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KINETICS AND MECHANISM OF DESULFURIZATION AND
DENITROGENATION OF COAL-DERIVED LIQUIDS

Fourteenth Quarterly Report for the Period September 21—December 20, 1978

By
Bruce C. Gates
James R. Katzer
Jon H. Olson
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March 16, 1979
Date Published

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Departments of Chemical Engineering and Chemistry
University of Delaware
Newark, Delaware

MASTER

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

Quantitative measurement of the reactivities of methyl-substituted dibenzothiophenes, under high pressure reaction conditions (102 atm, 300°C) representative of industrial practice, has been accomplished. The catalyst was sulfided commercial Co-Mo/ γ -Al₂O₃. Methyl groups in the 2 and 8 or 3 and 7 positions show little effect. Methyl groups in the 4 position, however, reduced the reactivity by an order of magnitude and methyl groups in the 4 and 6 positions reduced it somewhat more. Dibenzothiophene (DBT) was found to be self-inhibiting and results with the methyl-substituted compounds implies that there is competitive adsorption of DBT and the methyl-substituted DBT.

The reaction network involving benzonaphthothiophene and hydrogen has been determined. As before, the catalyst was typical commercial "cobalt molybdate" (sulfided CoO-MoO₃/ γ -Al₂O₃). The reaction conditions were 68 atm and 300°C. The important result was that in contrast to dibenzothiophene, benzonaphthothiophene experiences extensive hydrogenation accompanying hydrodesulfurization, even with Co-Mo/ γ -Al₂O₃, the most selective of the available hydrodesulfurization catalysts. The sulfur-containing compounds having 3 rings or fewer experience nearly stoichiometric hydrodesulfurization (hydrogenolysis without hydrogenation), whereas the sulfur-containing compounds having 4 rings or more experience hydrogenation and hydrodesulfurization at roughly equal rates, giving products which experience further hydrogenation (and/or hydrodesulfurization--as the compound allows), again at roughly the same rates.

II. OBJECTIVES AND SCOPE

The major objectives of this research are as follows:

- (i) To develop high-pressure liquid-phase microreactors for operation in pulse and steady-state modes to allow determination of quantitative reaction kinetics and catalytic activities in experiments with small quantities of reactants and catalyst.
- (ii) To determine reaction networks, reaction kinetics, and relative reactivities for catalytic hydrodesulfurization of multi-ring aromatic sulfur-containing compounds found in coal-derived liquids.
- (iii) To determine reaction networks, reaction kinetics, and relative reactivities for catalytic hydrodenitrogenation of multi-ring aromatic nitrogen-containing compounds found in coal-derived liquids.
- (iv) To obtain quantitative data characterizing the chemical and physical properties of aged hydroprocessing catalysts used in coal liquefaction processes and to establish the mechanisms of deactivation of these hydroprocessing catalysts.
- (v) To develop reaction engineering models for predicting the behavior of coal-to-oil processing and of catalytic hydroprocessing of coal-derived liquids and to suggest methods for improved operation of hydrodesulfurization and hydrodenitrogenation processes.
- (vi) In summary, to recommend improvements in processes for the catalytic hydroprocessing of coal-derived liquids.

SCOPE

A unique high-pressure, liquid-phase microreactor is being developed for pulse (transient) and steady-state modes of operation for kinetic measurements to achieve objectives (ii) through (iv). The relative reactivities of the important types of multi-ring aromatic compounds containing sulfur and nitrogen are being measured under industrially important conditions (300-450 °C and 500-4000 psi). The reaction networks and kinetics and several of the least-reactive multi-ring aromatic sulfur-containing and nitrogen-containing compounds commonly present in coal-derived liquids will be determined. Catalyst deactivation is an important aspect of the commercial scale upgrading of coal-derived liquids. Accordingly, the chemical and physical properties of commercially aged coal-processing catalysts are being determined to provide an understanding of catalyst deactivation; these efforts can lead to improved catalysts or procedures to minimize the problem. To make the results of this and related research most useful to DOE, reaction engineering models of coal-to-coal processing in trickle-bed and slurry-bed catalytic reactors including deactivation will be developed to predict conditions for optimum operation of these processes. Based on the integrated result of all of the above work, recommendations will be made to DOE for improved catalytic hydro-desulfurization and hydrodenitrogenation processing.

III. SUMMARY OF PROGRESS TO DATE

This summary is organized to parallel the task statements of the contract. A milestone chart is provided at the end of this section.

Microreactor Development

Three continuous-flow, liquid-phase, high-pressure microreactors have been built and operated under this contract. The work in this report confirms the success of these microreactors; the data from the batch autoclave runs are effectively identical to data from the flow microreactors. This task has been completed.

Catalytic Hydrodesulfurization

The hydrodesulfurization of dibenzothiophene (DBT) has been examined with a high-pressure microreactor and in batch, stirred-autoclave experiments. The range of data show that the reaction network is slightly more complex than the direct reduction of dibenzothiophene (DBT) to hydrocarbon products; the network is the following at 300°C and 100 atm where the rate constants for units of m^3/kg of catalyst·s:

The relative rates of hydrodesulfurization of a variety of the important sulfur-containing compounds in coal-derived liquids have been determined. The compounds include methyl-substituted dibenzothiophenes,

which evidently are among the least reactive compounds in hydrodesulfurization. The relative rate constants for the various reactants are the following: dibenzothiophene (DBT), 1; 4-MeDBT, 0.16; 4,6-diMeDBT, 0.10; 3,7-diMeDBT, 1.7; and 2,8-diMeDBT, 2.6. These results are largely explained by steric and inductive effects. Groups located β to the sulfur atom restrict its interaction with a surface anion vacancy and lower the reactivity. Inductive effects explain the higher reactivities of the compounds having methyl substituents where they exert no steric influence. The reactivities of the compounds have been determined with individual sulfur-containing compounds and with pairs of these compounds. The reactivities of these compounds are influenced by competitive adsorption determined by the previously mentioned steric and inductive effects.

More detailed study of the hydrodesulfurization of 4,6-dimethyl-dibenzothiophene, which is the least reactive sulfur-containing compound found so far, shows that the reaction network is similar to that of dibenzothiophene but that hydrogenation of the aromatic ring is more pronounced than for dibenzothiophene.

Results from batch-autoclave reactor studies on the hydrodesulfurization of multi-ring sulfur-compounds (with sulfided Co-Mo/ γ -Al₂O₃, 300°C and 70 $\pm$ 2 atm of H₂) show that the reactivity decreases from 1-ring to 3-ring compounds and then it increases for the 4-ring compound. Thus the three-ring sulfur-compound, dibenzothiophene and its methyl derivatives are the least reactive compounds studied so far. The first-order rate constants for the hydrodesulfurization of these compounds are given below:

<u>Reactant</u>	<u>Pseudo first-order rate Constant, cm³/g cat h</u>
thiophene	5000
benzothiophene	2900
dibenzothiophene	200
benzonaphthothiophene	600
7,8,9,10-tetrahydrobenzo- naphthothiophene	280

Three different catalysts, namely Co-Mo/ γ -Al₂O₃, Ni-Mo/ γ -Al₂O₃ and Ni-W/ γ -Al₂O₃ have been tested for the hydrodesulfurization of dibenzothiophene. The activities of these catalysts have been found to decrease in the order: Ni-Mo > Ni-W $\geq$ Co-Mo.

A new "three-point" adsorption of thiophenic compounds has been suggested to be important in the surface-catalyzed hydrodesulfurization mechanism. The new mechanism accounts for the observed substituent effects and the effects of the number of rings in the reactant; it also accounts for results of H-D exchange studies reported in the literature.

Our results show that in contrast to dibenzothiophene, benzonaphthothiophene experiences extensive hydrogenation accompanying hydrodesulfurization, even with Co-Mo/Al₂O₃, the most selective of the available hydrodesulfurization catalysts. Consequently, hydrogen consumptions (and processing costs) will unavoidably be high when feedstocks have appreciable concentrations of four-ring and larger sulfur-containing compounds.

Catalytic Hydrodenitrogenation

The hydrodenitrogenation of quinoline has been studied to yield a nearly complete identification of the reaction network and partial identification of the rate parameters in this network. The network is as follows:

This network shows that usually both the benzene and pyridine rings are saturated before the C-N bond in the (now) piperidine ring is broken. Thus, the hydrodenitrogenation of quinoline requires a large consumption of hydrogen before the nitrogen atom is removed from the hydrocarbon structure. The lack of selectivity encountered in hydrodenitrogenation stands in sharp contrast to the high selectivity in hydrodesulfurization.

The total rate of hydrodenitrogenation shows a maximum with respect to hydrogen partial pressure. This is because the pseudo first-order rate constants for the C-N bond scission reactions are reduced by increasing hydrogen pressure, the rate constants for the hydrogenation reactions, which increase with hydrogen pressure at lower hydrogen pressures, approach a maximum with increasing hydrogen pressure at the high hydrogen pressures, and because high hydrogen pressure shifts the quinoline $\rightleftharpoons$ 1,2,3,4-tetrahydroquinoline strongly to 1,2,3,4-tetrahydroquinoline which is not as reactive as quinoline for further reaction.

The pseudo first-order rate constants for 367°C and 136 atm are given associated with the reactions on the figure.

The pseudo first-order rate constants for hydrodenitrogenation (total nitrogen removal) of multi-ring nitrogen-containing aromatic compounds containing up to five rings at 367°C and 136 atm catalyzed by Ni-Mo/ γ -Al₂O₃ fall in the following order:

<u>Reactant</u>	<u>Pseudo first-order rate constant for total nitrogen removal, min⁻¹</u>
Dibenz[c,h]acridine	3.79
Quinoline	2.52
Carbazole	2.43
Acridine	1.62
Benz[c]acridine	1.54
Benz[a]acridine	1.08

Studies of competing hydroprocessing reactions catalyzed by Ni-Mo/ γ -Al₂O₃ and involving quinoline, indole, dibenzothiophene, and naphthalene in n-hexadecane show that marked interactions exist. The naphthalene hydrogenation rate is markedly reduced by the presence of quinoline; whereas the reactivity of quinoline is virtually unchanged by the presence of naphthalene. Similarly the rate of hydrodenitrogenation of indole, a non-basic nitrogen-containing compound, is strongly reduced by the presence of quinoline, whereas the rate of hydrodenitrogenation of quinoline, a basic nitrogen-containing compound, is unaffected by the presence of indole. The hydrogenation reactions in the dibenzothiophene reaction network are inhibited as severely as indicated by the reduction in their pseudo first-order rate constants as are the hydrogenation reactions for naphthalene. Thus the hydrogenation rate is reduced 30-fold by increasing the initial quinoline concentration from 0.0 to 0.5 wt % in naphthalene hydrogenation and in dibenzothiophene hydrodesulfurization. The rate of direct sulfur removal is reduced by only 3-fold by increasing the quinoline concentration from 0.0 to 0.5 wt %. These results clearly show that the rate expressions for the hydrotreating reactions are of the form

$$\text{Rate} = \frac{k_1 C_1 P_{H_2}^n}{[1 + K_j C_j K_Q C_Q] F(H_2)}$$

Catalyst Deactivation

A variety of physical techniques have been used to identify the aging process for catalysts used in the synthetic liquid fuel processes. Catalyst samples from three processes have been examined: a proprietary fixed-bed process, Synthoil, and H-Coal^R. The spent fixed-bed catalysts show the formation of an external crust which appears to be formed by columnar grain growth combined with the deposition of coal mineral matter, particularly clays and rutile. This external crust is absent from the H-Coal^R catalyst. The interior of the catalyst is altered by several

processes: coking, reactive deposition of mineral matter, passive deposition of mineral matter, and crack enhancement. These four processes are found in catalysts from all three processes. Coking fills the micropore volume of the catalyst. Reactive deposition of mineral matter penetrates about 200 μm from the outer surface into the interior of the catalyst. The concentration profile is approximately exponentially decreasing from the exterior surface. Passive cementing occurs within 50 μm of the surface unless the irregular concentration profiles. Finally, grain growth can occur inside the catalyst near the surface and tends to increase these cracks. When the surface cracks become a significant portion of the pore volume, passive deposition can penetrate further into the interior of the catalyst.

The activity of aged catalyst from the H-Coal^R process has been measured in batch experiments with dibenzothiophene and with quinoline. The activity was reduced 20-fold for hydrodesulfurization of dibenzothiophene and five-fold for hydrodenitrogenation of quinoline. Burning off of carbonaceous deposits increased the activity of the aged catalyst only three-fold for dibenzothiophene hydrodesulfurization, which implies that irreversibly deposited inorganic matter was responsible for most of the loss of catalytic activity.

Microreactor Engineering

The use of moments as a tool in interpreting pulse data from microreactors has been extended to fairly complex reaction networks. This work is now complete. The complex data from quinoline and acridine reactions have been reduced to rate parameters by extension of nonlinear regression analysis. Reaction engineering concerned with coal hydro-processing is now underway.

TIME PLAN* AND MILESTONE CHART**

Year 0	1	2	3
ACCOMPLISHMENT			
A. APPARATUS CONSTRUCTION			
1st High Pressure Microreactor	Completed month 6	100%	
2nd High-Pressure Microreactor	Completed month 10		
Batch Reactors	Completed month 4		
B. MICROREACTOR STUDIES OF HDS & HDN			
Definition of reaction procedures and operating conditions	month 8		
Choice of HDN Catalyst	month 8	100%	
Reaction Studies For:			
Benzothiophene	month 6 month 12	Started	100%
Quinoline		90%	100%
Dibenzothiophene	month 12	month 18	100%
Carbazole	10%	50%	100%
Naphthobenzothiophene	Synthesis Underway	month 18 month 24	Started 95%
Acridine		85%	month 24 month 28 100%
Higher molecular weight and methyl-substituted nitrogen and sulfur compounds	Synthesis Underway month 12	75%	month 28 month 30 100%
Reaction Kinetics			100%
Reaction Networks and Inhibitor Studies of Least Reactive Sulfur and Nitrogen Compounds		75%	85%
HDS-HDN: Simultaneously, Effect of Inhibitors	month 16	Started 20%	50% 100%
			month 36

TIME PLAN* AND MILESTONE CHART** (Continued)

Year	0	1	2	3
C. CATALYST DEACTIVATION				
SYNTHOIL				
CATALYST:				
Physical Properties	month 6	100%		
Chemical Properties	month 6	month 16 75%		100%
Other Deactivated Catalysts	90% month 10		month 24	100%
Catalyst Deactivation Studies	50%	month 14 70%		100% month 30
D. REACTION ENGINEERING				
Reactor Models for Pulse and Flow Microreactors	75%	month 14 90%	95%	100%
Process Reaction Engineering	5%	month 14 15%	30%	100% month 36

*Time Plan and Milestone Chart as Presented in Proposal.

**Hatching indicates that activity indicated is under active investigation; number in hatch region indicates the percentage completed; crosshatching indicates that the task has been completed.

CUMULATIVE EXPENDITURES*

Quarter	Personnel	Travel	Supplies & Expenses	Occupancy & Maintenance	Equipment	Information Processing	Transfers (Overhead)
First	\$ 5,807	\$ 28	\$ 4,674	\$ 6,110	\$ 610	\$ --	\$ --
Second	20,740	528	10,007	9,208	17,978	--	10,202
Third	37,396	1,152	19,582	10,108	30,704	--	20,035
Fourth	53,418	1,152	25,735	10,634	34,930	97	38,710
Fifth	91,593	1,521	37,291	13,755	50,614	154	75,839
Sixth	112,666	2,458	42,341	13,920	54,013	375	93,287
Seventh	132,669	3,140	51,589	14,396	54,013	1,180	113,830
Eighth	146,146	3,814	56,488	14,600	52,295	1,868	123,576
Ninth	167,884	5,119	54,778	16,325	54,977	2,044	117,681
Tenth	192,658	6,113	70,579	18,010	54,977	2,248	134,895
Eleventh	224,941	6,113	76,733	19,635	54,977	2,369	161,208
Twelfth	261,759	7,349	95,041	24,159	57,778	2,454	186,267
Thirteenth	301,587	7,700	101,622	26,016	57,778	2,462	203,391
Fourteenth	332,479	7,941	105,578	28,282	59,202	2,788	215,132

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. HYDRODESULFURIZATION OF METHYL-SUBSTITUTED

DIBENZOTHIOPHENES CATALYZED BY SULFIDED Co-Mo/ γ -Al₂O₃

The need for clean-burning fuels and the depletion of petroleum reserves are dictating the development of catalytic hydrodesulfurization processes for the heaviest petroleum fractions and for coal-derived liquids. These feedstocks require processing conditions much more severe than those used for petroleum distillates (Gates et al., 1979). The emerging technology demands desulfurization of relatively unreactive 3- and 4-ring aromatic compounds like dibenzothiophene and benzo[b]naphtho[2,3-d]thiophene (referred to as benzonaphthothiophene). As part of a systematic study of the reactivities of these and related compounds under high-pressure reaction conditions representative of industrial application, we have reported a reaction network for dibenzothiophene hydrodesulfurization (Houalla et al., 1978) and rates of reaction comparing 1-, 2-, 3-, and 4-ring compounds (Nag et al., in press) and methyl-substituted dibenzothiophene (Houalla et al., 1977). Continuing the study, we report here the results of experiments designed to provide a resolution of the reaction network involving benzonaphthothiophene and hydrogen. As before, the catalyst was a typical commercial "cobalt molybdate" (sulfided $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$) operated under conditions of practical interest with liquid-phase reactants.

Experimental

The reaction experiments were carried out with a one-liter high-pressure batch reactor (Autoclave Engineers); the design allowed charging of the catalyst after the reactants had been brought to reaction temperature, thereby virtually eliminating any heat-up period which would prevent

elucidation of isothermal kinetics (Shih et al., 1977).

The catalyst was particles of $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ (American Cyanamid HDS 16A) (2.3×10^{-4} kg), which was externally sulfided at 673 K with 10 vol % H_2S in H_2 at atmospheric pressure for two hours prior to being charged to the reactor.

The reactant solution (3.2×10^{-4} m³) contained 0.24 wt % benzonaphthothiophene [synthesized by the method of Campaigne and Osborn (1968)] in *n*-hexadecane (Humphrey Chemical Co., redistilled). This solution was saturated with hydrogen, providing a large stoichiometric excess of this reactant. The reactor was operated at 68 atm and 580 K.

Product samples were drawn periodically from the reactor and analyzed with an Antek gas chromatograph (glc) (440 L) equipped with a flame ionization detector and a column packed with methyl silicone fluid (with basic sites deactivated) on 100-120 mesh Supelcoport (GP 3%, SP-2100 DB, Supelco). Separate analyses to determine sulfur-containing compounds in the products was carried out with a Perkin-Elmer 3920B glc equipped with a sulfur-specific detector. Further details of the gas chromatographic analysis are as described previously (Houalla et al., 1978).

Results

Figure 1 shows typical chromatograms indicating the product spectrum obtained with a sample which had experienced a high conversion (about 95%). Peak (C) (Figures 1a and 1b) is identified with the major sulfur-containing product, which was formed from the beginning of each experiment and is therefore concluded to be a primary product. It has

been identified as 7,8,9,10-tetrahydrobenzo[b]naphtho[2,3-d]thiophene (referred to as 7,8,9,10-tetrahydrobenzonaphthothiophene) on the basis of its retention time and peak shape, which were determined for the authentic compound, synthesized by the methods of Campaign and Osborn (1968).

Peak (B), indicating a minor sulfur-containing product, was too small to be detectable in all but the chromatograms indicating the highest conversions; we infer that the peak indicates a partially hydrogenated species such as 7,8-dihydrobenzo[b]naphtho[2,3-d]thiophene, since it appeared between the benzonaphthothiophene peak and the 7,8,9,10-tetrahydrobenzonaphthothiophene peak. The primary hydrocarbon product has been identified (by comparison with the known) as 2-phenylnaphthalene, indicated as Peak (D) in Figure 1A. There were three other secondary hydrocarbon products not present in the early samples, but formed from (an) intermediate(s), indicated by peaks (E), (F), and (G) on Figure 1A. Experience with the analysis of the various sulfur-containing reactants and the products of their hydrodesulfurization has indicated that under these analytical conditions, the higher the degree of hydrogenation of the aromatic hydrocarbon, the more rapidly the compound is eluted. Lacking other analytical results, we tentatively identify peaks (E), (F), and (G), respectively, with 2-phenyltetralin, 2-phenyldecalin, and 2-cyclohexyldecalin.

The data are summarized in the conversion plot of Figure 2. In generating these data, we assumed (on the basis of analytical experience) that all the hydrocarbons had the same glc response factor as that measured for 2-phenylnaphthalene. The data clearly demonstrate that 7,8,9,10-tetrahydrobenzonaphthothiophene and 2-phenylnaphthalene are primary products which

experience further conversion into secondary products, which are aromatic hydrocarbons with various degrees of saturation.

Discussion

The appearance of both a hydrocarbon (2-phenylnaphthalene) and a partially hydrogenated sulfur-containing compound (7,8,9,10-tetrahydrobenzonaphthothiophene) as primary products demonstrates a strong similarity between the reaction networks of dibenzothiophene (Houalla et al., 1978) and benzonaphthothiophene. The striking qualitative difference is that hydrogenation is almost negligible in comparison with the parallel hydrodesulfurization of dibenzothiophene--3 orders of magnitude slower--(provided that the H_2S concentration is low), whereas the parallel hydrogenation and hydrodesulfurization of benzonaphthothiophene proceed at nearly equal rates. The maxima in the concentration-time plots for the primary products show that they are intermediates, undergoing conversion into hydrocarbons. From their structures, we infer that the primary products are both converted into a single secondary product, 2-phenyltetralin. These reactions are summarized in the network of Figure 3. The secondary product evidently undergoes further hydrogenation to give tertiary and quaternary products. Since their concentrations were always low (Figure 2) and their identities uncertain, all the hydrocarbons formed from the secondary product are lumped into one component for the modeling of the reaction network.

To provide a test of this model of the network, a few experiments were performed with each of the primary products (7,8,9,10-tetrahydrobenzonaphthothiophene and 2-phenylnaphthalene) used instead of benzonaphthothiophene as the

organic reactant. Otherwise, the procedures were the same as described above, except that carbon disulfide was added to the reaction mixture to maintain the sulfided state of the catalyst when 2-phenylnaphthalene was the reactant. In each case, the primary and major product was that which has been identified as 2-phenyltetralin, confirming the proposed network.

The conversion data for each of the organic reactants used separately can be represented very well by pseudo first-order kinetics (Figure 4). Therefore, in determining a quantitative model of the reaction network, it was assumed that each reaction was first order in the organic reactant. Assuming that the reactions and lumps were those indicated in Figure 3,* the pseudo first-order rate constants were estimated from the full set of data determined in the experiments with benzonaphthothiophene feed, as follows: (1) The data of Figure 2 were smoothed by fitting spline functions using the IMSL subroutine ICSMOU; this program performs one-dimensional data smoothing by error detection and is very effective in smoothing a data set which is only mildly contaminated with isolated errors. (2) The smoothed data were used with equal weighting in the Carlton 2 program (Himmelblau et al., 1967) to determine best values of the rate constants. The values of the rate constants are given in Figure 3, and the conversion-time curves predicted from the model compare well with the data (Figure 2).

The pseudo first-order rate constants determined from conversion

*To simplify the analysis further, the trace product suggested to be 7,8-dihydrobenzo[b]naphtho[2,3-d]thiophene was lumped with 7,8,9,10-tetrahydrobenzonaphthothiophene.

data for each of the individual reactants shown in Figure 4 agree within a factor of two with the values shown in the network of Figure 3. One should not expect exact agreement, since the reaction environments were different in the various experiments, and the competitive adsorption effects (causing inhibition of reaction) were not taken account of in the simple network model. We infer [on the basis of experience in determining the full nonlinear kinetics, with inhibition effects, for the simpler dibenzothiophene hydrodesulfurization (Broderick and Gates, to be published)] that a much larger set of data (probably as many as 10-100 times as many points) would be required to determine, with comparable precision, full rate equations [with estimates of rate constants and inhibition (adsorption) parameters] for the whole set of reactions in the benzonaphthothiophene + hydrogen network.

The important conclusion is that, in contrast to dibenzothiophene, benzonaphthothiophene experiences extensive hydrogenation accompanying hydrodesulfurization, even with Co-Mo/Al₂O₃, the most selective of the available hydrodesulfurization catalysts. Consequently, hydrogen consumptions (and processing costs) will unavoidably be high when feedstocks have appreciable concentrations of 4-ring and larger sulfur-containing compounds. These results, in combination with earlier results (Houalla et al., 1978; Kilanowski et al., 1978), lead to the recommendation of the following approximations for modeling the hydroprocessing of heavy petroleum and coal-liquid feedstocks: the sulfur-containing compounds having 3 rings or fewer experience nearly stoichiometric hydrodesulfurization (hydrogenolysis without hydrogenation), whereas the sulfur-containing compounds

having 4 rings or more experience hydrogenation and hydrodesulfurization at roughly equal rates, giving products which experience further hydrogenation (and/or hydrodesulfurization--as the composition allows), again at roughly the same rates. This recommendation is preliminary and requires critical evaluation by further experimentation.

Since the hydrogenation rates observed with benzonaphthothiophene are about 3 orders of magnitude greater than those observed with dibenzothiophene (Houalla et al., 1978), we conclude that there is extensive flat adsorption of benzonaphthothiophenic compounds, implying bonding of the molecules with the catalyst surface through the π electrons of the benzenoid rings. The importance of this kind of bonding of polycyclic aromatic compounds has been suggested earlier (e.g., Houalla et al., 1978; Singhal et al., 1978). The ideas are considered in detail elsewhere (Kwart et al., to be published).

Figure 1. Gas chromatographic analysis of the product of hydrodesulfurization of benzo(b)naphtho(2,3-d)thiophene at 580 K and 68 atm. A: The full organic product spectrum determined with a flame ionization detector; B: The sulfur-containing organic compounds, determined with a sulfur-specific detector. Details are given in the text.

Figure 2. Conversion of hydrogen and benzo (b)naphtho(2,3-d)thiophene in the presence of sulfided $\text{CoO-MoO}/\gamma\text{-Al}_2\text{O}_3$ in a batch reactor at 580 K and 68 atm. The solvent was *n*-hexadecane. The curves are the predictions of the reaction network model summarized in Figure 3.

Benzonaphthothiophene
 2-Phenylnaphthalene
 Tetrahydrobenzonaphthothiophene
 2-phenyltetralin
 2-phenyldecalin + 2-cyclohexyldecalin (postulated lump)

Figure 3. Conversion of benzo(b)naphtho(2,3-d)thiophene and hydrogen in the presence of sulfided $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ at 580 K and 68 atm: the reaction network. Each reaction is approximated as first order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in cubic meters per kilogram of catalyst per second.

Figure 4. Pseudo first-order kinetics of hydrodesulfurization and hydrogenation catalyzed by sulfided $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ in a batch reactor at 580 K and 68 atm. Each of the compounds shown was used separately as the organic reactant with hydrogen in a batch reactor. The conversion data were determined from the measured disappearance of reactant. The numbers next to the lines represent pseudo first-order rate constants in cubic meters per kilogram of catalyst per second.

B. HYDRODESULFURIZATION OF BENZO[b]NAPHTHO[2,3-d]THIOPHENE

CATALYZED BY SULFIDED $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$:

THE REACTION NETWORK

Although hydrodesulfurization of petroleum residues is widely practiced and the need for similar technology for coal-derived liquids is well recognized, there is only little literature reporting the relative reactivities of various sulfur-containing compounds found in the heavy feedstocks (1). Akhtar *et al.* (2) identified a number of the thiophenic compounds liberated from coal during liquefaction/hydroprocessing. These include thiophene, benzo[b]thiophene, dibenzothiophene (DBT), and benzo[b]naphtho[2,3-d]thiophene. Under typical hydroprocessing conditions (300°C, 71 atm), DBT has been found to be the least reactive of these compounds (3). Since methyl groups are the predominant substituent groups on the aromatic molecules of coal-derived liquids, abundant and relatively unreactive methyl-substituted dibenzothiophenes evidently represent the class of thiophenic compounds most in need of study.

Qualitative studies of the reactivities of these compounds with a pulse microreactor operated at low pressures (4) with sulfided Co-Mo/ γ -Al₂O₃ catalyst have shown that incorporation of methyl groups in the 4 or 4 and 6 positions of DBT

DBT

reduced the reactivity significantly, consistent with Beuther's (5) report (based on experiments for which the catalyst and reaction conditions were not specified) that incorporation of methyl groups in the 4 and 6 positions led to roughly a 100-fold decrease in the rate of hydrodesulfurization. Incorporation of methyl substituents in the 2 and 8 or 3 and 7 positions

of DBT, however, led to slightly increased activities, as measured by conversions in the pulse microreactor (4).

The objective of the experiments described here was to provide a quantitative measure of the reactivities of these compounds under high-pressure reaction conditions representative of industrial practice. A flow microreactor, described previously (6), was used with liquid feeds containing n-hexadecane (carrier oil), H_2 , and either a single sulfur-containing compound [e.g., 4-methyldibenzothiophene (4-MeDBT)] or a pair of sulfur-containing compounds, one of them being DBT.

The catalyst was commercial Co-Mo/ γ - Al_2O_3 (American Cyanamid HDS 16A), from the same batch used in related studies (3,4,6,7). The physical properties and composition are given elsewhere (7). A catalyst charge was 0.025 g diluted with 0.625 g of inert alundum particles; the catalyst particles were 149-178 μm in dimension, demonstrated experimentally to be small enough to ensure the absence of intraparticle mass transfer influence. The catalyst bed was 4.4 cm long with a volume of 0.32 cm^3 .

The catalyst was sulfided in situ prior to the hydrodesulfurization experiments; it experienced a flow of 10 vol % H_2S in H_2 at $400 \pm 1^\circ C$ for 2 hr. The hydrodesulfurization experiments were carried out with a liquid feed rate ranging from 0.6 to 12 cm^3/hr ; the reactor pressure was 102 atm, and the temperature was $300^\circ C$. All conversion data were obtained under steady-state operating conditions, as demonstrated by the agreement of several successive product analyses. Catalyst deactivation, measured by the decrease in a pseudo first-order rate constant, was typically < 10%.

The n-hexadecane was supplied by Humphrey Chemical Co. and was redistilled before use. Each feed solution was purged with H_2 and saturated with H_2 at 68 atm and room temperature. DBT (95%) was obtained from Aldrich Chemical Co. The 4-MeDBT (8) and the dimethyl-substituted dibenzothiophenes (9) were synthesized according to published methods.

In a typical kinetics run, after the catalyst had been sulfided in the reactor, the reactant mixture was supplied to the feed pump, and the desired flow rate was set. The liquid feed flowed through the catalyst bed to a dead-volume cylinder. In the routine experiments, the product stream was sampled every several hours, and the products (except H_2S) were analyzed with a gas chromatograph (glc) equipped with a flame ionization detector. Details are given elsewhere (7). Occasionally, more thorough analyses were done to obtain mass spectra of the individual products and to search for side products. Preparative glc was used, with a 5 ft X 1/4 in O.D. column packed with 10% SP2100 (Supelco) held at 200°C with a He flow rate of 40 cm³/min. The collected products were identified and analyzed with a glc-mass spectrometer system. Products were also occasionally concentrated by solvent extraction and dry-column chromatography prior to analysis by glc-mass spectrometry.

Integral conversion data were collected individually for each of the five reactant compounds listed in Table 1, and in separate experiments, DBT was mixed with each of the other four compounds. The observed conversions were calculated on the basis of disappearance of the respective sulfur-containing compounds. The H_2 concentrations in the liquid feeds were estimated from

the equilibrium solubility of hydrogen in n-hexadecane at room temperature (the temperature at which the feed solutions were prepared) (10). The lowest H_2 :sulfur-containing reactant ratio was about 35 moles/mole. Assuming a H_2 consumption of two molecules per molecule of sulfur-containing compound, the maximum decrease in the H_2 concentration in the reactant mixture was only 6% at 100% conversion of the sulfur-containing compound; consequently, the H_2 concentration was virtually constant in all the experiments.

Since the reactor operated in nearly piston flow [as determined by standard correlations (6)], the reaction order in the sulfur-containing reactant could be determined straightforwardly. The results of Fig. 1 show that pseudo first-order kinetics describes the conversion of each of the sulfur-containing reactants used singly; similar linear plots were obtained when pairs of the reactants were fed to the reactor. Table 1 summarizes the pseudo first-order rate constants calculated from the integral conversion data, with 95% confidence limits on the linear regression parameter (11).

The detailed reaction network for DBT hydrodesulfurization has been reported elsewhere (7). The results obtained here are consistent with the earlier results and show that, to a first approximation, the following network pertains to the whole group of methyl-substituted dibenzothiophenes:

For DBT, the pseudo first-order rate constant for the first of these two reactions is roughly 10 times greater than that for the second (7).

The product distribution data obtained with 2,8-DiMeDBT and 3,7-DiMeDBT conform closely to this network, but the product distribution data obtained with 4-MeDBT and 4,6-DiMeDBT are somewhat different. The yields of the substituted cyclohexylbenzene products formed from the latter two compounds were 5-10 times greater than the yield of cyclohexylbenzene formed from DBT under comparable conditions. These results suggest that the reactants with methyl groups in the 4 or in the 4 and 6 positions experienced more hydrogenation prior to sulfur removal than the others.

Increasing the feed concentration of DBT about twofold decreased the pseudo first-order rate constant more than threefold (Table 1), suggesting self-inhibition of reaction by DBT and qualitatively confirming the expectation based on the kinetics results of Espino *et al.* (12).

The data obtained with reactants used singly (Table 1) show that methyl groups added to the 2 and 8 positions of DBT hardly changed the reactivity, and methyl groups in the 3 and 7 positions also had only a small effect. Methyl groups in the 4 position, however, reduced the reactivity by an order of magnitude, and methyl groups in the 4 and 6 positions reduced it somewhat more. When DBT was added in turn to a solution of each of these methyl-substituted compounds, the order of the reactivities was the same as mentioned above, with the pseudo first-order rate constants of the substituted compounds being almost the same as those found in the experiments with these reactants used singly.

When DBT was in the reactant solution with 2,8-DiMeDBT or 3,7-DiMeDBT, the pseudo first-order rate constant for DBT (in contrast to those for the methyl-substituted compounds), was reduced significantly--about as much as when a corresponding amount of DBT itself was added to the reactant solution (Table 1). This result implies that there was competitive adsorption of DBT and the methyl-substituted DBT, as was expected from the occurrence of the self inhibition by DBT. The contrasting result that DBT did not strongly inhibit the reaction of 3,7-DiMeDBT or of 2,8-DiMeDBT (Table 1) indicates that these methyl-substituted compounds were more strongly adsorbed than DBT. The effect of 4,6-DiMeDBT on the reactivity of DBT, on the other hand, is almost negligible, demonstrating that it is more weakly adsorbed than DBT. Following this line of reasoning, we interpret the data of Table 1 as suggesting that 4-MeDBT has an adsorption strength between those of DBT and 4,6-DiMeDBT.

Although it is not clear why DBT appears to have almost no influence on the reactivity of the presumably less strongly adsorbed 4-MeDBT and 4,6-DiMeDBT (Table 1), it can be inferred that the reactivity depends on the rate of hydrogen transfer from the catalyst surface, which is apt to be affected by orientation of the reactant on the surface. We emphasize that the patterns of competitive adsorption and intrinsic reactivity of adsorbed reactants are still unresolved; more thorough kinetics and adsorption studies are required. The data presented here are, however, supportive of the idea [presented elsewhere (3,7,13-15)] that adsorption of the reactants involves

bonding of the catalyst surface with the π electrons of the benzenoid rings; mild steric effects explain the influence of methyl groups in the 4 and 6 positions.

TABLE 1. Pseudo first-order rate constants for hydrodesulfurization catalyzed by sulfided Co-Mo/ γ -Al₂O₃ at 300°C and 102 atm.

Sulfur-containing Reactant	Concentration, mole %	Pseudo first-order rate constant, cm ³ /(g of catalyst·hr) ^a	Second sulfur-containing reactant	Concentration, mole %	Pseudo first-order rate constant for second sulfur-containing reactant, cm ³ /(g of catalyst·hr) ^a
Dibenzothiophene	0.058	258.4 ± 10.3	none	--	--
Dibenzothiophene	0.130	77.5 ± 11.8	none	--	--
2,8-Dimethyldibenzothiophene	0.075	241.9 ± 23.5	none	--	--
5,7-Dimethyldibenzothiophene	0.072	126.5 ± 10.2	none	--	--
4-Methyldibenzothiophene	0.071	23.9 ± 1.2	none	--	--
4,6-Dimethyldibenzothiophene	0.064	17.7 ± 2.8	none	--	--
.....					
2,8-Dimethyldibenzothiophene	0.057	233.3 ± 9.2	Dibenzothiophene	0.065	88.1 ± 8.0
5,7-Dimethyldibenzothiophene	0.070	108.3 ± 11.5	Dibenzothiophene	0.074	66.4 ± 3.5
4-Methyldibenzothiophene	0.073	28.4 ± 1.9	Dibenzothiophene	0.081	100.8 ± 1.4
4,6-Dimethyldibenzothiophene	0.080	21.7 ± 5.0	Dibenzothiophene	0.071	213.8 ± 48.4

^aData are reported with 95% confidence limits.

Figure 5. Pseudo first-order kinetics of hydrodesulfurization of dibenzothiophene and methyl-substituted dibenzothiophenes. Reaction in a flow microreactor was catalyzed by sulfided Co-Mo/Al₂O₃ at 300°C and 102 atm.

C. LIQUEFACTION/HYDROGENATION OF COAL

The Bergius process for liquefaction/hydrogenation of coal has spawned several descendants with good prospects of commercial application, including the Exxon Donor Solvent (EDS), Gulf Solvent Refined Coal (SRC), and H-Coal^R processes (1). Coal particles slurried in recycled liquid product are broken up, accepting hydrogen and giving heavy, highly aromatic liquids with high contents of sulfur and nitrogen. Table 2 compares the developing processes and summarizes the reaction conditions. The following paragraphs address the chemistry of these processes, which is becoming well enough defined to allow identification of reaction types, illumination of the role of catalysts, and recognition of some opportunities for controlling the product distributions.

Even though there are frequent references to "catalytic liquefaction" of coal, it is clear that the initial break-up of the organic coal matrix cannot be accelerated by an added solid, since the intimate contacting required for catalysis cannot be achieved until the break-up has begun. The pyrolytic nature of this break-up has been suggested by a number of authors (e.g., 2,3), and recent work (4-6) provides strong evidence of its correctness. Measuring kinetics of the conversion of coal particles into gases plus benzene-soluble and pyridine-soluble liquids at 400°C (and avoiding the confusion of a long heat-up period), Neavel (5) collected precise data for reaction times as short as seconds. The results (Figure 6) show that about

10% of a bituminous coal was converted to gases + benzene-soluble liquids in about 20 seconds and 90% was converted to gases plus pyridine-soluble components in about 2 minutes. The rapid coal break-up has been investigated by microscopic examination of the solids at early stages of disintegration (5,6). The results demonstrate the physical nature of the initial break-up: gaseous pyrolysis products form within seconds, expanding the softened coal particles; organic material also dissolves. The initial rate of coal conversion is independent of whether a good hydrogen donor like Tetralin (1,2,3,4-tetrahydronaphthalene) is present (Figure 6). The results point to the pyrolytic nature of the initial break-up, a process accelerated neither by an added catalyst nor by a hydrogen-donor solvent. After longer times, however, the donor solvent gives much higher yields than a non-donor solvent like naphthalene, and in the presence of naphthalene, the yield even passes through a maximum (Figure 6). Behavior like this has been observed often and is attributed to formation of products like coke which are highly resistant to further conversion.

All the results mentioned above--and results obtained with model compounds under conditions similar to those of coal liquefaction (24)--support the idea that the intermediates in the disintegrating organic coal matrix are free radicals. Breaking of C-C and C-O bonds accounts for the following: (1) evolution of some light products directly split out of the coal matrix,

(2) production of highly reactive intermediates (free radicals) capable of abstracting hydrogen from molecules like Tetralin or from neighboring, hydrogen-rich groups in the coal itself, and (3) further reaction of the highly reactive intermediates with one another to give higher-molecular-weight materials, including coke.

Product analysis identified the several percent of organic material finally remaining unconverted (Figure 6) as mostly fusinite--macerals* roughly resembling charcoal. The other macerals, including the predominant one, vitrinite--derived in the coalification process from bark or woody tissue--were almost completely converted. Systematic studies of the reactivities of various coals (7,8) show patterns of reactivity in liquefaction depending both on the maceral content and the rank of the coal, which is a measure of the extent of coalification (Figure 7). (The lowest-rank coals are lignite; bituminous and anthracite coals have increasingly higher rank.) Work has already been reported (7,8a) suggesting how maceral content and rank can be of value in predicting the reactivities of new coals. One should not expect much accuracy in these predictions, however, since the correlations are rough and since coals are far from uniform even within a given seam.

Only recently have the products of coal liquefaction begun to yield to detailed chemical characterization (10). Farcasiu et al. (10a) fractionated products by liquid chromato-

*The term maceral refers to organic constituents of coal much as the term mineral refers to inorganic constituents in coal. Macerals are microscopically identifiable products of the coalification of what were originally organs and tissues of plants.

graphy, identifying 10 component classes, one having predominantly saturates, another aromatics, another polar aromatics plus nonbasic sulfur-, nitrogen-, and oxygen-containing compounds, another polyphenols, and so forth. The subgroup of component classes soluble in hexane was called oils, the remainder soluble in benzene was called asphaltenes (according to the familiar notation), and the remainder soluble in pyridine was called asphaltols, since it had a high concentration of -OH groups; this last fraction is often referred to as preasphaltenes, since it appears to be an intermediate in asphaltene formation (10a,11). There are few data to allow comparison of different coals or of the several liquefaction processes in terms of the yields of the various product fractions, but it seems to be fruitful to proceed assuming that there might be general validity in representing these fractions as characteristic liquefaction products. Further analytical work can be expected to provide better separation methods, more detailed characterization of the products, and improved definitions of the component classes. High-resolution mass spectrometry and ^{13}C nmr spectroscopy should be especially valuable.

With an understanding of the pyrolytic coal break-up, we can begin to understand the role of catalysts in liquefaction/hydrogenation processes. Many catalysts have been tested (12) and those most commonly used are hydroprocessing catalysts, typically prepared from a support of porous, high-surface-area ($\sim 200 \text{ m}^2/\text{g}$)

$\gamma\text{-Al}_2\text{O}_3$ with added oxides of Mo (or W) and Co (or Ni). Catalysts of this class were first applied in coal liquefaction/hydrogenation in prewar Germany, and they have found wide application for trickle-bed hydroprocessing of petroleum, especially hydrodesulfurization. In operation, the catalyst surfaces are converted from oxides into sulfides; these catalysts are the most active known hydrogenation catalysts in use with sulfur-containing compounds. Metals like Pt are intrinsically much more active hydrogenation catalysts than the metal sulfides, but they are strongly poisoned by sulfur and cannot be used in processing of coal or heavier petroleum fractions.

The sulfide catalysts are active for hydrogenation of the unsaturated products liberated in the break-up of the coal matrix. Compounds like naphthalene are transported rapidly to the catalyst surface, where they are converted into compounds like Tetralin. The catalytic hydrogenation taking place in a liquefaction reactor replenishes the donor solvent; Tetralin and similar hydrocarbons play the role of hydrogen carriers (4,5,24)--they give up hydrogen to the disintegrating coal matrix, return to the catalyst surface, where they react with dissociatively adsorbed hydrogen, and then shuttle back to the coal. This cycle is represented in a rough, schematic way in Figure 8.

We can now identify one of the critical questions in process design: how and where should the catalytic hydrogenation be carried out? One possibility, exemplified in the H-Coal^R

process, is to include the catalyst in the reactor where the liquefaction takes place. To some extent, this kind of operation is unavoidable, since the mineral matter of coal (including Pyrites, clays, and many minor constituents) has some activity as a hydrogenation catalyst (13,14). Another possibility, exemplified in the EDS process, is to confine the hydroprocessing catalyst within its own reactor and separately optimize the liquefaction and catalytic hydroprocessing operations.

The operation of the EDS process is reported (15,16) to be sensitive to an undefined "solvent quality index," surmised to be a measure of the reactivity (and perhaps also the capacity) of the recycle liquid acting as a hydrogen donor in the presence of the liquefying coal. The solvent quality index can be increased by increasing the amount of hydrogen added to the recycle solvent in a trickle-bed catalytic reactor (15). There is flexibility in the operation with regard to how much hydrogen is transferred to the coal in the liquefaction reactor and how much is transferred to the liquid product in a downstream reactor. The amount of hydrogen transfer required in the liquefaction reactor increases sharply with increased conversion (Figure 9), and for the optimum to be realized, some of the organic part of the coal must remain unconverted. The unconverted solid is separated from the liquid in the EDS process by vacuum distillation; it can be steam gasified to provide some of the hydrogen needed for hydroprocessing.

An essential difference between the H-Coal^R process and the EDS processes is therefore the lack of opportunity in the

former for separately optimizing the coal liquefaction and recycle solvent hydrogenation. But it may well be that the H-Coal^R process offers some undetermined advantage in having the hydrogenation catalyst immediately available to the fragments split out from the coal; perhaps a rapid catalytic conversion of some of these fragments leads to desirable products, whereas the fragments, allowed to react with each other when catalyst is absent, may give undesired products like coke.

The SRC process differs from both the EDS and H-Coal^R processes in lacking any added catalyst. Some attempts to increase the processing flexibility have been made in modifying the original SRC I process. In the modified process, called SRC II (17), liquid product is recycled and the contact between the catalytically active mineral matter and the liquid is regulated, providing some control over the hydrogen transfer and product distribution; the typical SRC I product is a friable solid at room temperature, but SRC II operation allows production of liquid, with the consumption of about twice as much hydrogen as SRC I (25).

There has been much thought given recently to modifying the SRC process to more closely resemble the EDS process (26). Reduction of the contact time in the SRC reactor minimizes the hydrogen consumption there and produces a feed for downstream catalytic hydroprocessing, which may be carried out in a slurry bed like that used in the H-Coal^R process.

The objectives in all these processes include production of clean-burning low-sulfur fuels, and even the SRC process, which uses no added catalyst, removes most of the organic sulfur (as well as almost all of the oxygen and the inorganic sulfur, but not a large fraction of the nitrogen). The EDS and H-Coal^R processes can be even more efficient in producing low-sulfur fuels, since the catalysts they employ may be selective for hydrodesulfurization. The selectivity of the sulfided CoO-MoO₃/Al₂O₃ catalyst is illustrated in Figure 10 which gives the reaction network for conversion of a typical reactant in the liquid product, dibenzothiophene. The catalyst directs the hydrodesulfurization reaction, the splitting out of H₂S (with the formation of biphenyl), almost to the exclusion of the accompanying hydrogenation reactions. There are many other reactants, such as hydrocarbons, however, which react with the expensive hydrogen. The optimum control of the hydrogen consumption between hydrodesulfurization and solvent hydrogenation could probably best be obtained by use of a catalyst like sulfided CoO-MoO₃/Al₂O₃ in a separate trickle-bed reactor, as in petroleum refining.

Using the catalyst in a separate reactor instead of including it in the liquefaction reactor offers the further advantage of preventing catalyst activity loss resulting from accumulation of coal mineral matter (but not of carbonaceous deposits). The mineral deposits in used H-Coal^R catalysts have been examined by electron microscopy, electron microprobe analysis, and energy

dispersive x-ray analysis (EDAX) (19); other catalysts have also been examined (20) and other characterization techniques applied (21). The results show that deposits form within the catalyst pore structure (Figure 11), including mineral matter (primarily iron sulfide and clays) and the ever-present carbonaceous material (coke); titanium deposits also form, probably from conversion of soluble organotitanium components liberated from the coal matrix during liquefaction. The deposits can cause rapid catalyst deactivation, covering the catalyst surface and perhaps blocking the pore mouths. Deposits within the particles can also enlarge cracks and break up the particles. They are a serious disadvantage of the slurry-bed process.

The liquids produced from coal are potentially valuable as replacements for petroleum to be used as feedstocks for further refining. Appropriate catalytic refining operations like cracking and hydrocracking, however, require feeds which are almost free of nitrogen-containing compounds, since many of these are basic and poison the catalysts by combining with acidic surface sites. Petroleum feeds for hydrocracking usually undergo catalytic hydrodenitrogenation prior to contacting the hydrocracking catalyst. A similar pretreatment may be applied to coal-liquefaction products (22), but the conditions are much more severe than those required for petroleum; the severity results from the relatively high nitrogen contents (as much as a few weight percent) and the lack of reactivity of some of the multiring nitrogen-containing compounds, such as acridine. Figure 12 shows a reaction network

determined for catalytic hydrodenitrogenation of acridine. The comparison with hydrodesulfurization (Figure 10) is striking; hydrodenitrogenation takes place with much lower selectivity--the reactant undergoes extensive hydrogenation (which is needed to weaken the C-N bonds) prior to denitrogenation. There are no known catalysts which are able to coordinate nitrogen and selectively break the C-N bonds as they break C-S bonds; development of such catalysts would have a major impact on the processing of coal-derived liquids.

Table 2

Processes for Liquefaction/Hydrogenation of Coal

Process	Reactor Type(s)	Typical Catalyst	Typical reaction conditions		Distinctive Characteristics
			temp., °C	pressure atm	
Bergius--single stage for liquefaction	Stirred batch reactor	Iron oxide	465	200	Severe conditions, throw-away catalyst
SRC--single stage for liquefaction and hydrogenation; recycle of product liquid	Tubular flow reactor	Coal mineral matter	450	140	No added catalyst; lack of specificity in hydrogenation
H-Coal ^R --one or more stages; liquefaction of coal and catalytic hydroprocessing of product liquid occur in the same reactor	Continuous flow slurry bed reactor	Hydroprocessing catalyst like sulfided $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$	450	200	Liquefaction and catalytic conversion of products in the same reactor; rapid catalyst aging
EDS--first stage for liquefaction in the presence of hydrogen-rich donor solvent (recycle liquid) and second stage for catalytic hydroprocessing of liquid product	First stage, continuous tubular flow reactor; second stage trickle-bed flow reactor	In liquefaction stage, coal mineral matter; in trickle bed reactor, hydroprocessing catalyst like $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$	450	120	Liquefaction in the presence of good hydrogen-donor species for high yields of liquid products; catalytic hydroprocessing of liquids in a separate reactor for selective hydroprocessing with relatively slow catalyst deactivation

Figure 6. Conversion of a bituminous coal (rank HVCB) at 400°C; comparison of a hydrogen-donor solvent (Tetralin) with a non-donor naphthalene solvent (5).

Figure 7. Dependence of conversion in coal liquefaction/hydrogenation on coal rank and maceral content: conversion at 385°C and 238 atm was determined in the presence of hydrogen, partially hydrogenated anthracene oil, and an unspecified catalyst (9).

Figure 8. Schematic representation of the reaction cycles of coal liquefaction/hydrogenation.

Figure 9. Dependence of coal conversion to benzene solubles and gases on the amount of hydrogen transferred from Tetralin donor; the coal sample and reaction conditions were as specified in Figure 6 (5).

Figure 10. Reaction network prevailing in the hydrodesulfurization of dibenzothiophene in *n*-hexadecane carrier oil catalyzed by sulfided $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ at 300°C and 103 atm. The numbers next to the arrows are pseudo first-order rate constants in units of m^3/kg of catalyst. The hydrogenation reactions, denoted with red arrows, are almost negligibly slow in comparison with the hydrodesulfurization reactions (18).

Figure 11. Qualitative composition profiles in a used H-Coal^R catalyst, determined by electron microprobe analysis. The profiles indicate the deposition of mineral matter from the coal preferentially near the pore mouths (19).

Figure 12. Reaction network prevailing in the hydrodenitrogenation of acridine in paraffinic white-oil carrier catalyzed by sulfided $\text{NiO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ at 364°C and 137 atm. The numbers next to the arrows are pseudo first-order rate constants in units of m^3/kg of catalyst. The hydrogenation reactions, denoted with red arrows, precede breaking of C-N bonds (23).

V. REFERENCES

SECTION A

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VII. PERSONNEL

There have been no changes in personnel during this quarter.