogen chemically interacted with the catalyst (coal minerals or other added catalyst), hydrogen on the hydroaromatic

portion of a hydrogen donor solvent or perhaps hydrogen on the hydroaromatic portion of coal (5, 6, 7, 10, 11). The major role of catalyst in liquefaction appeared to be the replenishment of the hydrogen donor solvent in order to maintain the proper level of hydroaromatics (1, 12). The hydrogen atmosphere, the hydrogen donor ability of the solvent and the hydrogenation activity of the catalyst seem to be most important variables among others in liquefaction process.

A series of experiments using the autoclave reactor was performed to evaluate the sensitivity of the rates of hydrogenation and hydrodesulfurization and to a lesser degree, liquefaction of a coal/oil slurry to variations in atmospheric composition ( $H_2$  or  $N_2$ ), type of solvent (light recycle oil, LRO, or creosote oil), and presence of different catalysts (Table I). The selectivity of different catalysts in terms of overall effect on product distribution (gas, oil, asphaltene, preasphaltene, and pyridine insolubles) was also examined. Creosote oil and LRO were simply assumed to exist as oil after reaction. Creosote oil contains, however, about 3.5% by weight of asphaltene, affecting significantly the oil and asphaltene portions in runs B and D. In runs A, B, C, and D, as to be expected, both liquefaction (based on pyridine soluble degree) and hydrogenation (based on benzene soluble degree) occurred to a larger extent in a hydrogen atmosphere than in an inert nitrogen atmosphere -- the pyridine solubles yield being 35% higher and the benzene solubles yield, 25% higher -- irrespective of the type of solvent used, LRO or creosote oil.

Hydrogen donor species like tetralin and hydrophenanthrene are present in significant amounts in LRO; whereas only trace amounts of these species are present in creosote oil. As a result, LRO is considered to be a much better SRC solvent than creosote oil, which is used as an SRC startup and makeup solvent. Extent of liquefaction and hydrogenation are strongly dependent on solvent characteristics, or type. For example, the pyridine soluble yield was increased by 27% and the benzene soluble yield was increased by 21% -- irrespective of the atmosphere,  $H_2$  or  $N_2$  -- when LRO was used instead of creosote oil.

The results of runs A and E clearly demonstrate the pronounced effect of the presence of presulfided Co-Mo-Al -- a well known hydrogenation catalyst -- on product distribution: the oil fraction is increased by about 76% over that resulting in the absence of the catalysts; the preasphaltene fraction is decreased by about 71%; and the pyridine insoluble fraction is decreased from 12.5% to practically zero percent, with the asphaltene fraction remaining essentially the same. The presence of Fe (run F) and SRC residue (run G) had, on the other hand, a much less pronounced effect on product distribution. Most interestingly, in the presence of Fe the pyridine insoluble fraction decreased to practically zero; and the oil fraction increased by about 27%, with the asphaltene and preasphaltene fractions remaining essentially the same. Within the limits of experimental error, in the presence of SRC residue product distribution remained practically the same. Based on these results, Fe appears to be more effective than SRC residue in accelerating oil and pyridine soluble yields, with both being much less effective than presulfided Co-Mo-Al.

In Table II hydrogen consumption during reaction was compared, based on  $H_f/H_0$  value (the ratio of final hydrogen partial pressure to that in the initial charge at reaction temperature). The justification for using this value to gauge hydrogen consumption was presented in an earlier work (13) in which the kinetics of hydrogenation were described in detail. The presence of SRC residue and coal ash had significant effects on hydrogen consumption, being next to that of presulfided Co-Mo-Al and significantly higher than that of Fe. In fact, the presence of Fe had little, or no effect on hydrogen consumption ( $H_f/H_0$ ) as compared to that occurring during non-catalytic reaction. Apparently, based on the gas analyses and in light of the above results with regard to product distribution (Table I), the higher hydrogen consumption that resulted in the presence of SRC residue are due partly to higher yields of gaseous products ( $H_2S$ ,  $CH_4$ ,  $CO_2$ ,  $C_2-C_5$ , etc.). The results from previously reported (1) catalyst screening studies (Table IV) also support the hydrogen consumption data in Table II. In addition, the results of earlier HPLC analyses of creosote oil after hydrogenation in the presence of different catalysts (Table V)(14) indicated that the degree of hydrogenation was greater in the presence of SRC residue and coal

ash than in the presence of Fe (pyrite). The peak height ratio of tetralin to naphthalene in the gas chromatographic analyses of the liquid products (Table II) indicated a similar trend to that observed in the HPLC analyses (Table IV) and the Hf/H<sub>0</sub> values (Table II), that is, that hydrogenation reactions are accelerated significantly more by SRC residue and coal ash than by Fe. In conclusion then, despite the more significant effect of Fe than that of SRC residue on overall product distribution, as was discussed earlier, the presence of Fe during reaction has little effect on hydrogen consumption; whereas that of SRC residue causes a significant increase in hydrogen consumption. Also, apparently based on the results given in Table III, solvent-to-coal ratio has little effect on hydrogen consumption.

Table VI shows the results from a series of runs in which 2:1 coal/oil slurries were reacted in the presence of different concentrations of Fe catalyst. Samples used to perform gas analyses and for determining the sulfur content of the liquid fraction (that fraction which passed through Whatman #51 filter paper) were collected immediately upon completion of the specified reaction period (2 hrs). In agreement with the findings of the other studies discussed earlier, the presence of Fe catalyst did not have an appreciable effect on gas make (CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub>-C<sub>5</sub>) or Hf/H<sub>0</sub> values. Also, as was observed earlier, Fe served to completely scrub out any H<sub>2</sub>S produced.

Table VII shows the results of a set of experiments in which a small tubing-bomb reactor was used. When a vertical agitation rate in the range of 100-500 cycles per minute was used, with an air atmosphere the presence of Fe catalyst did not affect the product distribution. More importantly, even with a hydrogen atmosphere and in the presence of Co-Mo-Al catalyst, the product distribution was not drastically different from that obtained with an air atmosphere and in the absence of the catalyst. This insensitivity apparently is due to the poor mass transfer obtained at this low agitation rate; for with an agitation rate of above 1000 cycles per minute, the product distribution changed significantly, with substantially more hydrogenation occurring. Further reaction studies using the tubing-bomb reactor are currently in progress.

#### Hydrodesulfurization

As shown in Table VIII the rate of hydrodesulfurization (HDS) of a 3:1 coal/oil slurry was the same in a N<sub>2</sub> atmosphere as that in a H<sub>2</sub> atmosphere when no catalyst was present during reaction. An earlier more detailed study of non-catalytic HDS (13) showed that the rate of HDS is indeed insensitive to not only hydrogen partial pressure but also the concentration of hydrogen donor species in the solvent. However, as shown in both Table I and VIII, in the presence of Co-Mo-Al catalyst the rate of HDS was significantly higher in the presence of a H<sub>2</sub> atmosphere than that in a N<sub>2</sub> atmosphere. In fact, for a 3:1 coal/oil slurry the sulfur content of the liquid reaction products was lower even under a N<sub>2</sub> atmosphere when Co-Mo-Al catalyst was present during reaction. For a 2:1 coal/oil slurry, in the other hand, no detectable lowering in the sulfur content of the liquid products due to catalytic activity under a N<sub>2</sub> atmosphere was observed (Table I and VIII). This insensitivity of HDS reactions to catalytic activity at the lower solvent-to-coal ratio could be due to the rapid depletion of hydrogen donor species that occurs under a N<sub>2</sub> atmosphere. For instance, as shown in Table IX, the degree of conversion of coal to liquids (cresol solubles) under a nitrogen atmosphere was the same after two hours of reaction as that after 15 minutes, presumably because of the rapid depletion of donor species; for, in the presence of a H<sub>2</sub> atmosphere, a significant increase in conversion resulted when the reaction time was increased from 15 minutes to two hours. If the catalyst can serve to accelerate HDS reactions by facilitating the transfer of hydrogen from donor species to active sulfur bearing species, then the concentration of donor species does take on importance, and the observed decrease in catalytic activity with a decrease in the solvent-to-coal ratio should be expected. Further experiments are in progress to ascertain the extent to which HDS catalysts can serve to accelerate reactions in this capacity. The major role of HDS catalysts appears nevertheless to be the acceleration of the transfer of gaseous hydrogen to reactive sulfur bearing

species. Thus, a  $H_2$  atmosphere must be present for a catalyst to be most effective in accelerating HDS reactions.

Apparently from Table II, Fe proved to be about as effective as a desulfurization catalyst as did presulfided Co-Mo-Al. Among the liquid products, Co-Mo-Al was selective in accelerating desulfurization reactions in that it affected the asphaltene fraction the most in both percentage of sulfur ( $0.92 \rightarrow 0.50\%$ ) and absolute weight of sulfur ( $0.12 \rightarrow 0.07$  gr). The selectivity of Fe catalyst among the liquid products was not as apparent as that of Co-Mo-Al catalyst.

In an earlier study (13)  $H_2S$  was shown to inhibit the activity of HDS catalysts. This inhibition by  $H_2S$  could be due to either the blocking of active hydrogenation centers or back reaction by  $H_2S$  product. Fe reacts with product  $H_2S$  to form non-stoichiometric  $FeS_{1+x}$ , and as a result, is a much more effective HDS catalyst than either pyrite or reduced pyrite (Table IV), each of which rapidly form non-stoichiometric  $FeS_{1+x}$  during HDS (13). Further evidence of the inhibition of catalytic activity by  $H_2S$  is provided by comparing the results given in Table II and IV: during the HDS of a coal/oil slurry in the presence of coal ash too much  $H_2S$  was apparently produced for the ash to scrub out (Table II), and because of  $H_2S$  inhibition the coal ash was totally ineffective as an HDS catalyst; whereas during the HDS of creosote oil all of the  $H_2S$  product was scrubbed out by the coal ash (Table IV), and the coal ash was a very effective HDS catalyst. For similar reasons, as shown in Table II, SRC residue is essentially ineffective as a HDS catalyst. Because of the scrubbing action of  $H_2S$  product by Fe then, it is a very effective HDS catalyst. In fact, as shown in Table VI, Fe Catalyst appears to be selective in accelerating HDS reactions more than hydrogenation reactions, in that as its concentration was increased from one to 13.3 percent, sulfur removal increased significantly with little change in hydrogen consumption ( $H_f/H_0$ ).

#### Process Application

During startup of the Wilsonville SRC pilot plant it has been observed that mineral matter accumulates in the dissolver until steady state conditions are achieved. This mineral matter has been found to exert some catalytic activity, particularly with regard to liquefaction and hydrogenation reactions. This finding is in complete agreement with the results discussed above. Actual SRC residue obtained from the Wilsonville plant as well as several minerals indigenous to coal and even coal ash, for example, were shown to act as effective hydrogenation catalysts. However, two major disadvantages to the use of SRC residue were observed: 1) it is ineffective as a HDS catalyst; 2) it is not selective in the catalytic activity and contributes to excess hydrogen consumption due to excess gas formation, etc. The results obtained for SRC residue should be indicative of the catalytic behavior of the mineral matter that exists in the SRC dissolver. To illustrate: an appreciable  $H_2S$  atmosphere exists in the SRC dissolver during normal steady state operation. Like pyrite, reduced pyrite, and coal ash as well as SRC residue then -- all of which were observed to be ineffective HDS catalysts in a  $H_2S$  atmosphere -- indigenous mineral matter does not scrub out  $H_2S$  product, and as a result, should not exert a significant catalytic activity for HDS reactions. In addition, the hydrogen consumption required to obtain the typical conversion yields obtained at Wilsonville have been estimated using non-catalytic kinetics to be about one half of that actually required (15). The catalytic activity existed by indigenous coal minerals was suggested to be the major cause of this higher hydrogen consumption.

In contrast to the minerals indigenous to coal, Fe has been shown here to be most attractive as a catalyst for the SRC process: 1) it is an effective HDS catalyst 2) it is somewhat selective with regard to accelerating hydrogenation reactions, with minimal contribution to increased hydrogen consumption.

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Figure 1: Block Diagram for Separation Procedures

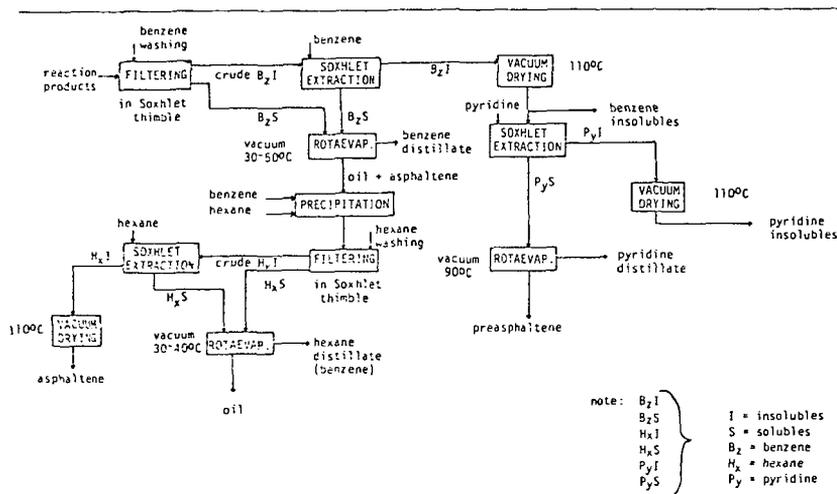


Table 1. Product and Sulfur Distribution by Different Solvent and Catalyst in Autoclave Reactor

solvent/coal = 2, T = 410°C, 120 minutes, 1000 rpm

runs	A	B	C	D	E	F	G
solvent	LRO	creosote	LRO	creosote	LRO	LRO	LRO
catalyst (14.3%)	-	-	Co-Mo-Al*	Co-Mo-Al*	Co-Mo-Al*	Fe	SRC residue
gas (psig)	H <sub>2</sub> (2000)	H <sub>2</sub> (2000)	H <sub>2</sub> (1000)	H <sub>2</sub> (1000)	H <sub>2</sub> (2000)	H <sub>2</sub> (2000)	H <sub>2</sub> (2000)
product, %**							
oil	32.6	7.1	16.5	4.0	57.4	41.4	33.0
asphaltene	38.4	42.5	28.7	19.3	37.8	38.5	45.2
preasphaltene	16.6	11.1	8.5	2.3	4.8	19.3	12.8
insolubles	12.5	39.3	46.3	74.4	0.0	0.9	9.1
sulfur, %							
oil	0.31	0.49	0.34	0.51	0.25	0.25	0.31
asphaltene	0.92	0.98	0.89	0.78	0.50	0.75	0.90
preasphaltene	0.55	0.63	0.65	0.99	0.78	0.30	0.63
insolubles	4.07	2.46	2.82	2.42	4.01	4.00	3.82
total sulfur, grams							
reactants	1.28	1.59	1.84	2.14	1.84	1.28	1.78
products (except gases)	0.80	1.03	1.56	1.71	1.32	1.36	1.60
oil	0.28	0.40	0.29	0.42	0.25	0.24	0.29
benzene solubles	0.40	0.55	0.38	0.47	0.32	0.34	0.41
pyridine solubles	0.43	0.57	0.40	0.48	0.33	0.36	0.44

\*: presulfided Co-Mo-Al

\*\* : based on dmf coal and solvent-free

Table II. Effect of Type of Catalyst on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry

solvent (LRO)/coal = 2, T = 410°C, 120 minutes, 1000 rpm

Catalyst	Initial Pressure (1x10 <sup>-3</sup> psig)	Final Pressure (1x10 <sup>-3</sup> psig)	Partial Pressures (psig)					Sulfur Content Of Liquid Products**	Hf/Ho***	Tetralin/Napthalene Ratio****
			H <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>5</sub>			
Co-Mo-Al*	2.00	1.32	0.783	70	48	172	108	0.24	0.42	
" "	2.02	1.32	0.523	151	97	234	175	0.19	0.28	0.49
SRC Residue	2.01	1.52	0.842	41	115	244	132	0.38	0.45	
" "	2.00	1.36	0.739	35	115	206	125	0.37	0.40	
" "	2.02	1.51	0.834	48	132	219	137	0.39	0.44	0.33
Coal Ash	2.02	1.38	0.812	23	131	168	106	0.37	0.43	
" "	2.00	1.48	0.919	25	80	190	127	0.37	0.49	
" "	2.01	1.32	0.830	11	57	178	104	0.37	0.44	0.29
Fe	2.00	1.48	1.08	0.0	42	136	87	0.24	0.58	
" "	1.99	1.44	1.01	0.0	45	156	92	0.27	0.55	
" "	2.01	1.46	1.02	0.0	45	157	99	0.24	0.55	0.25
None	2.28	1.71	1.21	35	49	167	114	0.374	0.57	
" "	1.92	1.59	1.11	37	56	155	95	0.417	0.62	0.16
" "	2.09	1.70	1.25	36	44	135	90	0.350	0.64	
" "	2.02	1.65	1.19	48	53	141	83	0.411	0.63	
" "	2.01	1.54	--	--	--	--	--	0.402	--	

\* Presulfided Co-Mo-Al

\*\* Liquid products: those that pass through a Whatman #51 filter paper

\*\*\* Hf/Ho: the ratio of the final hydrogen partial pressure to the original

\*\*\*\* The peak height ratio in the gas chromatograph analysis of liquid products

Table III. Effect of Catalyst and Solvent (LRO)-to-Coal Ratio on Hydrogen Consumption

T = 410°C, 120 minutes, 1000 rpm

Co-Mo-Al* Catalyst	Solvent-to-Coal Ratio	Initial Pressure (10 <sup>-3</sup> psig)	Final Pressure (10 <sup>-3</sup> psig)	Partial Pressures (psig)					Hf/Ho**
				H <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>5</sub>	
None	3:1	2.02	1.72	1.16	31.3	37.4	280	73	0.62
None	3:1	2.00	1.70	1.34	7.4	41.8	108	68	0.72
15.0%	3:1	2.00	1.229	0.56	127	58	198	144	0.30
15.0%	3:1	2.02	1.360	0.82	54	55	169	118	0.44
None	2:1	2.00	1.48	0.95	50	45	137	93	0.62
15.0%	2:1	2.00	1.320	0.783	70	48	172	108	0.42
15.0%	2:1	2.02	1.320	0.523	151	97	234	175	0.28

\*,\*\* same as in Table II

Table IV. Catalyst Screening Runs: Liquid % Sulfur, Final Total Pressure, Final Gas Composition, and Fractional Decrease in Hydrogen Pressure

15 grams catalyst, 100 grams creosote oil, T = 425°C,  
 Pi = 3000 psig H<sub>2</sub>, 120 minutes, 2000 rpm

Mineral	% Sulfur*	Final Total Pressure (10 <sup>-3</sup> psig)	H <sub>2</sub> (10 <sup>-3</sup> )	H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>5</sub>	H <sub>F</sub> /H <sub>0</sub> **
None	0.52	2.40	2.13	10.	2.5	64.	18.	0.74
None	0.46	2.42	2.23	7.1	2.0	62.	24.	0.78
Muscovite (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.	0.68
Iron (-325)	0.27	1.98	1.75	< 1.	12.	16.	20.	0.61
Reduced Pyrite	0.36	1.96	1.85	17.	0.4	61.	18.	0.65
Coal Ash	0.23	1.92	1.72	< 1.	1.4	57.	15.3	0.60
Siderite	0.34	1.81	1.61	< 1.	67.	93.	29.	0.56
SRC Solids (-325)	0.32	1.73	1.48	13.	24.	85.	30.	0.52
Co-Mo-Al (-80, +150)	0.02	1.12	0.92	< 1.	1.9	128.	74.	0.32
Co-Mo-Al (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.	0.26

\* Liquid products: those that pass through a Whatman #51 filter paper  
 \*\* H<sub>F</sub>/H<sub>0</sub>: the ratio of the final hydrogen partial pressure to the original

Table V. HPLC Analysis of Treated Creosote Oil

Compound	A	B	C	Wt. %	D	E	F
1 and 2-naphthantrile	0.611	0.458	0.243	trace	0.046	trace	
carbazole	0.423	0.366	0.418	0.386	0.443	0.526	
naphthalene	8.92	7.49	6.55	4.16	4.01	4.17	
2-methylcarbazole	0.106	0.084	0.059	0.067	0.102	trace	
1-methylnaphthalene	5.23	4.56	3.14	3.13	2.33	2.08	
2-methylnaphthalene	8.00	6.21	7.63	5.42	4.61	4.37	
acenaphthene	6.28	4.15	1.56	2.38	2.24	2.08	
fluorene	5.22	5.02	3.78	3.62	3.64	4.55	
dibenzochiaphene	1.27	0.888	0.720	trace	0.576	0.622	
phenanthrene	12.4	9.10	7.95	8.05	7.11	5.96	
anthracene	1.86	1.88	1.31	2.17	1.50	1.53	
Total	50.32	40.23	33.36	29.39	26.61	25.89	

A-original oil  
 B-oil heated with hydrogen, no catalyst  
 C-oil heated with hydrogen and pyrite  
 D-oil heated with hydrogen and cobalt molybdate  
 E-oil heated with hydrogen and coal ash  
 F-oil heated with hydrogen and SRC solids

Three runs were made for each treatment with a relative standard deviation between runs of ± 8% of the determined mean weight per cent.

Table VI. Effect of Iron Concentration on Hydrogen Consumption and Rate of Hydrodesulfurization of a Coal/Oil Slurry

solvent (LR0)/coal = 2, T = 410°C, 120 minutes, 1000 rpm

Wt. % Fe	Initial Pressure (x10 <sup>-3</sup> psig)	Final Pressure (x10 <sup>-3</sup> psig)	Partial Pressure (psig)					Sulfur Content of Liquid Products*	H <sub>2</sub> /H <sub>0</sub> **	
			H <sub>2</sub> (10 <sup>-3</sup> )	H <sub>2</sub> S	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -C <sub>5</sub>		Average	Average
0.	2.28	1.71	1.21	35	49	167	114	0.374	0.57	
0.	1.92	1.59	1.11	37	56	155	95	0.417	0.62	0.62
0.	2.09	1.70	1.25	36	44	135	90	0.350	0.39	0.64
0.	2.04	1.65	1.19	48	53	141	83	0.411		0.63
0.	2.01	1.54	--	--	--	--	--	0.402		--
1.0	2.21	1.70	1.19	5.9	54	200	114	0.374	0.37	0.57
2.0	1.52	1.23	0.773	0.0	42	172	102	0.318	0.35	0.56
2.0	1.66	1.34	0.851	0.0	64	189	112	0.373		0.56
4.0	1.98	1.41	0.923	0.0	50	189	107	0.360	0.35	0.50
4.0	1.48	1.22	0.863	0.0	24	120	73	0.329		0.64
7.7	2.10	1.62	1.15	0.0	49	172	107	0.294	0.28	0.59
7.7	2.04	1.55	1.11	0.0	46	152	98	0.273		0.58
13.3	2.01	1.46	1.02	0.0	45	157	99	0.237		0.55
13.3	1.99	1.44	1.01	0.0	45	156	92	0.271	0.25	0.55
13.3	2.00	1.48	1.08	0.0	42	136	87	0.24		0.58

\*,\*\* same as in Table II

Table VII. Product and Sulfur Distribution in Small Tubing-Bomb Reactor

solvent(tetralin)/coal = 2, T = 410°C, 30 minutes

runs	solvent(tetralin)/coal = 2, T = 410°C, 30 minutes			
	A**	B	C	D
catalyst (7.7%)	-	Fe	Co-Mo-Al	Co-Mo-Al
gas (Psi)	air (1atm)	air (1atm)	H <sub>2</sub> (1360 psig)	H <sub>2</sub> (1200 psig)
cycles per minute	100-500	100	100	-1000
product, %				
oil + gases	21.0	23.0	22.4	31.4
asphaltene	18.2	17.4	23.8	33.3
presphaltene	45.8	43.4	31.4	24.8
insolubles	15.1	16.2	22.4	10.5
sulfur, %				
oil	0.14	0.13	0.06	-
asphaltene	1.76	1.41	1.39	-
presphaltene	0.53	0.31	0.91	-
insolubles	4.29	3.66	3.38	-
total sulfur, grams				
reactants	0.080	0.081	0.065	-
products (except gases)	0.055	0.075	0.062	-
oil	0.009	0.009	0.003	-
benzene solubles	0.017	0.015	0.010	-
pyridine solubles	0.023	0.019	0.016	-
naphthalene/tetralin (GC peak ratio)	0.57	0.59	0.29	-

\*: based on dmmf coal and solvent-free

\*\* : average value of 4 runs at 100, 250, 350 and 500 cycles per minute.

Table VIII. Effect of Catalyst, Hydrogen Atmosphere, and Solvent-to-Coal Ratio on Rate of Hydrodesulfurization of a Coal/Oil Slurry

T = 410°C, 120 minutes, 1000 rpm

Weight Percent of Catalyst (Co-Mo-Al*)	Atmosphere	Solvent-to-Coal Ratio	Percent Sulfur Content of Liquid Fraction of Reaction Product **	Tetralin/Naphthalene Ratio***
None	2000 psig H <sub>2</sub>	3:1	0.42	0.190
None	2000 psig H <sub>2</sub>	3:1	0.42	
None	2000 psig H <sub>2</sub>	3:1	0.42	0.066
15.0	1000 psig N <sub>2</sub>	3:1	0.30	0.066
15.0	1000 psig H <sub>2</sub>	3:1	0.29	
15.0	2000 psig H <sub>2</sub>	3:1	0.17	-
15.0	2000 psig H <sub>2</sub>	3:1	0.17	
None	2000 psig H <sub>2</sub>	2:1	0.39(avg of 4 runs)	0.16
15.0	2000 psig H <sub>2</sub>	2:1	0.24	0.49
15.0	2000 psig H <sub>2</sub>	2:1	0.19	
15.0	1000 psig H <sub>2</sub>	2:1	0.36	-
15.0	1000 psig H <sub>2</sub>	2:1	0.36	

\*,\*\*,\*\*\* same as in Table II

Table IX. Effect of Reaction Time and Atmosphere on Conversion of Coal to Liquid

Atmosphere	Reaction Time	Cresol Solubles(%)	Cresol Soluble Yield (%)*
H <sub>2</sub>	2 hrs.	96.20	95.81
N <sub>2</sub>	2 hrs.	89.78	66.81
H <sub>2</sub>	15 min.	92.3	78.23
N <sub>2</sub>	15 min.	89.73	66.58

Reaction Conditions:

Temperature = 410°C  
 Solvent-to-Coal Ratio = 2:1  
 Non-Catalytic

\*Cresol Soluble Yield =  $\frac{C - A}{1 - M} \times 100$  where C = charge of moisture free coal; A = the recovered insoluble residue; M = the fraction of mineral matter in dry coal.