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

Eighth Quarterly Report, March 21—June 20, 1977

By
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August 25, 1977
Date Published

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MASTER

U. S. DEPARTMENT OF ENERGY

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Prepared for

Fossil Energy
Energy Research and Development Administration
Washington, D.C.

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I. ABSTRACT

Three high-pressure flow microreactors and two batch autoclave reactors have been used to study the reaction networks and kinetics of (1) catalytic hydrodesulfurization of dibenzothiophene and methyl-substituted dibenzothiophenes and (2) catalytic hydrodenitrogenation of quinoline, methyl-substituted quinolines, and carbazole. The catalysts were commercial, sulfided $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{NiO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$, and $\text{NiO-WO}_3/\gamma\text{-Al}_2\text{O}_3$.

At the typical conditions of 300°C and 104 atm, dibenzothiophene reacts to give H_2S and biphenyl in high yield, but there is some hydrogenation preceding desulfurization. Methyl-substituted dibenzothiophenes react similarly, and each reaction is first-order in the sulfur-containing compound. Two methyl groups near the sulfur atom (in the 4 and 6 positions) reduce the reactivity tenfold, whereas methyl groups in positions further removed from the sulfur atom increase reactivity about twofold. The results are consistent with steric and inductive effects influencing adsorption. The data indicate competitive adsorption among the sulfur-containing compounds.

In quinoline hydrodenitrogenation, both rings are saturated before the C-N bond is broken. Similarly, in acridine conversion, a large amount of hydrogenation precedes nitrogen removal. Breaking of the carbon-nitrogen bond is evidently one of the slower reactions in the network. The Ni-Mo catalyst is about twice as active as the Co-Mo catalyst for ring hydrogenation, and the two catalysts are about equally active for breaking the carbon-nitrogen bond.

Reactivity of carbazole is similar to that of quinoline and lower than that of acridine. Again, extensive hydrogenation precedes heteroatom removal.

Aged catalysts taken from the H-Coal^R and Synthoil processes contained coke and deposits of mineral matter (primarily FeS and clays). The H-Coal catalysts were examined, for example, in experiments with dibenzothiophene hydrodesulfurization and quinoline hydrodenitrogenation. The activity of the used catalyst was reduced 20-fold for hydrodesulfurization of dibenzothiophene and fivefold for hydrodenitrogenation of quinoline. Most of the loss of hydrodesulfurization activity was associated with the mineral deposits and not with the coke.

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 hydro-sulfurization 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 of 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 ERDA, reaction engineering models of coal-to-oil 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 ERDA for improved catalytic hydrodesulfurization 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 micro-reactors 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 data show that the reaction network is slightly more complex than the direct reduction of DBT to hydrocarbon products; the network is the following at 300°C and 100 atm:

The relative rates of hydrodesulfurization of a variety of the important 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: BT, very large; 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 near the S 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.

Three different catalysts, namely Co-Mo/ γ -Al₂O₃, Ni-Mo/ γ -Al₂O₃ and Ni-W/Al₂O₃ have so far 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.

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 HDN of quinoline requires a large consumption of hydrogen before the N atom is removed from the hydrocarbon backbone. The lack of selectivity encountered in hydrodenitrogenation stands in sharp contrast to the high selectivity in hydrodesulfurization.

The total rate of HDN shows a maximum with respect to hydrogen partial pressure. However, the only individual reaction in the network which decreases in rate with increasing hydrogen partial pressure is the conversion of 1,2,3,4-tetrahydroquinoline to ortho-n-propylaniline; this reaction dominates the overall network at high pressure.

Also in hydrodenitrogenation of acridine, a large amount of hydrogenation precedes nitrogen removal, and the carbon-nitrogen bond breaking reactions are relatively slow. In the presence of Co-Mo/ γ -Al₂O₃ catalyst, heteroaromatic ring hydrogenation is favored, and with a Ni-Mo/ γ -Al₂O₃ catalyst, aromatic ring hydrogenation is favored. For both acridine and quinoline, little effect of replacing Co with Ni could be detected in the nitrogen removal reaction, although Ni-Mo/ γ -Al₂O₃ is roughly twice as active for hydrogenation as Co-Mo/ γ -Al₂O₃.

The hydrodenitrogenation of carbazole has been examined under conditions similar to those used for acridine. Both carbazole disappearance and total nitrogen removal can be represented as first order reactions. Tetrahydrocarbazole was the major intermediate compound present in the dry column extract. Both Cis hexahydrocarbazole and octahydrocarbazole were identified as minor products. Reactivity of carbazole is similar to that of quinoline, and acridine is the least reactive.

Preliminary experiments have been carried out to characterize hydrodenitrogenation of substituted quinolines. The conditions used were similar to those used for quinoline HDN. 2,6-, 2,7- and 2,8-dimethylquinoline were studied and products identified were analogous to those observed in quinoline network. The reactivity of these compounds to HDN is comparable to that of quinoline.

Catalyst Deactivation

A variety of physical techniques have been used to identify the aging processes for catalysts used in 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 cracks have been enlarged by grain growth; this deposition yields 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 HDS of dibenzothiophene and five-fold for HDN of quinoline. Burning off of carbonaceous deposits increased the activity of the aged catalyst only three-fold for dibenzothiophene HDS, 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 for quinoline and acridine reactions have been reduced to rate parameters by extension of nonlinear regression analysis.

TIME PLAN* AND MILESTONE CHART**

8

month 28

month 28

month 28

TIME PLAN* AND MILESTONE CHART** (cont)

Year 0 1 2 3

C. CATALYST DEACTIVATION

SYNTHOIL

CATALYST:

Physical Properties	month 6		
Chemical Properties	month 6	month 16	
Other Deactivated Catalysts	90% month 10	75%	month 24
Catalyst Deactivation Studies	50%	month 14	70%
REACTION ENGINEERING			
Reactor Models for Pulse and Flow Microreactors	75%	month 14	90%
Process Reaction Engineering	5%	month 14	15%

month 30

month 36

*Time Plan and Milestone Chart as Presented in Proposal.

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

CUMULATIVE EXPENDITURES*

Item	Quarter							
	First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth
Personnel	\$5,807	\$20,740	\$37,356	\$53,418	\$91,593	\$112,666	\$132,669	\$146,146
Travel	28	528	1,152	1,152	1,521	2,458	3,140	3,814
Supplies & Expense	4,674	10,007	19,582	25,735	37,291	42,341	51,589	56,488
Occupancy & Maintenance	6,110	9,208	10,108	10,634	13,755	13,920	14,396	14,600
Equipment	610	17,978	30,704	34,930	50,614	54,013	54,013	52,295
Information Processing	--	--	--	97	154	375	1,180	1,868
Transfers (Overhead)	--	10,202	20,035	38,710	75,839	93,287	113,830	123,576

*Includes encumbrances

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. HYDROPROCESSING MICROREACTOR DEVELOPMENT

All three flow microreactors are now in regular, nearly continuous operation. The first microreactor is being used to study the reactivity of various mono- and di-methyl substituted dibenzothiophenes. In the preceding quarterly report, the relative reactivities of substituted dibenzothiophenes (DBT) and DBT in the presence of one another were given. During the current quarter, the reactivities of these methyl-substituted DBT's have been studied separately, as is discussed later in this report. Further, two industrial catalysts besides the standard Co-Mo/ γ -Al₂O₃ were tested for DBT hydrodesulfurization (HDS). From the earlier studies of the HDS of DBT with the Co-Mo/ γ -Al₂O₃ catalyst, a reaction network has been proposed which might be expected to be similar to those prevailing for the various substituted DBT's under our experimental conditions. This part of the work is currently underway, and data are expected to appear in the next quarterly report.

The second microreactor continues to be used for characterization of hydrodenitrogenation (HDN) of quinoline and methyl-substituted quinolines. Some results appear in the following pages.

The third microreactor has been used for studies concerning the attainment of suitable experimental conditions to measure differential HDS conversions of DBT to determine reaction rates. Results are included in a following section of this report.

B. CATALYTIC HYDRODESULFURIZATION

1. Experimental

a. First high-pressure flow reactor

During this quarter, the first flow reactor was utilized in measuring pseudo first-order rate constants for conversion of DBT, possible DBT HDS intermediates, and methyl-substituted DBT's. The operating conditions (except for the modifications to be explained) remained the same as those described previously and are summarized below (unless otherwise mentioned):

- Catalyst: HDS 16A; mass: 25mg; volume of reactor bed: 0.325 cm³; length of bed: 4.1 cm; catalyst particle size: 149-178 μ m.
- Catalyst pretreatment: catalyst sulfided in situ with 10% H₂S in H₂ for two hours at 400°C. Flow rate was 30-50 cm³/min.²
- Liquid flow rate: 1.2 to 7.2 cm³/hr.
- Saturation pressure applied to liquid feed: 1000 psig.
- Reactor temperature: 300 $\pm$ 1°C.

- Reactant mixture (unless otherwise specified): 0.122 wt% DBT in n-hexadecane carrier oil.

Since a number of different runs were made with compounds other than DBT, or different catalysts, the catalyst and reactant(s) for the individual runs made during this quarter are listed in Table 1.

B.a-I. Reactivities of Methyl-Substituted Dibenzothiophenes:

Experiments were performed to determine the reactivities in catalytic hydrodesulfurization (HDS) of various methyl-substituted dibenzothiophenes. The first flow microreactor was used with the experimental conditions the same as those reported earlier (see the 7th quarterly report in this series). In the 7th quarterly report, results of the catalytic HDS of binary mixtures of these methyl-substituted DBT's with DBT were given. From those data we have an idea about the relative reactivity of each of the methyl-substituted compounds relative to DBT. In this quarter, the same catalyst (Co-Mo/ γ -Al₂O₃) was used to determine the reactivities of the compounds separately. These results offer an opportunity to elucidate the effects of competitive adsorption of the compounds in the DBT family. The experimental conditions for each run were maintained constant, and they are the ones summarized earlier in this section.

RESULTS AND DISCUSSION

As will be shown later, it has been found that DBT can react in two ways; namely,

- (i) With sulfur extrusion preceding hydrogenation of the aromatic ring(s).
- (ii) With hydrogenation of aromatic ring(s) preceding the S-removal.

The first reaction is predominant at all the conditions investigated. The importance of the second reaction depends on the catalyst composition and the concentration of H₂S in the reactant mixture. Detailed discussion of the DBT reaction network is given in a following section, and now it is assumed that substituted dibenzothiophenes are characterized by reaction networks analogous to that stated above for DBT. More data are necessary to test this assumption (and the experiments are underway), but it is already clear from preliminary results that for the substituted compounds (possibly with the exception of 4-Me- and 4,6-diMeDBT), the predominant reaction is the one involving the removal of sulfur, and this is followed by hydrogenation of the aromatic ring(s). The formation of methyl biphenyls can account for approximately 90 - 95% of the reaction products.

The kinetics of hydrodesulfurization of the various methyl DBT's was tested with the first-order rate equation for a piston

flow reactor (see the 7th quarterly report, pp. 21 and 28). The integrated rate equation:

$$-\ln(1 - x) = k_1 (W/F) \quad (i)$$

where

x = fractional conversion of S-compound

k_1 = first order rate constant

W = mass of catalyst

F = liquid flow rate, cm^3/hr

was found to be applicable in all cases. Figs. 1-5 demonstrate the applicability of this rate equation for the various S-compounds. The first-order rate constants for different compounds under the two different experimental conditions are summarized in Table 2.

From Table 2, several important conclusions follow regarding the reactivity vis-a-vis the position(s) of the substituent methyl group(s) in the DBT. (The following structure of DBT indicates the positions of the substituents.)

The conclusions are as follows:

(1) The reactivity of DBT is decreased when it is substituted by one or more methyl groups.

(2) The reactivities of methyl-substituted DBT's are strongly dependent on the positions of the substituents. For example, 2,8-diMeDBT is about 18 times more reactive (judged from the k_1 values) than is 4,6-diMeDBT, which is the least reactive sulfur-containing compound studied. The considerably lower reactivities of 4-MeDBT and 4,6-diMeDBT can be explained by the steric hindrance caused by the substituents near the S-atom, which is believed to interact with a Mo^{3+} ion underlying a surface anion vacancy in the adsorption step. The steric effect is also reflected by the fact that 4-MeDBT has a higher reactivity than 4,6-diMeDBT. The higher reactivities of 2,8- and 3,7-diMeDBT have been explained (see the 7th quarterly report) by the increase of electron density around the adsorbing S-atom by virtue of the hyperconjugation effect caused by the methyl groups.

(3) From the results of the activity measurements of DBT in the presence of one of the methyl-substituted DBT's, it is evident that the rate of reaction of the former is considerably depressed by the presence of the latter. This depression is again dependent on the reactivity of the methyl-substituted dibenzothiophene. For example, 2,8-diMeDBT, which is more reactive than 4-MeDBT, depresses the rate of reaction of DBT more than does 4-MeDBT. From these

TABLE 1
Reactants and Catalysts Used in Flow Reactor No. 1

Run No.	Reactant	Concentration (wt%)	Catalyst
1-45	DBT	0.122	CoMo (HDS 16A ¹)
1-46	DBT	0.122	NiMo (HDS 9A ¹)
1-47	DBT	0.122	NiW (ND 550 ²)
1-48	4H DBT	0.127	CoMo (HDS 16A)
1-49	o-mercapto BPh	0.125	"
1-50	2,8-diMeDBT	0.071	"
1-51	4-MeDBT	0.052	"
1-52	3,7-diMeDBT	0.0714	"
1-53	DBT	0.0544	"
1-54	DBT	0.115	"
1-55	DBT	0.164	"

¹HDS 16A and HDS 9A are American Cyanamid catalysts

²ND 550 is a Nalco catalyst. For all the catalysts the support material is γ -alumina

Notes: Abbreviations used throughout the report are:

DBT (dibenzothiophene), 4H DBT (tetrahydrodibenzothiophene), 6H DBT (hexahydrodibenzothiophene), BPh (biphenyl), CHB (cyclohexylbenzene), BCH (bicyclohexyl), o-mercaptoBPh (orthomercapto-biphenyl), 2,8-diMeDBT (2,8-dimethyldibenzothiophene), etc.

Figure 1. Pseudo First-Order Kinetics of Hydrodesulfurization of Dibenzothiophene; x is the Fraction of Sulfur-Containing Compound Converted and WHSV is the Weight Hourly Space Velocity (g of catalyst hr/cm³ of feed).

Figure 2. Pseudo First-Order Kinetics of Hydrodesulfurization of 4-Methyldibenzothiophene.

Figure 3. Pseudo First-Order Kinetics of Hydrodesulfurization of 2,8-Dimethyldibenzothiophene.

Figure 4. Pseudo First-Order Kinetics of Hydrodesulfurization of 3,7-Dimethyldibenzothiophene.

Figure 5. Pseudo First-Order Kinetics of Hydrodesulfurization of 4,6-Dimethyldibenzothiophene.

TABLE 2

Comparison of the First Order Rate
Constants for DBT and Methyl-Substituted DBT's

No:	Compound	k_1 (cm ³ /g of catalyst hr)		
		Alone	With DBT	DBT with others
1	DDT	256	-	-
2	2,8-diMeDBT	188	234	89
3	3,7-diMeDBT	123	114	67
4	4-MeDBT	24	27	100
5	4,6-diMeDBT	9	20	198

Notes: (1) S-compound concentrations:

- a. In binary mixtures $\approx 6.5 \times 10^{-6}$ moles/cm³.
- b. In single compound solution $\approx 3.2 \times 10^{-6}$ moles/cm³.

(2) Other reaction conditions were those given earlier

(3) Rates are calculated on the basis of the rate of disappearance of the sulfur-containing compounds.

results, it follows that the various sulfur-containing compounds are adsorbed on the same catalytic sites and that there is a correlation between reactivity and the strength of adsorption.

(4) While the inhibition effect of the methyl-substituted DBT's on DBT is quite clear and consistent, the same effect of DBT on the methyl-substituted compounds is not yet understood. In some cases, the rate is depressed and in some other cases it is increased by DBT. It is expected that this point will be clarified by the results of current experiments.

B.a-II. HDS of DBT catalyzed by Ni-Mo/ γ -Al₂O₃ and Ni-W/ γ -Al₂O₃

The Co-Mo/Al₂O₃ catalyst is the standard being used for studying the HDS reactivities of sulfur-containing compounds; two other catalysts, Ni-Mo/Al₂O₃ and Ni-W/Al₂O₃, have been tested for comparison in hydrodesulfurization of dibenzothiophene under the experimental conditions which have been summarized earlier.

RESULTS AND DISCUSSION

(i) Activity

Since the experimental conditions were the same, the pseudo first-order rate constants can be taken as the criteria for comparing the activities of the three catalysts. Fig. 6 shows the activities of the three catalysts. Fig. 7 demonstrates the validity of the first order rate equation for each catalyst. The rate constants have been calculated from the Fig. 7 and summarized in Table 3.

From the information obtained from Table 3, the catalysts can be arranged in order of decreasing activities as follows:

$$\text{Ni-Mo} > \text{Ni-W} \geq \text{Co-Mo}$$

It is to be noted, however, that the comparison is based on unit mass of the catalysts and not on the unit surface areas which are not yet known for all the catalysts.

(ii) Selectivity

In this report, selectivity for a product 'P' is defined as follows:

$$(\%) \text{Selectivity} = \frac{\text{number of moles of sulfur-containing compound converted to product 'P' x 100}}{\text{total number of moles of sulfur-containing compound reacted}}$$

Figure 6. Comparison of the Activities of Different Catalysts for the Hydrodesulfurization of Dibenzothiophene.

Figure 7. Pseudo First-Order Kinetics of Hydrodesulfurization of Dibenzothiophene in the Presence of Various Catalysts.

TABLE 3

First-Order Rate Constants for the
Hydrodesulfurization of Dibenzothiophene with Different Catalysts:

Wt. of Catalyst = 0.025gm Temp. = 300±1°C

Catalyst	Reactant Concentration	Rate Constant	
		cm ³ /hr gm	cm ³ /hr cm ²
Co-Mo/ γ -Al ₂ O ₃	0.115 wt%	109	0.545
Ni-W/ γ -Al ₂ O ₃	0.120 wt%	135	—
Ni-Mo/ γ -Al ₂ O ₃	0.120 wt%	190	1.117

The selectivities for the major products of hydrodesulfurization of DBT, namely, biphenyl (BPh) and cyclohexylbenzene (CHB), are plotted in Fig. 8 as a function of contact time ($1/\text{WHSV}$) for three different catalysts.

From the figure it is evident that the selectivities for BPh formation gradually decrease toward a constant value in the case of Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$ and Ni-W/ $\gamma\text{-Al}_2\text{O}_3$ catalysts; the reverse trend is evident in the case of the $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The selectivity curves for the Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst reveal that with increasing contact time, more and more of the BPh is hydrogenated to CHB. But it is not known to what extent the alternative route of the network is important in this case; it is possible that at higher contact time, CHB is increasingly generated directly from DBT. To settle this issue, relative hydrogenation rates of BPh and DBT are to be determined.

It is already clear, however, from these data that Mo-containing catalyst promoted with Ni acts as a better hydrogenation catalyst than the others.

B.1(b) Third high-pressure flow microreactor

With the third microreactor operating satisfactorily, continued work was done toward measuring DBT hydrodesulfurization (HDS) kinetics in the differential conversion regime. The operating conditions for the third microreactor are identical to the previously mentioned conditions for the first flow reactor, except for the catalyst loading, i.e.:

*Catalyst: HDS 16A ; mass: 10mg; volume of reactor bed: 0.158cm^3 ; length of bed: 4.1 cm; catalyst particle size (unless otherwise stated): 149-178 μm .

In two cases the particle sizes of the catalyst and of the inert alundum packing were different from that given above and are given in Table 4.

2. Analytical

Besides the glc analysis described previously, the glc-mass spectrometer identification work was continued. This technique was explained in the 7th quarterly report in this series. Emphasis was placed on identifying the products from HDS of methyl-substituted DBT and intermediates in HDS of DBT.

3. Results and Discussion

(1) Partial study of particle size effect on HDS of DBT.

Using the third flow reactor, experiments similar to those reported in the 5th quarterly report in this series were performed with various catalyst particle sizes. The early experiments were

Figure 8. Comparison of the Selectivity Pattern for the Formation of the Major HDS Products in the Presence of Various Catalysts.

TABLE 4
Catalyst Particle Sizes
Surveyed in Flow Reactor No. 3

Run	Catalyst Particle Size (μm)		Alundum Mesh Size
	Range	Mean	
3-13	208-295	252	60
3-14	105-149	127	100-140
Standard Cond.	149-178	164	90

questionable due to lack of agitation in the H_2 -sparged liquid feed autoclave, as was explained in the 5th quarterly report. To confirm the absence of an influence of intraparticle diffusion on rates of HDS, activity was measured for the same weight of catalyst for two new particle sizes, one larger and one smaller than the standard (see Table 4). A plot of percent sulfur removal vs. time in Fig. 9 confirms the absence of intraparticle diffusion effects.

(ii) Confirmation of differential reactor conditions for DBT HDS. A differential reactor is defined as one in which the reaction rate is nearly constant throughout the reactor. Such a condition exists only when the change in reactant concentration through the bed is minimal. The mass balance equation for such a reactor is:

$$F(C_{s_0} - C_s) = r W$$

where F = volumetric flow rate in cm^3/hr , C_s is the concentration of DBT, C_{s_0} is the inlet concentration of DBT, W is the weight of catalyst and r is the reaction rate in $moles\ hr^{-1}\ cm^{-3}$. Solving for r gives:

$$r = \frac{F}{W} (C_{s_0} - C_s) = \frac{WHSV}{\rho_{C_{16}}} C_{s_0} X$$

where

$$X = (C_{s_0} - C_s) / C_{s_0}$$

$\rho_{C_{16}}$ is the density of hexadecane, and WHSV is the weight hourly space velocity with units hr^{-1} . If r is a constant then a plot of X vs. $(WHSV)^{-1}$ should give a straight line through the origin with slope of $r\rho_{C_{16}}/C_{s_0}$. Such a plot is shown in Fig. 10. Con-

tinuation of differential reactor conditions into higher levels of sulfur removal (5-10%) is possible, and the range of conversions in the differential range remains to be determined by further experimentation.

d. Reaction Network for DBT HDS catalyzed by Co-Mo/ γ - Al_2O_3 .

Completion of the study of possible intermediates in the DBT HDS reaction network, which includes the analytical determination of the products of each, has made possible a nearly complete determination of the reaction network under the conditions of these experiments. The observed reaction network is as follows.

Figure 9. Effect of Particle Size on the Catalytic Activity for HDS of DBT.

Figure 10. Demonstration of the Achievement of Differential Reactor Conditions in HDS of DBT.

A run with the possible intermediate o-mercaptoBPH gave complete conversion to BPh and CHB. CHB amounted to 2-3% of the products at flow rates of 3.6 - 7.2 cm³/hr, compared to 5% when DBT was the reactant. This result agrees with the results of the run made previously with BPh in which hydrogenation to CHB was substantially less than expected based on the DBT run (see 7th quarterly report). Again an alternative route for formation CHB from DBT is suggested.

In the DBT batch experiments reported earlier (see the 6th quarterly report), tetrahydrodibenzothiophene (4HDBT) was identified as a sulfur-containing intermediate by the dry column, glc/mass spectrometer technique; correspondingly, the CHB selectivity was of the order of 4-12%. An important difference in the operating conditions between the batch and flow experiments is the H₂ concentration in the liquid, with the concentration being about three times greater in the batch experiments. This explains why 4HDBT has not been observed in the product of a standard flow experiment.

From the study of tetrahydrodibenzothiophene (4HDBT) and hexahydrodibenzothiophene (6HDBT) made in the flow reactor, it has been shown that these two compounds rapidly reach equilibrium with one another. Evidence of the equilibrium (summarized in Table 5) includes a constant ratio of 4HDBT to 6HDBT--independent of the starting material and WHSV--and equal conversion to CHB. No BCH product was observed. The reactivity of 4HDBT and 6HDBT compared to DBT is about four times as great, as determined from the ratio of pseudo first-order rate constants. In Fig. 11, the straight line fit of the data confirms the suggestion of a first-order expression for HDS of 4HDBT and 6HDBT.

Partial hydrogenation of DBT prior to heteroatom removal thus explains the observed data by supplying an alternate route for HDS of DBT and CHB production. A final confirmation of this parallel path in the reaction network was observed in a recent experiment which is to be discussed completely in the 9th quarterly report: addition of H₂S to the feed in an H₂S/H₂ mole ratio of 0.084 suppressed direct hydrogenolysis in favor of the slower preliminary hydrogenation route. 4HDBT was detected in very low concentrations, and CHB selectivity increased to more than 13% at a flow rate of 1.2 cm³/hr (see Table 6).

TABLE 5
Evidence of 4HDBT - 6HDBT Equilibrium

Reactant	Avg. Ratio of Peak Areas $A_{4\text{HDBT}}/A_{6\text{HDBT}}$	First-Order Rate Constant $\text{cm}^3 \text{gm}^{-1} \text{hr}^{-1}$	% Selectivity CHB Avg.
4HDBT	4.6	380	68.1
6HDBT	4.8	420	71.2
Avg.	4.7	400	69.7

Notes: Experimental Conditions:

- (i) Catalyst: 0.025 g of Co-Mo/ γ - Al_2O_3 (HDS-16A) diluted by 0.625 g of alundum
- (ii) Temperature: $300 \pm 1^\circ\text{C}$.
- (iii) H_2 -saturation pressure: 1000 psig (at room temperature).
- (iv) Pressure during operation: ~ 1500 psig
- (v) Catalyst sulfided in situ at 400°C for 2 hr by 10% $\text{H}_2\text{S}/\text{H}_2$ (v/v) at a flow rate of $30\text{-}50 \text{ cm}^3/\text{hr}$.

Figure 11. Pseudo First-Order Kinetics for HDS of Hexahydrodibenzothiophene and Tetrahydrodibenzothiophene.

TABLE 6
H₂S Effects on CHB Selectivity

Run	H ₂ S/H ₂ mole ratio	Selectivity for CHB (%)	
		1.26cm ³ /hr	7.2cm ³ /hr
3-10	0.00	8.3	2.3
3-15	0.014	9.8	2.5
3-16	0.084	16.2	4.5

Notes: Experimental Conditions:

- (i) 0.010 g of Co-Mo/ γ -Al₂O₃ (HDS-16A) diluted by 0.28 g of alundum.
- (ii) Temperature: 300 $\pm$ 1°C.
- (iii) Pressure during operation: $\approx$ 1500 psig.
- (iv) Initial concentration of DBT: 0.12 wt% in n-hexadecane.

C. CATALYTIC HYDRODENITROGENATION (HDN)

1. Carbazole

Carbazole hydrodenitrogenation (HDN) was investigated under the same conditions as acridine (i.e., 367°C, 2000 psig) in the 1L batch reactor. The run lasted 12 hours, and after 3.5 hours, the samples were clear, with no crystalline material. Another run was made under milder pressure conditions, $P = 1000$ psig, so as to determine the reaction products by means of the gas chromatograph (g.c.) - mass spectrometer (m.s.). The oil remaining after the run, approximately 460ml admixed with the same volume of hexane, was introduced into a dry column made up using alumina (Alumina Woelm for Dry Column Chromatography, Activity 111/20mm ICN). The dimensions were 3.1cm x 50 cm. After all the oil had been adsorbed, it was eluted using 1 liter of hexane. Three distinct zones were detected using a UV lamp, and subsequent extraction and m.s. analysis yielded carbazole for the most polar fraction, 1,2,3,4-tetrahydrocarbazole and hexahydrocarbazole with intermediate polarity and octahydrocarbazole for the fraction with the least polarity. The reactor samples were analyzed on a 50m OV101 2x WCOT column on the PE 3920B chromatograph equipped with a N_2 -specific detector. The samples that showed crystallized material were treated with a few drops of acetone until they showed clear. All the weights of the samples before and after solution were recorded so as to correct the completed concentrations for dilution. The substrate was by far the most abundant compound in the reactor samples, and tetrahydrocarbazole and octahydrocarbazole could also be detected; all other cited species (e.g. 5th quarterly report) were present, but the quantitative measurements are beyond the instrument's capability. For the total nitrogen and carbazole, first order rate plots are shown in Fig. 12. The carbazole and tetrahydrocarbazole concentration vs. time profiles are shown in Fig. 13.

It is apparent that when carbazole is compared to acridine, acridine is the more reactive of the two. The reactivity of carbazole compares to quinoline under these conditions.

Total nitrogen removal rate constant for 3 hours at 367°C,

2000 psig / Ni-Mo/ γ Al₂O₃

		$\frac{\text{g oil}}{\text{min g cat}}$
<u>Acridine</u>	1.62	
<u>Carbazole</u>	2.43	"
<u>Quinoline</u>	2.52	"

A tentative network for carbazole could be the following:

An explanation for the enhanced reactivity of carbazole as compared to acridine could be that once hydrogenation of the aromatic ring is accomplished, the partially hydrogenated carbazole resembles a substituted indole, which would then react faster than the corresponding quinoline-type analog attached by acridine (A. K. Aboul Gheit and K. Abdou, 1973). These results show that in coal-derived liquids, acridine and its analogs are the most refractory compounds towards catalytic hydrodenitrogenation.

Figure 12. First-Order Rate Plot for Total Nitrogen Removal From Carbazole.

○ CARBAZOLE

● TETRAHYDROCARBAZOLE

10⁶ CONCENTRATION, g mole/g of oil

20

15

10

5

0

0

100

200

300

TIME, min

Figure 13. Conversion Plot for Carbazole and Tetrahydrocarbazole.

2. Substituted Quinolines

To study the effect of methyl group substitution on hydrodenitrogenation of quinoline, experiments have been planned with the following compounds:

- 1) 2-methylquinoline

- 2) 2,6-dimethylquinoline

- 3) 2,7-dimethylquinoline

- 4) 2,8-dimethylquinoline

One experiment for each of the three dimethylquinolines was carried out under the following conditions in batch autoclave:

Reactant concentration: ~0.5 wt% in white oil

Reaction temperature: 342°C

Total pressure: 500 psig

CS₂ concentration: 0.05 wt%

Catalyst: Ni-Mo/γ-Al₂O₃ presulfided in 10% H₂S/H₂ at 400°C for 2 hours

Reaction mixtures at the end of the experiments were acid extracted and concentrated for GC-mass spec identification of compounds. The work is not completed to date, but preliminary results suggest the presence of five nitrogen compounds analogous to those found in quinoline network, e.g., for 2,6-dimethylaniline, the following compounds were identified:

2,6-DMQ.

1,2,3,4-tetrahydro
2,6-DMQ.

5,6,7,8-tetrahydro
2,6-DMQ.

Decahydro 2,6-DMQ

O-butyl p-methyl aniline

The product samples were analyzed on 50m OV 101 2X WCOT column maintained at 140°C in PE 3920 B gas chromatograph equipped with a nitrogen specific detector. The complete product distributions will be presented in the next quarterly report when analysis and mass-spec identification is completed. Some precipitation was observed in the early samples of these runs, although the compounds (initial reactants) are soluble in white oil. This indicates that some products may not be soluble in white oil to the extent they are formed. The results will be presented at a later date when analysis is completed.

3. HDN of Quinoline in the Flow Microreactor

As mentioned in the preceding quarterly report, a flow micro-reactor run was carried out for HDN of quinoline under the following conditions:

Quinoline concentration: 0.43 wt% in white oil

Saturation pressure : 2900 psig (1% H_2S/H_2)

Reaction temperature : 342°C

Catalyst: HDS-9A; Ni-Mo/ γ - Al_2O_3 , 60-80 mesh (8.4 mg) in situ
sulfided at 400°C for 2 hr

LHSV : ~ 140 - 7900 $\frac{cm^3 \text{ of feed}}{g \text{ of catalyst-hr}}$

With such a large range of LHSV, it was possible to observe the concentrations of intermediate hydrogenated products going through a maximum. In fact, LHSV of ~ 7900 cm^3 of feed (g of cat-hr) corresponds to a sample at 0.72 minute in standard batch autoclave runs for quinoline HDN. It is clear, therefore, that the fast hydrogenation reactions can be studied conveniently in this reactor. Figure 14 gives the product distribution for the experiment.

The detailed reaction network is the one reported earlier for quinoline. Total rate of nitrogen removed is about 30% faster in the flow reactor compared to that in the batch reactor. All other rate constants are within a factor of 3 at most. Since sulfiding of catalyst is done in situ in the flow reactor, the catalyst is more active for cracking and less so for hydrogenation of aromatic rings (see also, effect of sulfiding and CS_2 concentration in HDN, 7th quarterly report). Also, hydrogen concentration in the two reactors is difficult to control. A run will be performed to match the conditions as closely as possible for comparison purposes.

Figure 14. Product Distribution in Hydrodenitrogenation of Quinoline in White Oil Carrier at 342°C and approximately 165 atm. The concentrations are reported relative to an initial value of 100 for quinoline.

D. POISONING REACTION ENGINEERING:

This section continues the study of the aged H-Coal^R catalyst samples used for hydrogenation of coal (or coal derived liquid). As mentioned in the 7th quarterly report, the activity of the aged catalyst was significantly lower than that of fresh catalyst. The activity of regenerated catalyst shows that the permanent poisoning by the deposition of the inorganic mineral matter is responsible for most of the loss of the catalyst activity for H-Coal Run No. 130-73 (3036 lb coal/lb catalyst). In this report, detailed study of the aged catalyst in hydrodenitrogen (HDN) is investigated. The catalyst used was from the H-Coal Run No. 130-78 (1502 lb coal/lb catalyst) with a short run duration of 274 hours and a high space velocity of 78 lb coal/ft³ reactor/hr. This study combined with that discussed in the 7th quarterly report shows the apparent effect of both hydrocarbon poison and mineral matter deposition on the performance of H-Coal catalyst in the hydro-treating process.

Since the reaction network of HDN for quinoline has been well developed in previous reports, the choice of quinoline as the typical nitrogen compound to elucidate the activity of spent catalyst in an HDN process seems proper. The rate of removal of total nitrogen can be measured from a batch reactor experiment. This can be used as a criterion for catalyst deactivation by comparison with the result of fresh catalyst. The recovery of catalyst activity was carried out by burning off the reversible hydrocarbon poison. The burning off procedure is the same as that described in the 7th report. Each catalyst was presulfided at the same conventional temperature--325°C. Additional information about the activity of low temperature (168°C) presulfided fresh catalyst (LTS catalyst) has also been measured in order to demonstrate the effect of catalyst deactivation by mineral matter.

The total loss of mass from the catalyst during the burning process was measured to be 21.9 wt%, which shows that there had been significant deposition of hydrocarbon in Run No. 130-78 catalyst. When compared to the 11 wt% loss during the burning process of catalyst from Run No. 130-73, the different ratio of coal/catalyst in the feed stream is seen to account for the different durability of catalyst. The recovery of activity for catalyst of Run No. 130-78 is much higher than that for Run No. 130-73, which demonstrates that the effect of coking and mineral matter deposition depends strongly on the input coal/catalyst ratio.

The effect of deposition on the catalyst on the individual reactions of the HDN process can be elucidated by the comparison of the empirical rate parameters for each reaction for the different catalysts as specified below:

Consistent with earlier reports, the reaction rates are assumed to be first order in each component, and rate parameters can be evaluated by computer by comparing the experimental curves with those predicted for a set of rate parameters. The comparison of experimental and theoretical profiles shows fair agreement. Table 8 lists the values of the rate constants of the individual reactions in the HDN process for each catalyst examined. The relative activities for individual reactions are listed in Table 9. The experimental results are shown in Figures 15 - 23 with initial concentrations listed in Table 7. Some remarks and conclusions are given below.

Comparison of Figs. 15, 17, and 19 shows the apparent loss of activity in spent catalyst for the quinoline and 1,2,3,4THQ reactions. From Table 9, it is shown that the activity of catalyst has different effects on the specific reactions of the HDN network. The activity for spent catalyst is only 20% for the quinoline and 1,2,3,4THQ reactions, whereas the regenerated catalyst shows higher activity, which suggests the high recovery of the activity.

Profiles in Figs. 16, 18, and 20 show the significant effect of catalyst deposits on the production of secondary components. The apparent decrease of the OPA concentration in the presence of spent catalyst suggests that this particular reaction is affected significantly. Since the reaction of OPA contributes to the removal of nitrogen in the HDN network, the low activity for this reaction accounts for the observed lower rate of total nitrogen removal. From Table 9, it is clear that the activity for hydrogenation in spent catalyst is strongly reduced, whereas the high activity in denitrogenation, as represented by k_8 , suggests the denitrogenation durability of H-coal catalyst is not affected strongly by the deposits. The results for regenerated catalyst show the burning off of the hydrocarbon leads to recovery of most of the activity for hydrogenation while the denitrogenation activity is little affected.

Figs. 21 and 22 demonstrate that the empirical rate of removal of total nitrogen depends strongly on the over-all efficiency of the catalyst. While the data for the spent catalyst fit the first order reaction, $r = -kC$, quite well, the results for fresh catalyst appear to indicate a higher order, $r_n = -k'C^{2.3}$. For the sake of systematic comparison of the catalytic activity in the over-all HDN process, the comparison of fractional conversion

of total nitrogen becomes a better criterion. Fig. 23 shows the fractional conversion for total nitrogen with varying catalytic activity. The catalyst activity can not be recovered completely even though there is only a small amount of mineral matter deposition.

TABLE 7: Prepared and Estimated Initial Concentrations of Quinoline for the Experiments with Various Catalysts

Type of catalyst	Initial concentration prepared (g-mole/g of oil)	Initial concentraion estimated experimentally (g-mole/g of oil)	Efficiency
spent	72.5×10^{-6}	65×10^{-6}	89.6%
regenerated	79.6×10^{-6}	74×10^{-6}	92.8%
fresh	77.8×10^{-6}	72×10^{-6}	92.5%

TABLE 8: Comparison of the Rate Constants for the Individual Reactions in the Quinoline Network with Different Catalysts

	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
spent catalyst	17.7	3.78	.157	.066	.396	.0179	.0156	2.94
regenerated catalyst	62.0	15.5	.518	.066	.650	.0460	.0500	2.90
fresh catalyst	92.0	20.0	.670	.137	.840	.1100	.1000	3.47

* The unit of rate parameter is (g of oil)/(g of catalyst)/(minute)

TABLE 9: Comparison of the Relative Rate Constants (referred to fresh catalyst) for the Individual Reactions in the Quinoline Network with Spent and Regenerated Catalysts.

	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8
spent catalyst	19.3%	18.9%	23.4%	48.2%	47.1%	16.3%	15.6%	84.7%
regenerated catalyst	67.4%	77.5%	77.3%	48.2%	77.4%	41.8%	50.0%	84.1%

Figure 15. Predicted and Experimental Conversion Plots for Quinoline and 1, 2, 3, 4THQ for Fresh Catalyst. The sharp change of profiles at the initial time interval suggests the reaction rate is very fast for these components.

Figure 16. Observed and Predicted Conversion Plots for Secondary Components for Fresh Catalyst.

Figure 17. Predicted and Experimental Conversion Plots for Quinoline and 1, 2, 3, 4THQ for Regenerated Catalyst.

Figure 18. Observed and Predicted Conversion Plots for Secondary Components for Regenerated Catalyst

Figure 19. Predicted and Experimental Conversion Plots for Quinoline and 1, 2, 3, 4THQ for Spent Catalyst.

Figure 20. Observed and Predicted Conversion Plots for Secondary Components for Spent Catalyst (cf. Fig. 18).

Figure 21. Conversion Plot Showing Total Nitrogen Removal with Spent Catalyst.

figure 22. Conversion Plot for Total Nitrogen Removal with Fresh Catalyst.

Figure 23. Fractional Conversion of Total Nitrogen in HDN for Various Catalysts.

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<u>Compound</u>	<u>Supply</u>	<u>Structure (see accompanying key)</u>
2,8-Dimethyldibenzothiophene	0.5g	1
3,7-Dimethyldibenzothiophene	0.5g	2
4,6-Dimethyldibenzothiophene	1.0g	3
4-Methyldibenzothiophene	0.5g	4
Tetrahydrodibenzothiophene	0.2g	5
Hexahydrodibenzothiophene	0.5g	6
O-Phenylthiophenol	0.1g	7
Benzo[b]naphtho[2,3-d]thiophene	1.0g	8
7,8,9,10-Tetrahydrobenzo[b] naphtho[2,3-d]thiophene	1.5g	9
2,3,4-Triphenylthiophene	3.0g	10
1,2-Dimethylnaphtho[2,1-b]thiophene	5.0g	11
Phenoxthin	8.0g	12
Dihydrobenzothiophene	1.0g	13
3,7-Dimethylbenzothiophene	3.0g	14
2-Methylbenzothiophene	0.5g	15
7-Methylbenzothiophene	2.0g	16
3-Methylbenzothiophene	2.0g	17
2,3-Cyclohexylbenzenethiophene	2.0g	18
O-Propylaniline	7.0g	19
Decahydroquinoline	CIS:None	20
	Trans:1.0g	
	Mix:10.0g	
Sym-octahydroacridine	5.0g	21
Perhydroacridine	0.1g	22
1,9-Dimethylacridine	5.0g	23
4-Methylcarbazole	5.0g	24
4,6-Dimethylcarbazole	1.0g	25
Cis-Hexahydrocarbazole	20.0g	26

Compounds in Process of Preparation

4-Methylbenzo[b]naphtho[2,3-d]thiophene	27
4,6-Dimethylbenzo[b]naphtho[2,3-d]thiophene	28
7-Methylbenzo[b]naphtho[2,3-d]thiophene	29
6-Methylbenzo[b]naphtho[2,3-d]thiophene	30
Benz[c]acridine	31
Benz[a]acridine	32
Dibenz[c,h]acridine	33

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21

22 23 24 25 26 27 28 29 30 31 32 33

V. CONCLUSIONS

1. Hydrodesulfurization (HDS) of dibenzothiophene (DBT) at 300°C and 104 atm can be carried out selectively with commercial catalysts like Ni-Mo/ γ -Al₂O₃ and Co-Mo/ γ -Al₂O₃. The activity (i.e., the first order rate constant) of Ni-Mo/ γ -Al₂O₃ (HDS-9A) is roughly two times higher than that of Co-Mo/ γ -Al₂O₃ (HDS-16A). Detailed studies of the reaction network revealed that although S-extrusion almost exclusively precedes the hydrogenation of aromatic rings, under certain conditions (e.g., with Ni-Mo catalyst or a relatively high H₂S/H₂ ratio in the feed), the hydrogenation of the reactant prior to S-extrusion can be a significant reaction. All these results have been summarized in a reaction network for the hydrodesulfurization of dibenzothiophene.

2. In the catalytic hydrodenitrogenation (HDN) of carbazole (with Ni-Mo/ γ -Al₂O₃ and a batch autoclave reactor) large amount of hydrogenation product was detected. Under identical experimental conditions, carbazole shows higher reactivity than acridine. In coal-derived liquids, therefore, acridine and its analogs are among the most refractory compounds towards catalytic HDN.

The HDN reaction networks for methyl-substituted quinolines were found to be analogous to those observed for the HDN of quinoline.

3. From the studies of the activities of the aged catalyst from the H-Coal^R process for the HDN of quinoline, it can be concluded that deposition of coke and coal mineral matter both cause the loss of catalyst activity. A small fraction of the activity loss can be regained by burning off the coke.

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VIII. PERSONNEL

There have been two changes in personnel this quarter: Dr. Stuart Shih and Dr. Rainer Zawadski have left the group. They are now employed by Mobil and by American Cyanamid, respectively.