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FOSSIL ENERGY

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

Quarterly Report, June 20—September 19, 1976

October 1, 1976

Work performed under Contract No. E(49-18)-2028

University of Delaware
Newark Delaware

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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

Quarterly Report for Period

June 20, 1976, to September 19, 1976

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I. ABSTRACT

Two high-pressure flow microreactors are functioning efficiently in studies of dibenzothiophene hydrodesulfurization and quinoline hydrodenitrogenation. Assembly of a third microreactor is scheduled for completion in about three months.

Dibenzothiophene hydrodesulfurization at conditions such as 1,000 psig and 300-350°C takes place in the absence of mass transfer influence. The rate is surprisingly high, requiring temperatures of 300°C or less for determination of differential conversions with the existing apparatus.

Batch reaction studies have shown that nitrogen removal from quinoline is characterized by an apparent activation energy of about 20 kcal/mole, whereas the rates of accompanying hydrogenation reactions are almost independent of temperature. Nitrogen removal from acridine and from carbazole is much slower than nitrogen removal from quinoline; the outer rings of the three-ring compounds (acridine and carbazole) are hydrogenated relatively rapidly.

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 hydrosulfurization and hydrodenitrogenation processes.

vi) In summary, to recommend improvements in processes for the catalytic hydroprocessing of coal-derived liquids.

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.

TABLE 1 TIME PLAN* AND MILESTONE CHART**

Year 0 — 1 — 2 — 3

ACCOMPLISHMENT

A. APPARATUS CONSTRUCTION

1st High-Pressure Microreactor Completed → month 6

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

Reaction Studies for:

Benzothiophene month 6 ←→ month 12

Quinoline >50%

60%

Dibenzothiophene month 12 ←→ month 18

Carbazole start

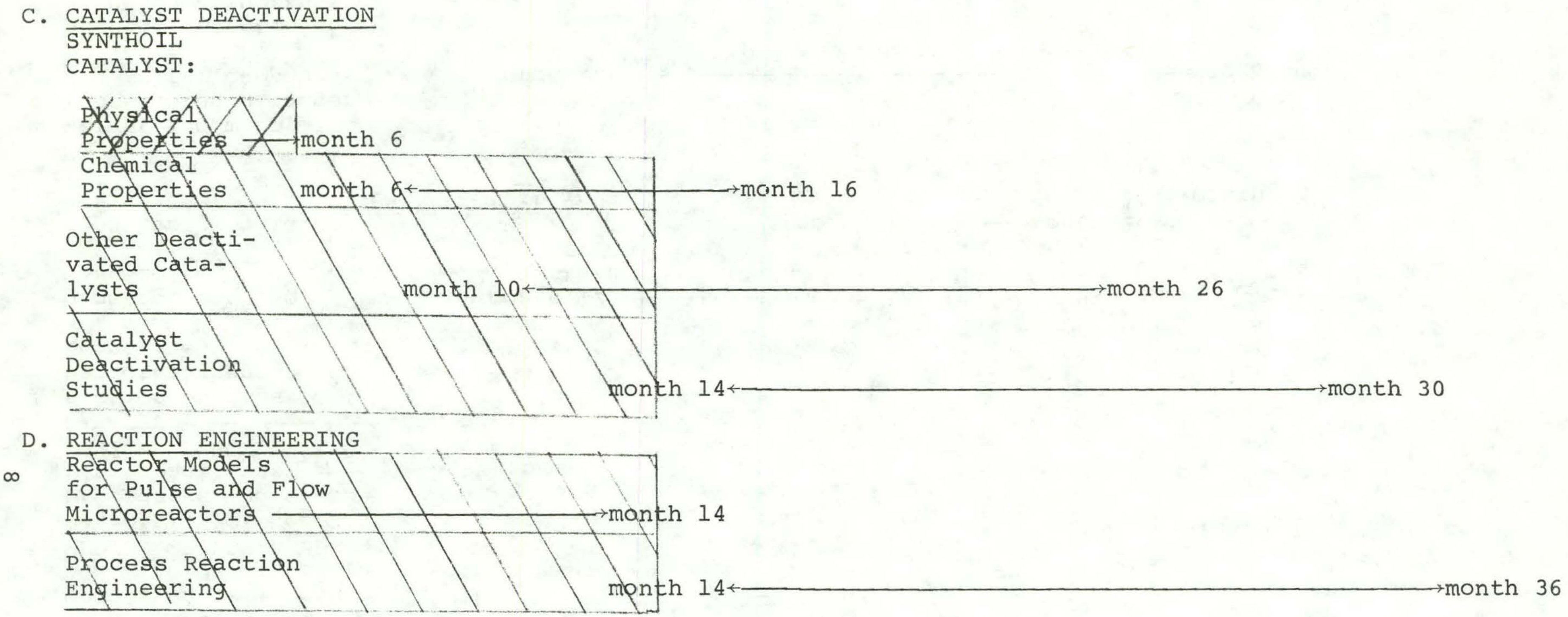
Naphthobenzothiophene month 18 ←→ month 24

Acridine start month 24 ←→ month 28

Higher molecular weight and methyl substituted nitrogen and sulfur compounds start month 12 ←→ month 28

Reaction Kinetics, Reaction Networks and Inhibitor Studies of Least Reactive Sulfur and Nitrogen Compounds month 18 ←→ month 28

HDS-HDN: Simultaneously, Effect of Inhibitors month 16 ←→ month 36



C. CATALYST DEACTIVATION
SYNTHOIL
CATALYST:

Physical Properties → month 6

Chemical Properties month 6 ←→ month 16

Other Deactivated Catalysts month 10 ←→ month 26

Catalyst Deactivation Studies month 14 ←→ month 30

D. REACTION ENGINEERING

Reactor Models for Pulse and Flow Microreactors → month 14

Process Reaction Engineering month 14 ←→ 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.

TABLE 2 CUMULATIVE EXPENDITURES

ITEM / QUARTER	First	Second	Third	Fourth	Fifth
Personnel	$ 5,807	20,740	37,396	53,418	91,809
Travel	28	528	1,152	1,152	1,352
Supplies & Expenses	4,674	10,007	19,582	25,735	30,711
Occupancy & Maintenance	6,110	9,208	10,108	10,634	11,374
Equipment	610	17,978	30,704	34,930	41,951
Information Processing	--	--	--	97	231
Transfers (Overhead)	--	10,202	20,035	38,710	75,651

III. SUMMARY OF PROGRESS TO DATE

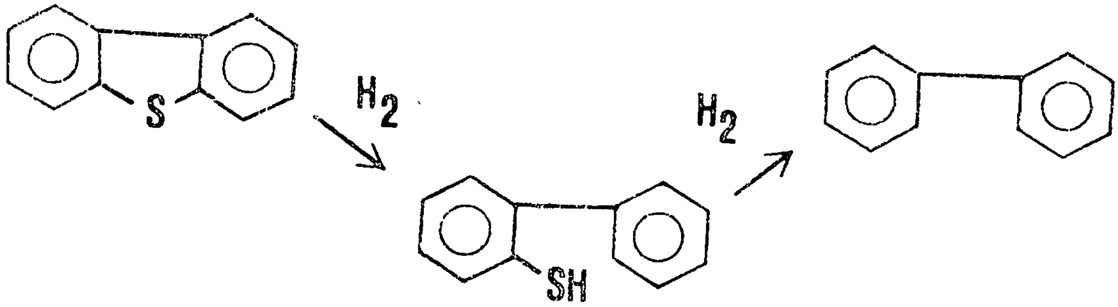
This summary is organized to parallel the task statements of the contract. It includes results of this report and the four preceding quarterly reports. A milestone chart is provided at the end of this section (Table 1).

Microreactor Development

The microreactor design has been perfected, and a paper describing the design and operation has been prepared for publication; it is appended. The first two units are operating routinely, and assembly of the third unit has begun.

Hydrodesulfurization

Dibenzothiophene hydrodesulfurization in a flow microreactor has been characterized at pressures of 300 to 1050 psig and temperatures of 300 to 350°C. The reactivity of dibenzothiophene is at least 50 times greater than expected from consideration of the literature. The reaction rate is independent of mass transfer influence at the conditions which have been investigated. The hydrodesulfurization reaction gives biphenyl as the primary hydrocarbon product, and the results so far are consistent with the following reaction network:



Hydrodenitrogenation

The reaction network for the hydrodenitrogenation of quinoline on a Ni-Mo/Al_2O_3 (HDS-9A) catalyst was determined, and it involves equilibrium hydrogenation to 1,2,3,4-tetrahydroquinoline; other ring hydrogenations are much slower and do not reach equilibrium. The saturated nitrogen-containing ring is then cracked forming o-propylaniline and γ-phenyl-n-propylamine, which then undergoes denitrogenation. The apparent first-order rate constants of the kinetically more important steps in the reaction network have been evaluated as a function of H_2 and H_2S concentration, initial quinoline concentration, and catalyst type. The results show that the rate of each reaction in the network can be largely understood in terms of nitrogen-carbon bond reactivity.

The quinoline reaction studies have been extended to a flow microreactor. Studies of acridine and carbazole hydrodenitrogenation in batch reactors have begun. The results show that (1) nitrogen removal from the three-ring compounds is slow compared to nitrogen removal from quinoline and (2) hydrogenation of the outer rings is fast.

Catalyst Deactivation

The deactivation of Synthoil pilot plant catalysts is associated with cementing of coal mineral matter to the surface of the catalyst, buildup of FeS_x on the external suface, and deposition of inorganic substances within the pore mouths. Plans are to extend the aged catalyst analyses to include H-Coal samples.

Microreactor Engineering

The moment analysis of pulse microreactor has been summarized to give a basis for investigation of fairly complex reaction networks. In particular, the film model was extended to describe a two-phase catalyst. The transport with reaction in a spherical catalyst was compared critically to the film mode.

Table 1 is the milestone chart and time plan prepared for the work at the beginning of the contract period (in the Proposal). Hatching on the chart indicates that the activity (task) indicated is under active investigation; the number in the hatched region is an estimate of the percentage completion of this particular activity. Crosshatching on the chart indicates that an activity (task) has been completed. Table 2 gives the cumulative expenditures.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. HYDROPROCESSING MICROREACTOR DEVELOPMENT

The first of the two operating microreactors is now being used for studies of dibenzothiophene hydrodesulfurization as described subsequently in this report. It has been tested after the modification reported in the fourth quarterly report. Further, a new gear box has been purchased and installed in the Ruska feed pump; it will allow feed delivery at flow rates as high as 7 ml/hr. These flow rates are expected to be appropriate for determination of differential conversion data and therefore reaction rate data. An oil reservoir was added to the system to allow reloading of the feed autoclave without disassembling it.

The second flow microreactor is being used in studies of quinoline hydrodenitrogenation (as described subsequently), and a third flow microreactor is now under construction. It is expected that the third unit will be in operation by the end of the next quarter, but delays in equipment delivery could force a revision of this time plan.

The experiments with the two microreactors have convincingly demonstrated their operability and the appropriateness of the design. Therefore, it has been considered timely to prepare a report of the microreactor design and operation for publication. The paper has been drafted. It will be submitted to *Industrial and Engineering Chemistry Fundamentals*.

B. CATALYTIC HYDRODESULFURIZATION

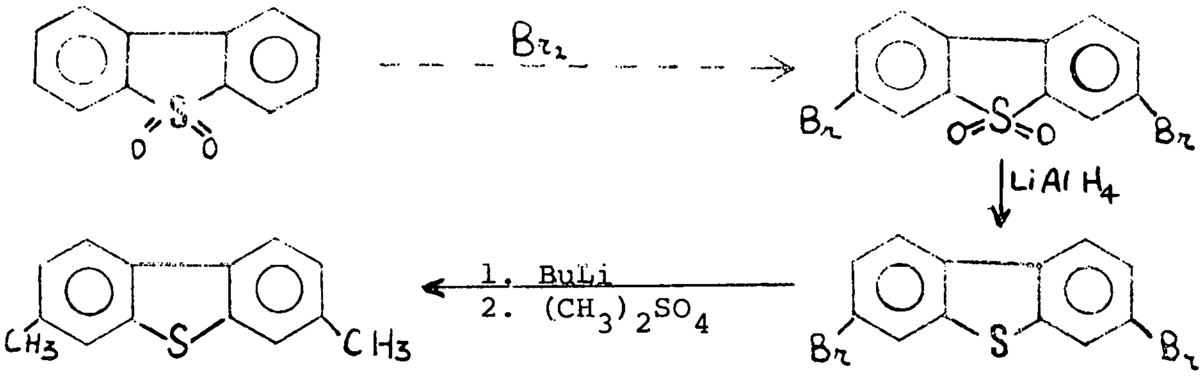
1. Experimental

a. Synthesis of sulfur-containing compounds

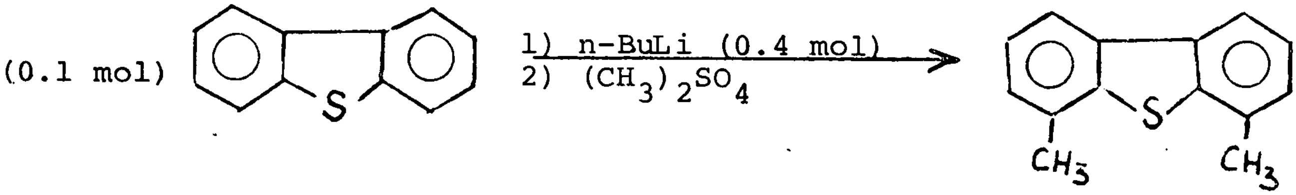
The current microreactor studies of high-pressure hydrodesulfurization are being done with dibenzothiophene as a reactant, and a series of related compounds will be tested for their relative reactivities in the next quarters. Most of the compounds are not available commercially, and therefore a considerable fraction of this quarter's effort has been devoted to organic synthesis. Specifics follow:

Dihydrobenzothiophene has been prepared from benzothiophene via its 1,1-dioxide.

3,7-Dimethylbenzothiophene has been obtained from dibenzothiophene sulfone by the following route:

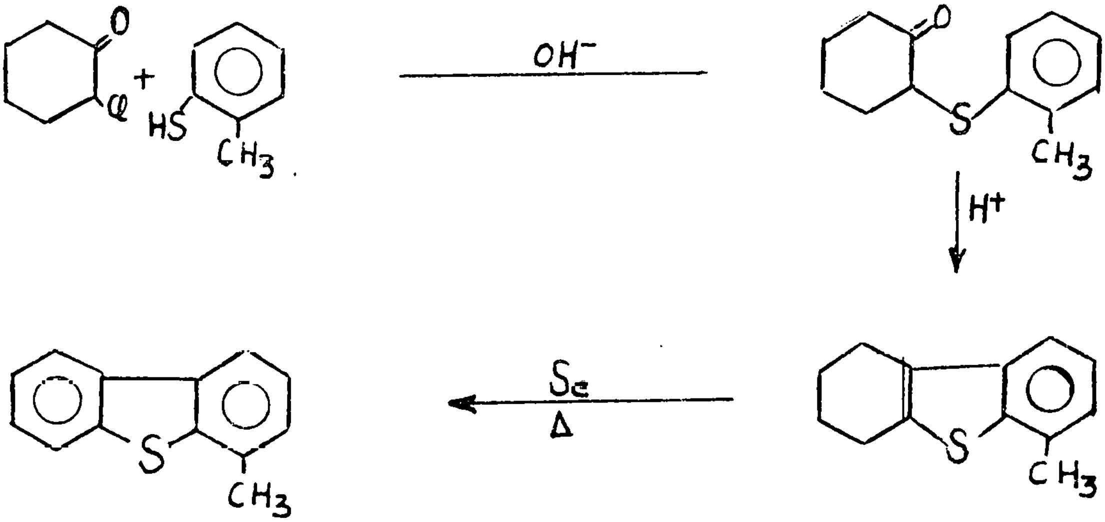


4,6-Dimethyldibenzothiophene has been obtained directly from dibenzothiophene:



However, the product is only about 95% pure, and further purification is underway.

The synthesis of 4-methyldibenzothiophene is in progress by the following route:



At this writing, the tetrahydro compound (A) has been obtained.

An inventory of the compounds now on hand is given in the Appendix in Table B1. A priority list of planned syntheses is also included in the Appendix as Table B2.

b. Liquid-phase high-pressure flow microreactor operating conditions

The experiments reported in this report were carried out under conditions that are different from those reported previously. Catalyst pretreatment, mass and particle size; composition of the feed mixture; feed flow rate; and reaction temperature were modified. The new conditions are summarized as follows:

- Catalyst: HDS-16A; catalyst mass, 25 mg; catalyst particle size ranges 149-178, 105-149, 350-420 microns. Catalyst was diluted with quartz chips having the same particle size ranges.
- Catalyst pretreatment: <u>in situ</u> sulfidation with 10% H_2S in H_2 for 2 hours at 400°C
- Liquid flow rate: 1.2ml/hr to 3 ml/hr.
- Reactant mixture: 0.122 wt% dibenzothiophene in n-hexadecane solvent.
- Reaction temperature: 300°C.
- H_2 "saturation[1]" pressure: 1000 psig

c. Analysis

The flame ionization gas chromatograph (Antek 440L; see fourth quarterly report) has been calibrated, checked, and optimized. The chromatograph has been modified to accommodate an open tubular column. A Spectro physics integrator and a Sargent-Welch recorder were purchased, delivered and installed. The chromatograph is operating properly and was used to carry out the analysis of products of hydrodesulfurization of dibenzothiophene reported here. Fig. A1 of the appendix shows the detector response for dibenzothiophene and biphenyl dissolved in n-hexadecane.

2. Results and Discussion

a. Catalyst activity

Reaction conditions giving low (differential) conversions are being sought for the reaction kinetic studies. Since the first run

---

[1] In the runs reported in previous and present quarterly reports, the H_2 content of the feed is unknown, since there was no mechanical stirring during the saturation. The equipment malfunction was discovered this quarter.

has shown a surprisingly high dibenzothiophene conversion, the operating conditions were modified as mentioned in the preceding paragraphs.

The results are exemplified by the following:

Run (10) was carried out at 350°C and with 1.2 cm^3/hr flow rate. Nearly 100% conversion of dibenzothiophene was obtained with 25 mg of catalyst. Since no useful kinetic measurement can be achieved under these conditions, the reaction temperature in all the following runs was decreased to 300°C. Lowering the temperature dropped the conversion to a workable range. Going to very high flow rate is less effective in reducing conversion, since it reduces available run time with a limited reactant supply and leaves little flexibility in further increasing space velocity.

b. Reproducibility

Runs M11, M14, and M15 were all carried out under the same conditions, as summarized in Fig. 1 and Table 3. Only the purging procedure in Run M11 was different from the standard. Runs M14 and M15 gave the same conversion within 12% error. The high conversion obtained in Run M11 could be attributed either to the inconsistent purge procedure or to the fact that all these runs were carried out without mechanical stirring of the reactant mixture during the saturation with hydrogen.

c. Catalyst particle size effect

In order to ensure that future kinetic studies will be free from mass transfer limitations, we have studied the effect of catalyst particle size on the rate of dibenzothiophene hydrodesulfurization. Runs M12 and M13 were carried out using, respectively, 350-420 μm and 149-177 μm catalyst particle sizes. The results were compared with the average of the conversion levels obtained in Runs M14 and M15, for which the catalyst particle size range was 149-177 μm. The conversion based on the disappearance of dibenzothiophene was used as the basis for determining a particle size effect.

Fig. 2 shows that as the catalyst particle size was varied within the range 105 to 420 μm, no change in the conversion of dibenzothiophene was observed. Although these results indicate the absence of an intraparticle diffusion effect, the experiments will be checked again now that the problems with the saturator have been eliminated.

d. Reaction network

The gas chromatographic analysis of the products of Runs M10

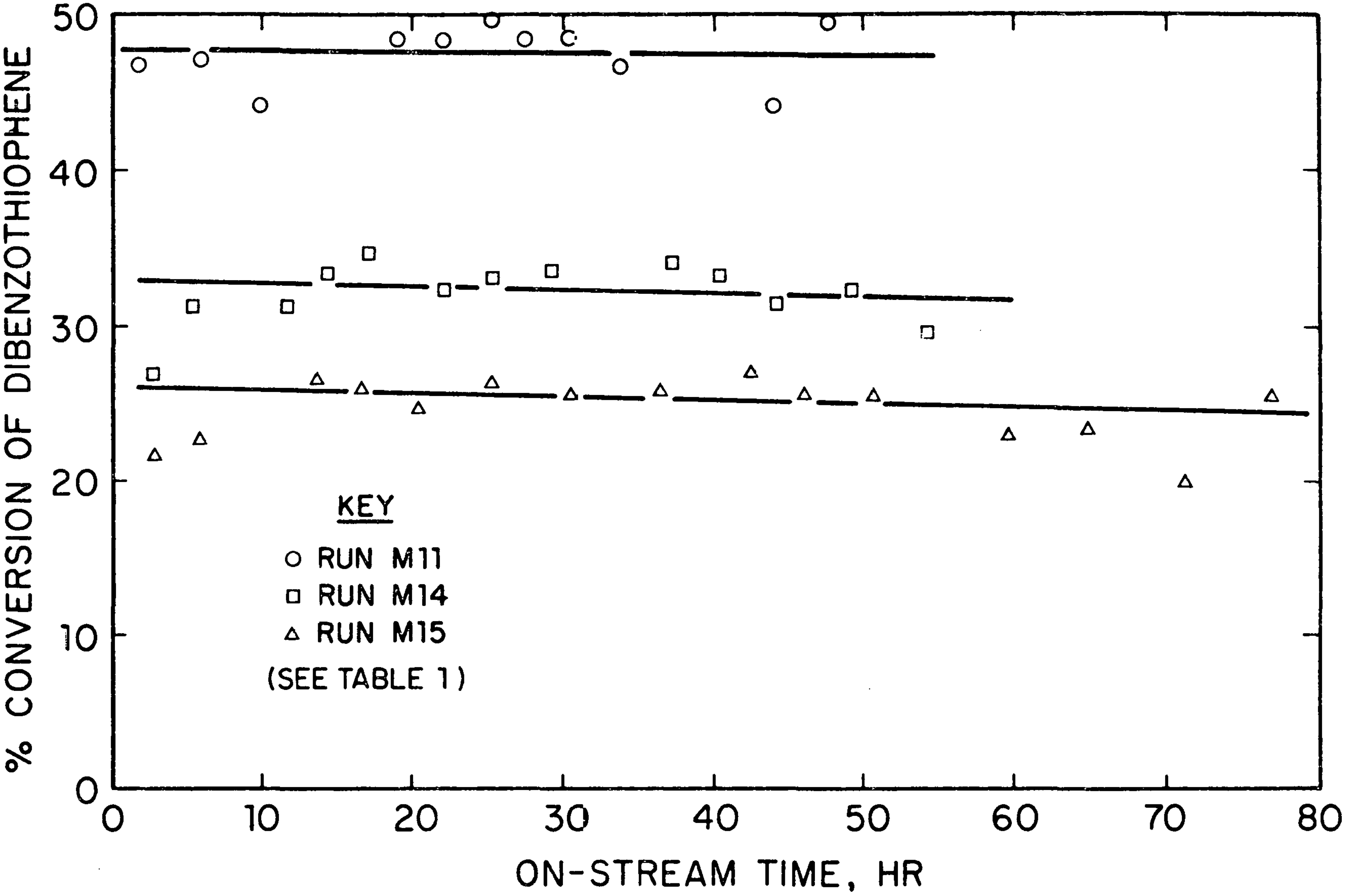


Figure 1. Hydrodesulfurization of Dibenzothiophene in a Flow Microreactor

TABLE 3

OPERATING CONDITIONS FOR DIBENZOTHIOPHENE HYDRODESULFURIZATION

Run	T,°C	Feed Saturation Pressure PH_2, psig	Feed Flowrate ml/hr	Cat. Particle Size, Micron	% Conversion of D.B.T.	% Conversion to Biphenyl
M-10	352	1000	1.2	350-420	~95	
M-11	300	"	"	149-177	47.5	39.3
M-12	"	"	"	350-420	30	23.1
M-13	"	"	"	105-149	27.7	19.0
M-14	"	"	"	149-177	32.4	25
M-15	"	"	"	149-177	24.6	20

Notes:

1. The actual H_2 content of the feed liquid is not known, since a malfunction of the stirrer in the saturator probably prevented saturation of the feed by H_2 in the time allowed.
2. The carrier liquid was n-hexadecane.

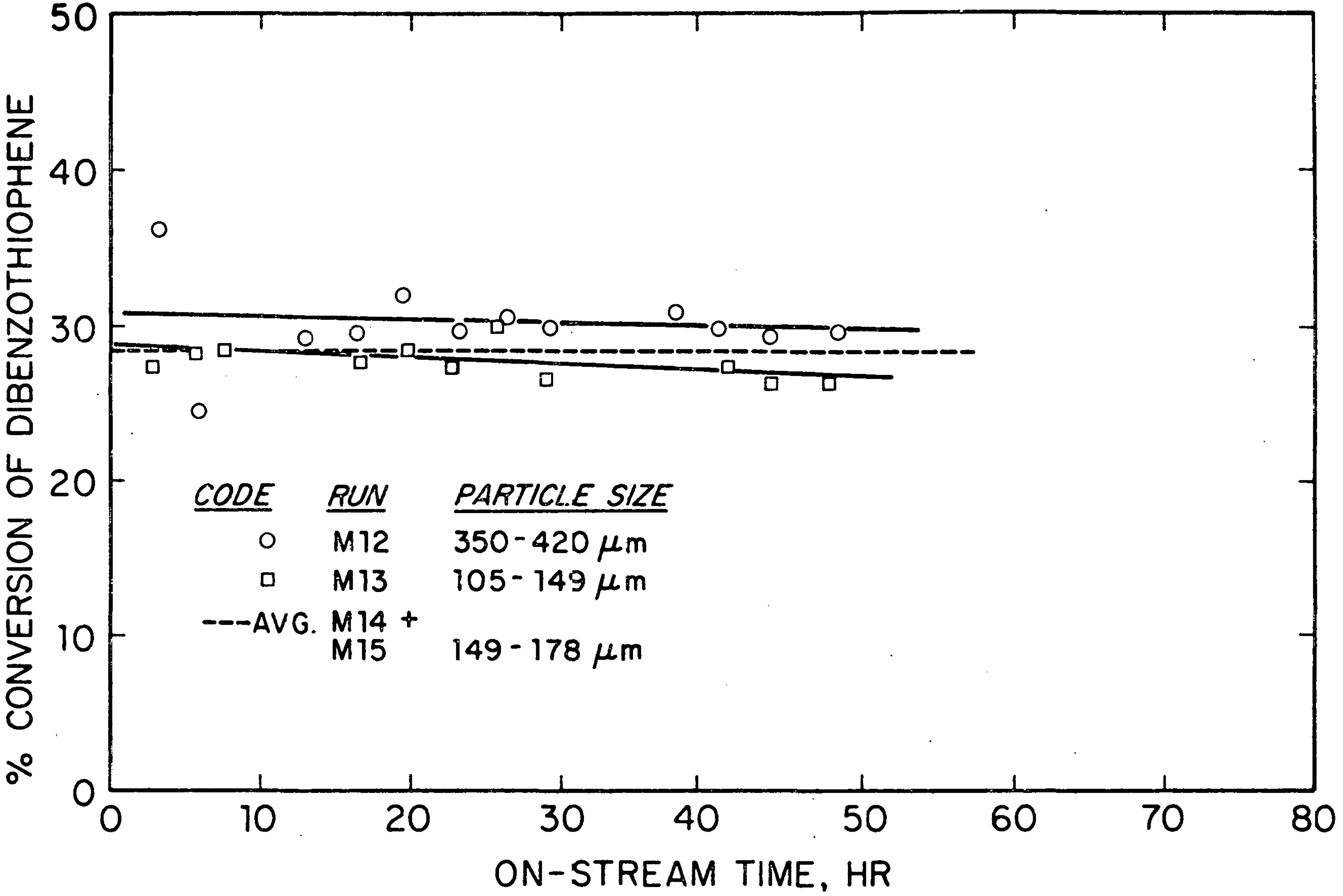


Figure 2. Lack of an Effect of Catalyst Particle Size on Conversion of Dibenzothiophene in a Flow Microreactor

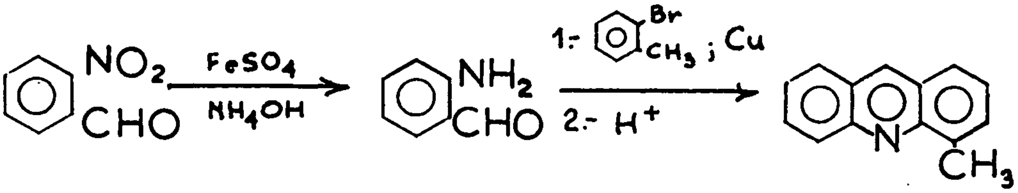
-M16 shows, in agreement with the previous results, the presence of biphenyl as a primary reaction product. No hydrogenated dibenzothiophene was found among the products, even at low temperature (300°C) and a relatively high flow rate (3 cm^3/hr).

C. CATALYTIC HYDRODENITROGENATION

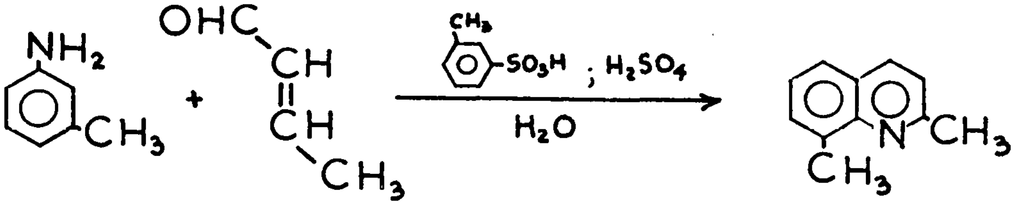
1. Synthesis of nitrogen-containing compounds

The reaction studies have progressed beyond quinoline to include the three-ring compounds carbazole and acridine. Studies with a number of related compounds are planned, and so the synthesis work is proceeding apace. Specifically, the recent synthesis work has include the following.

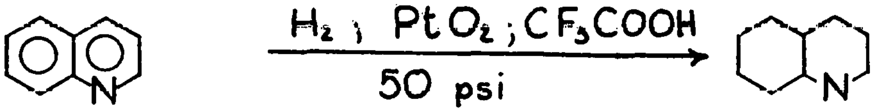
4-Methylacridine has been synthesized by the following procedure;



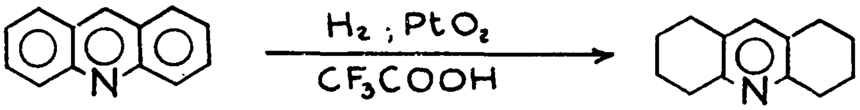
2,8-Dimethylquinoline was prepared by the condensation of crotonaldehyde with o-toluidine:



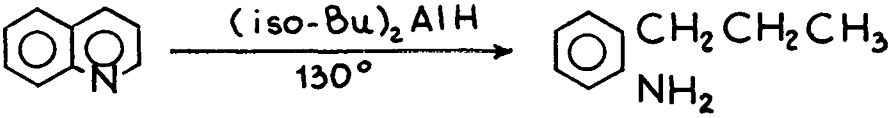
Decahydroquinoline has been obtained by hydrogenation of quinoline:



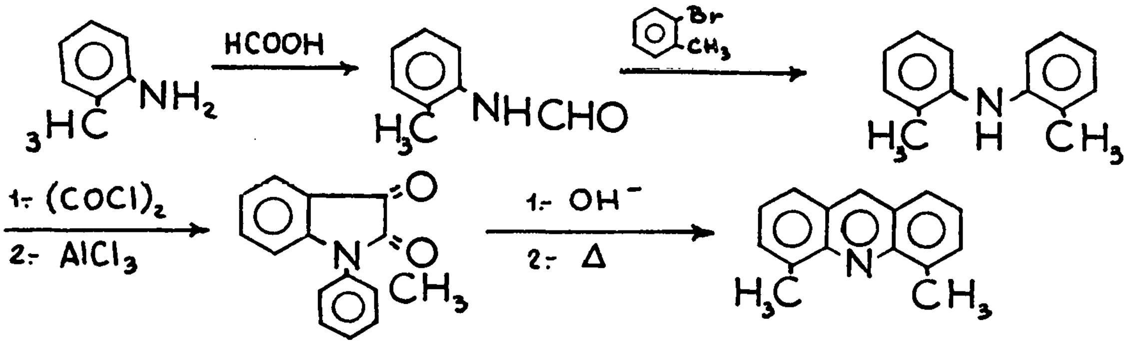
Sym-Octahydroacridine has been obtained by similar hydrogenation of acridine:



O-Propylaniline was prepared from quinoline:

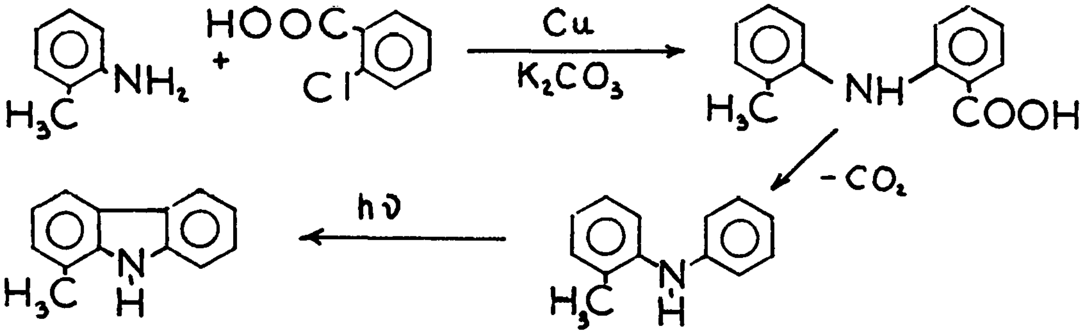


The synthesis of 4,5-dimethylacridine by the following sequence of reactions is presently in progress:



The crude product has been isolated and purification is underway.

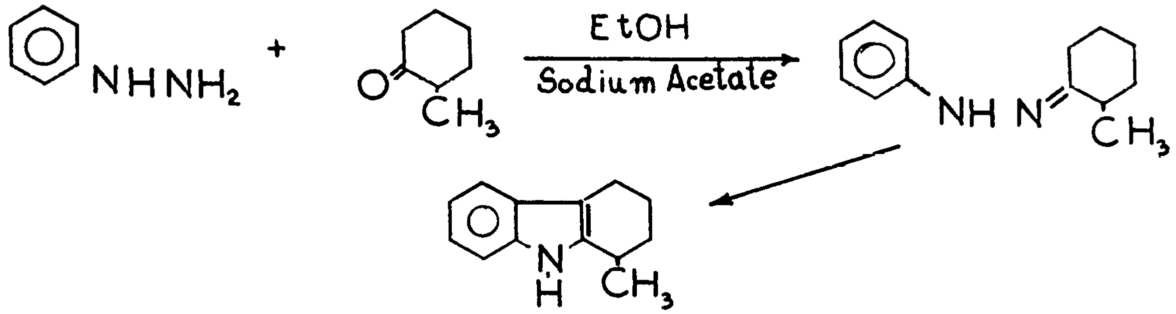
The preparation of 1-Methylcarbazole was first attempted by the following method:



The yield of the product was very low, and so a third procedure promising higher yield has been undertaken.

8-Methyl 1,2,3,4-Tetrahydrocarbazole has already been isolated in good yield.

By a similar procedure, 1-Methyl 1,2,3,4-Tetrahydrocarbazole has been prepared:



2. Reaction studies

Batch autoclave reaction studies to determine reaction networks and kinetics of hydrodenitrogenation reactions are proceeding with the methods described in previous reports. The methods have been extended to include work with the second flow microreactor, which is now fully operational and producing data routinely. Work with quinoline reactant is continuing, and work with carbazole and with acridine is now well underway. Results for each reactant are given in turn in the following paragraphs.

a. Quinoline hydrodenitrogenation in a batch reactor

The effect of temperature on the kinetics of quinoline hydrodenitrogenation has been investigated in four runs with a temperature range from 300 to 365°C. The reactions were carried out in a one-liter autoclave at a constant total pressure (and, approximately, hydrogen partial pressure) of 500 psig. Data from three of the runs have been collected, and analysis of the fourth set of samples is underway.

The kinetic data are summarized as apparent first-order rate constants, as explained in previous reports. The results (Table 4) surprisingly show that the apparent activation energies of all hydrogenation reaction steps are very low. The hydrogenolysis (cracking) of 1,2,3,4-tetrahydroquinoline to give o-propylaniline and the denitrogenation of o-propylaniline both have activation energies of about 35 kcal/mole. The hydrogenation reactions have activation energies too low to be determined quantitatively.

The literature provides a few data indicating activation energies of hydrodenitrogenation reactions. Aboul-Gheit and Adbou (1973) reported an activation energy of 30 kcal/mole for hydrodenitrogenation of quinoline diluted in paraffin oil catalyzed by an unsulfided Co-Mo/Al_2O_3 catalyst; the estimate

Table 4

Effect of Temperature on Rate of Reaction Accompanying Quinoline Hydrodenitrogenation

Reaction	Apparent First-Order Rate Constants $\frac{\text{g-oil}}{\text{g-catalyst min}}$			Estimated Activation Energy kcal/mole
	363°C	342°C	325°C	
Total fractional N-removal	0.96	0.56	0.42	20
Quinoline plus 1,2,3,4 tetrahydroquinoline removal	1.77	0.88	0.63	25
Quinoline $\xrightarrow{2H_2}$ 5,6,7,8 tetrahydroquinoline	0.68	0.76	0.65	very low
1,2,3,4 tetrahydroquinoline $\xrightarrow{2H_2}$ decahydroquinoline	0.28	0.27	0.26	very low
5,6,7,8 tetrahydroquinoline $\xrightarrow{2H_2}$ decahydroquinoline	~0	0.045	~0	very low
decahydroquinoline $\xrightarrow{H_2}$ H.C. + NH_3	2.05	1.39	1.30	20
0-propyl aniline $\xrightarrow{H_2}$ H.C. + NH_3	2.31	1.28	0.38	35

Operating conditions:

catalyst: HDS-9A (cyanamid)
$Ni\text{-}Mo/Al_2O_3$

presulfiding conditions: 325°C in 10% H_2S/H_2 for 2 hrs.

solvent: hydrotreated white oil

total pressure (H_2 pressure): 500 psig

reactor: stirred batch autoclave

is based on total nitrogen removal. The present results indicate an activation energy of 20 kcal/mole for total nitrogen removal from quinoline, but since the catalyst was sulfided, agreement with the literature results is not expected. (Qader, Wiser and Hill (1968) investigated the hydrodenitrogenation of coal tar catalyzed by unsupported tungsten disulfide and reported activation energy of 10 kcal/mole for temperatures between 300 and 400°C.)

b. Quinoline hydrodenitrogenation in a high-pressure flow microreactor

A 100-hr quinoline hydrodenitrogenation run has been carried out in the second flow microreactor to determine the behavior of the reactor system and to establish operating conditions for future runs. The conditions for the run are summarized in Table 5.

Hydrogen sulfide was introduced into the feed liquid so that the catalyst would be maintained in the sulfided state, as was proposed in third quarterly report. Under the operating conditions more than 95% of the nitrogen was removed in all cases. This result indicates the need for reducing the catalyst loading for all measurements of differential conversion for a meaningful kinetic study.

A 400-hr quinoline hydrodenitrogenation run in flow microreactor will be carried out during the next quarter with a reduced catalyst loading (~25 mg of Ni-Mo/Al_2O_3 sulfided in situ). The reactant mixture will be saturated with hydrogen containing ~1% H_2S. Two different concentrations of quinoline will be studied to demonstrate the usefulness of the reactor system as proposed in the second quarterly report. Results of the proposed run will be compared to data obtained in the batch autoclave reactor.

c. Acridine hydrodenitrogenation in a batch reactor

Preliminary experiments concerning the hydrodenitrogenation of acridine were performed with the batch autoclave reactor. The purposes were to establish the acridine reaction network; (relying on product identification by mass spectrometry and NMR) and to define reaction conditions (especially temperature and pressure) appropriate for studying the kinetics of acridine hydrodenitrogenation.

The mass spectrometry and NMR work is not yet completed, but initial results suggest that the acridine reaction network

TABLE 5

OPERATING CONDITIONS FOR HYDRODENITROGENATION OF QUINOLINE IN A FLOW MICROREACTOR

1) Reactant compound and initial concentration: quinoline in white oil, 6.35×10^{-6} g mole/cm^3

2) Catalyst: HDS 9-A, Ni-Mo/Al_2O_3
   Weight of catalyst: 0.312 g
   In situ sulfiding at 325°C for 2 hr
   Catalyst size: 60-80 mesh

3) Saturation pressure: 1500 psig (2% H_2S/H_2)
   Total operating pressure: 2500 psig

4) Reaction temperature: 300-342°C

5) Feed flow rate: 1.6 cm^3/hr to 16 cm^3/hr
   LHSV: 6 to 60 hr^{-1}

is as shown in Figure 3. Preliminary gas chromatographic analysis of the reactor samples is shown in the conversion plot of Figure 4. These data indicated that at reaction conditions of 340°C and 500 psig, acridine is readily hydrogenated to give 1,2,3,4,5,6,7,8-octahydroacridine. This compound is relatively unreactive, however, and the total nitrogen removal is small. No significant concentration of a cracked product could be detected, although the results of mass spectrometry indicate that trace quantities of 1-(methylenecyclohexyl)aniline were formed. (For comparison, the total nitrogen removal from quinoline at these same reaction conditions was approximately 50-60%.)

Further acridine experiments have indicated that cracking does occur more readily at 2000 psig and 355°C, but this result is qualitative since the product analyses remain to be done.

d. Carbazole hydrodenitrogenation in a batch reactor

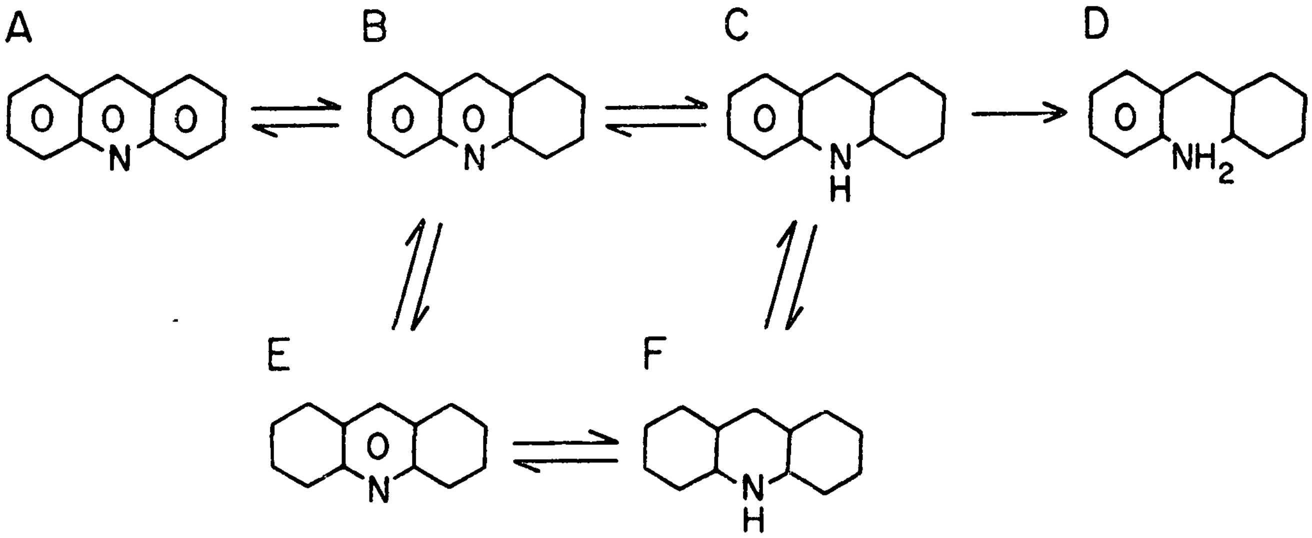
Carbazole has a very low solubility in white oil at the concentration levels used previously for quinoline. This lack of solubility presents a problem during sampling because, even though 1% wt of carbazole is soluble at 300°C in white oil, it does precipitate out at room temperature. It was therefore deemed necessary to determine a solubility curve of carbazole in various solvents and solvent mixtures to guide future experiments. The results are shown in the Appendix in Figure A2.

It is concluded that a concentration lower than 0.05% could lead to analytical problems, and a concentration of 0.5% carbazole was chosen for the standard one-liter autoclave run. The problem of having a solid in the reactor samples was solved by adding a known amount of toluene to each sample, making the solution homogeneous and therefore facilitating the analysis. Under these concentration conditions, the search for appropriate temperature and H_2 partial pressure conditions was initiated.

It was found that with P=2000 psig, T=365°C, H_2S concentration=0.05%, catalyst loading=0.4%, and carbazole concentrations=0.5%, extensive reaction based on solid disapearance in the samples could be observed. Quantitative results have not yet been determined. The reaction temperature seems to be limited by the stability of the white oil under the reaction conditions. At temperatures exceeding 370°C, extensive cracking and coloration of white oil could be seen.

An acid extraction procedure was applied to the reaction products, but since only a few milligrams of material were obtained, difficulties were encountered. A search for more effective extraction procedures is continuing. Basic and non-basic extraction techniques are to be tested.

Even though the methods must be developed further, pre-



A = ACRIDINE
B = 1, 2, 3, 4 - TETRAHYDROACRIDINE
C = 1, 2, 3, 4, 9, 10, 11, 12 - OCTAHYDROACRIDINE
D = 1 (METHYLENECYCLOHEXYL) ANILINE
E = 1, 2, 3, 4, 5, 6, 7, 8, - OCTAHYDROACRIDINE
F = TETRADECAHYDROACRIDINE

Figure 3. Preliminary Reaction Network for Acridine Hydrogenation

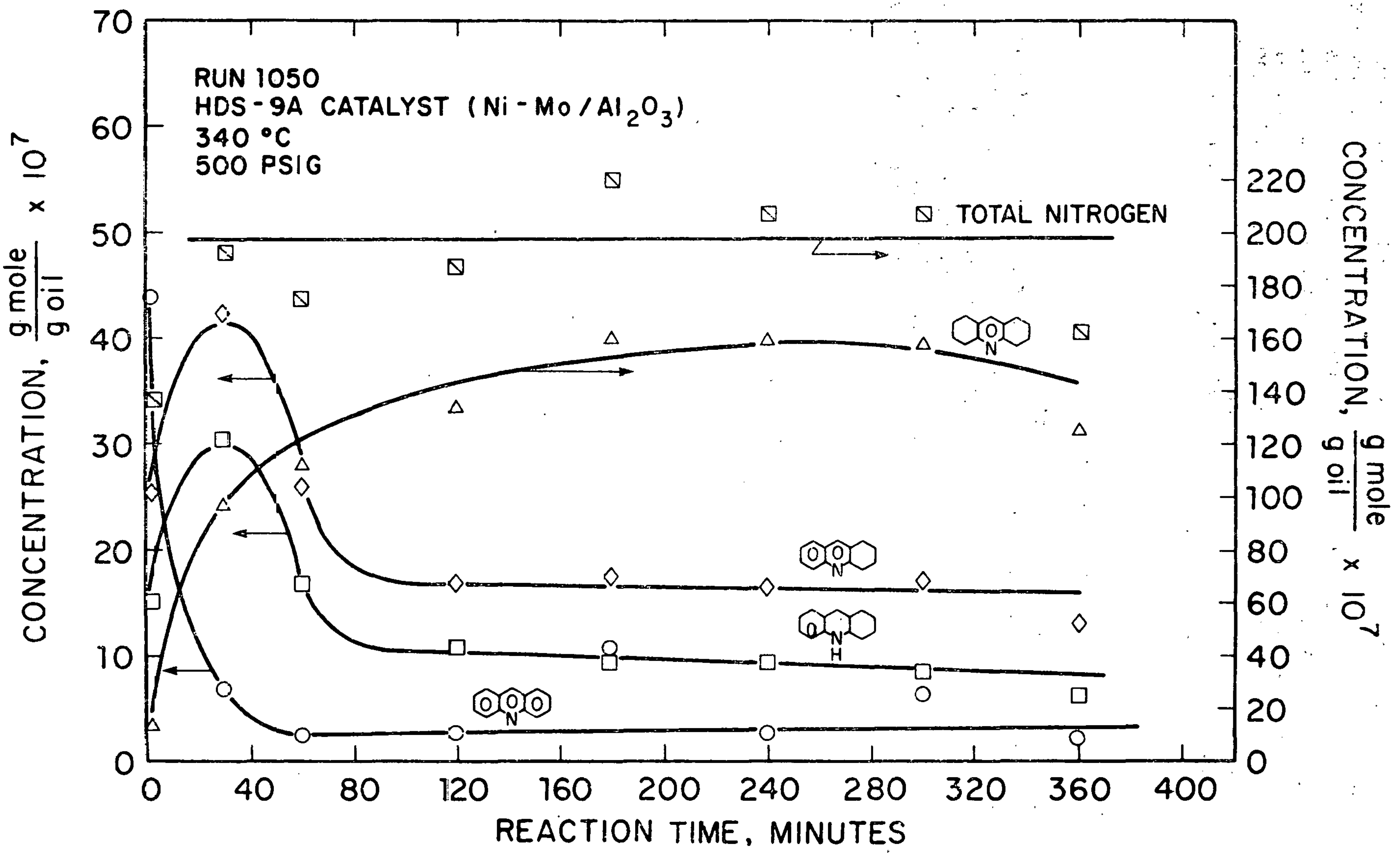


Figure 4. Conversion of Acridine in a Batch Autoclave Reactor

liminary information was obtained from the early experiments. Products were analyzed on a gas chromatograph-mass-spectrometer system. A typical chromatogram is shown in Figure 5. Peaks 17, 16, 15, and 13 were identified as carbazole, 1,2,3,4-tetrahydrocarbazole, 1,2,3,4,12,13-hexahydrocarbazole, and 1,2,3,4,5,6,7,8-octahydrocarbazole, respectively. Peaks 17, 16, and 15 were confirmed by spiking the original sample with the authentic compounds. From these results, a preliminary and tentative network can be suggested for carbazole hydrodenitrogenation (Figure 6).

D. CATALYST DEACTIVATION

It has been shown previously by the analysis of aged Synthoil pilot-plant catalyst that rapid deposition of mineral constitients of coal takes place on catalyst surfaces (see Stanulonis *et al.* (1976)). The deposits are considered likely to deactivate the catalyst rapidly, and this hypothesis is to be tested in future microreactor experiments. The only available Synthoil catalyst samples had been used in the pilot plants for periods of only several weeks, however, and there is strong motivation for investigating catalyst used for longer periods. Samples of catalyst used in the H-Coal process are potentially of value to this investigation, and so efforts are being made with the assistance of Bill Wu of ERDA to obtain appropriate samples of used H-Coal catalysts.

E. HYDROPROCESSING REACTION ENGINEERING

Effort in this quarter has been devoted to consolidating the work given in earlier quarterly reports. The result is a working draft of a paper intended for later publication.

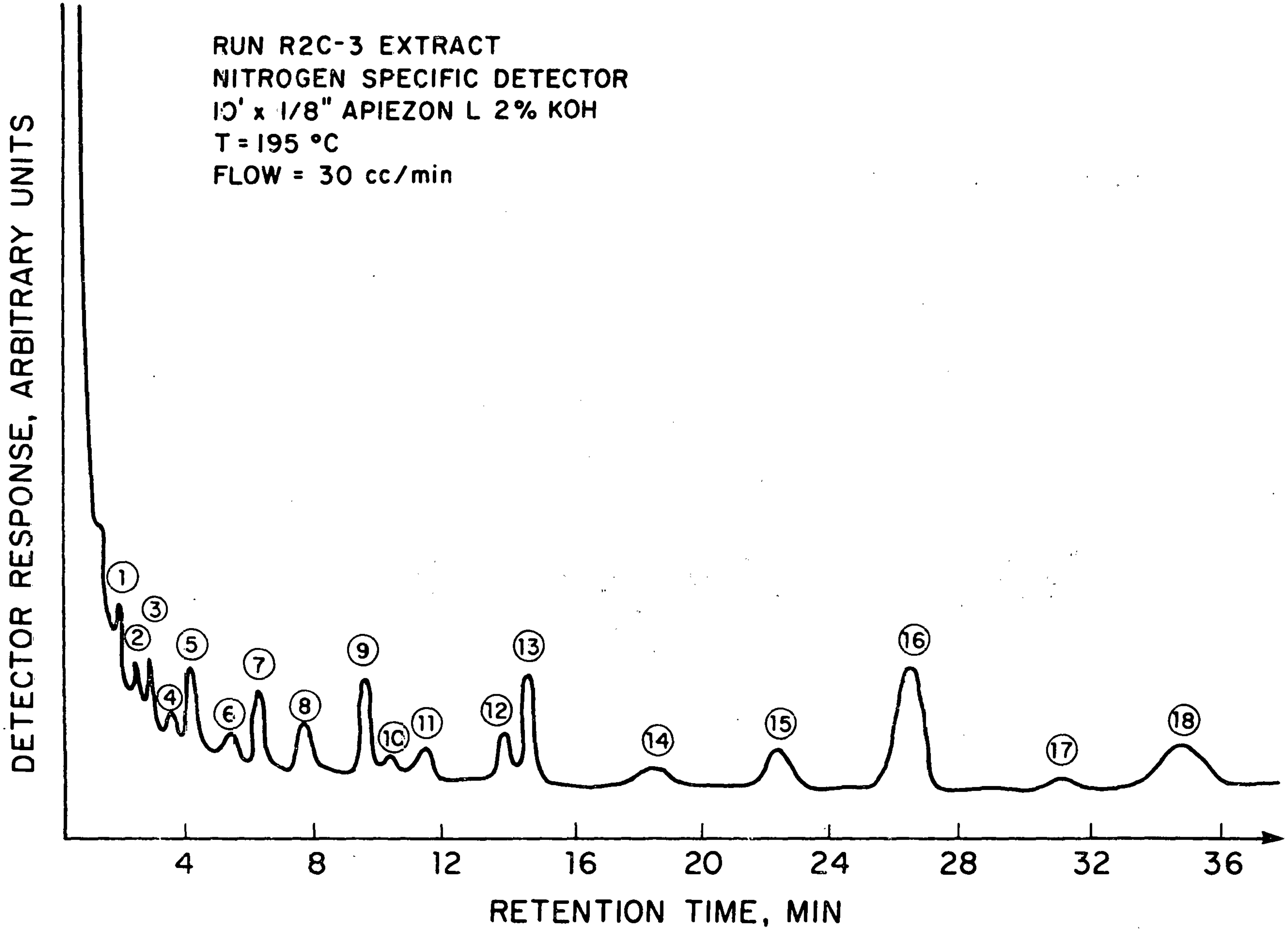


Figure 5. Typical Chromatogram of Carbazole Reaction Products

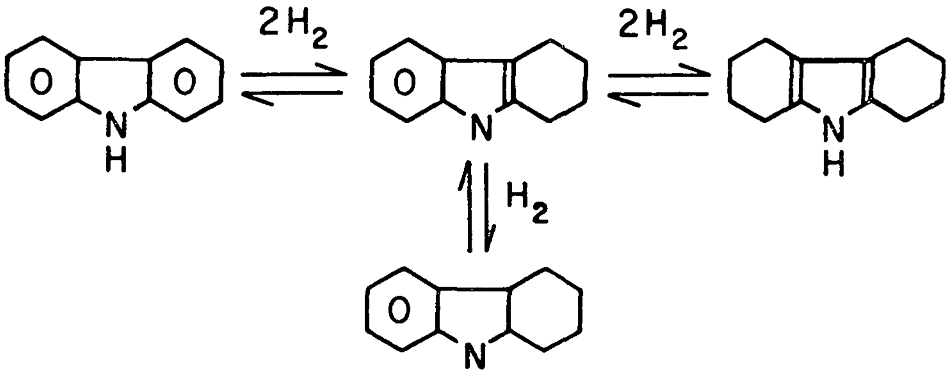


Figure 6. Tentative Reaction Network for Carbazole Hydrogenation

V. CONCLUSIONS

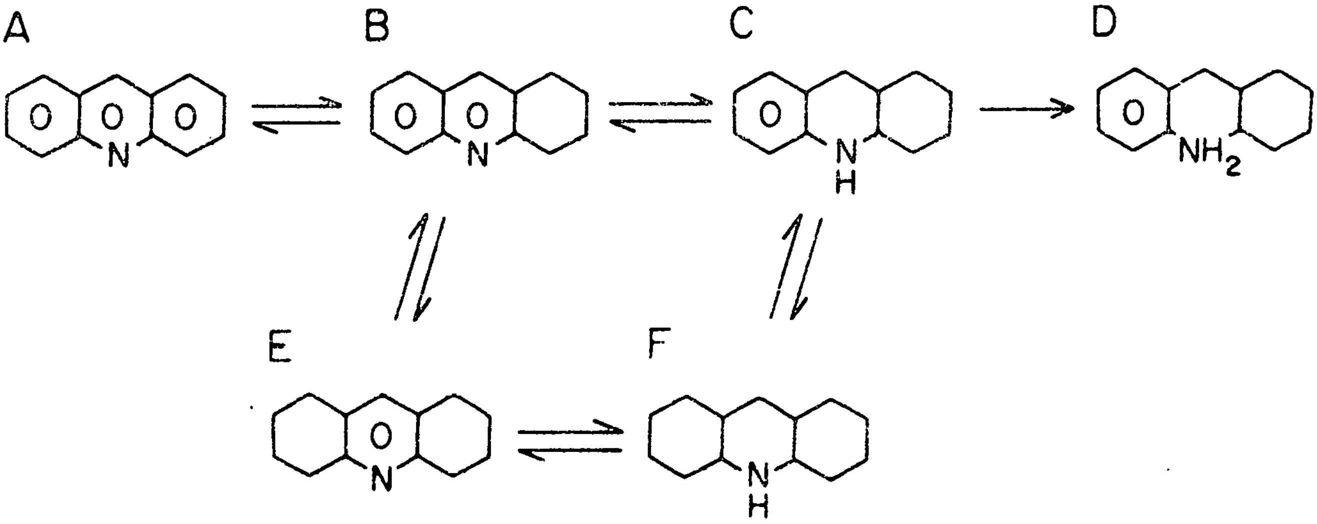
1. Dibenzothiophene has a surprisingly high reactivity in hydrodesulfurization, and with only 25 mg of catalyst in the flow microreactor, a temperature of 300°C or even less is required to give differential conversion data at the pressures and space velocities of interest.

2. The rate of dibenzothiophene hydrodesulfurization is not affected by intraparticle diffusion at the reaction conditions of interest when the catalyst particles are less than about several hundred microns in dimension.

3. Overall nitrogen removal from quinoline is characterized by an apparent activation energy of about 20 kcal/mole, but the rates of hydrogenation reactions in the quinoline networks are nearly independent of temperature.

4. The second flow microreactor has performed well in extended quinoline hydrodenitrogenation runs, and conditions have been established for kinetics experiments.

5. Preliminary results of batch autoclave reaction experiments suggest the following reaction network for acridine:



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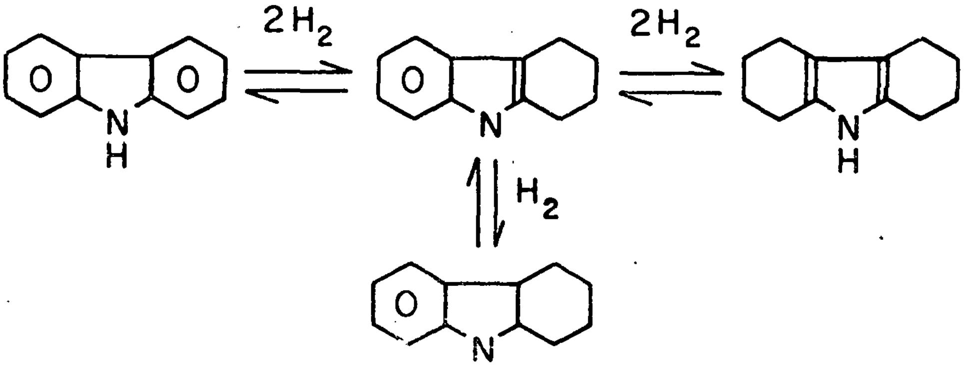
D = 1 (METHYLENECYCLOHEXYL) ANILINE
E = 1, 2, 3, 4, 5, 6, 7, 8, - OCTAHYDROACRIDINE
F = TETRADECAHYDROACRIDINE

6. Under conditions for which 50% nitrogen removal from quinoline was observed, only a small fraction of nitrogen was removed from acridine: evidently hydrodenitrogenation of three-ring compounds is slow and hydrogenation of the outer rings is fast.

7. Preliminary results of batch autoclave reaction experiments lead to the following <u>tentative</u> suggestion of a reaction network for carbazole:



Carbazole is similar to acridine in that it experiences relatively rapid hydrogenation of the outer rings but only slow denitrogenation.

VI. LITERATURE CITED

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Stanulonis, J. J., B. C. Gates and J. H. Olson, "Catalyst Aging in a Process for Liquefaction and Hydrodesulfurization of Coal," *A.I.Ch.E. J. 19*, 417 (1976).

VII. PUBLICATIONS

1. Stanulonis, J. J., B. C. Gates, and J. H. Olson, "Catalyst Aging in a Process for Liquefaction and Hydrodesulfurization of Coal," A.I.Ch.E. Journal 19, 417 (1976).

2. Eliezer, Kenneth F., Manoj Bhinde, Marwan Houalla, Dennis Broderick, Bruce C. Gates, James R. Katzer, and Jon H. Olson, "A Flow Microreactor for Study of High-Pressure Catalytic Hydroprocessing Reactions," to be submitted to Ind. Eng. Chem. Fundamentals.

VIII. PERSONNEL

There have been no changes in personnel during this quarter. It is expected that Ed Reiff will finish his M.Ch.E. thesis and leave the group in the next quarter. A new graduate student is expected to join the group at about the same time; he will do hydrodesulfurization work. An offer of a post-doctoral position has been made to Dr. N. K. Nag, a chemical engineer who is now working in Enshede, The Netherlands, at the Twente University of Technology. Dr. Nag is doing research in the group of Professor Mars, and his project is concerned with characterization of supported "monolayer" catalysts very similar to those used in the present research.

APENDIX A

Supplementary Data

Figures A1 and A2

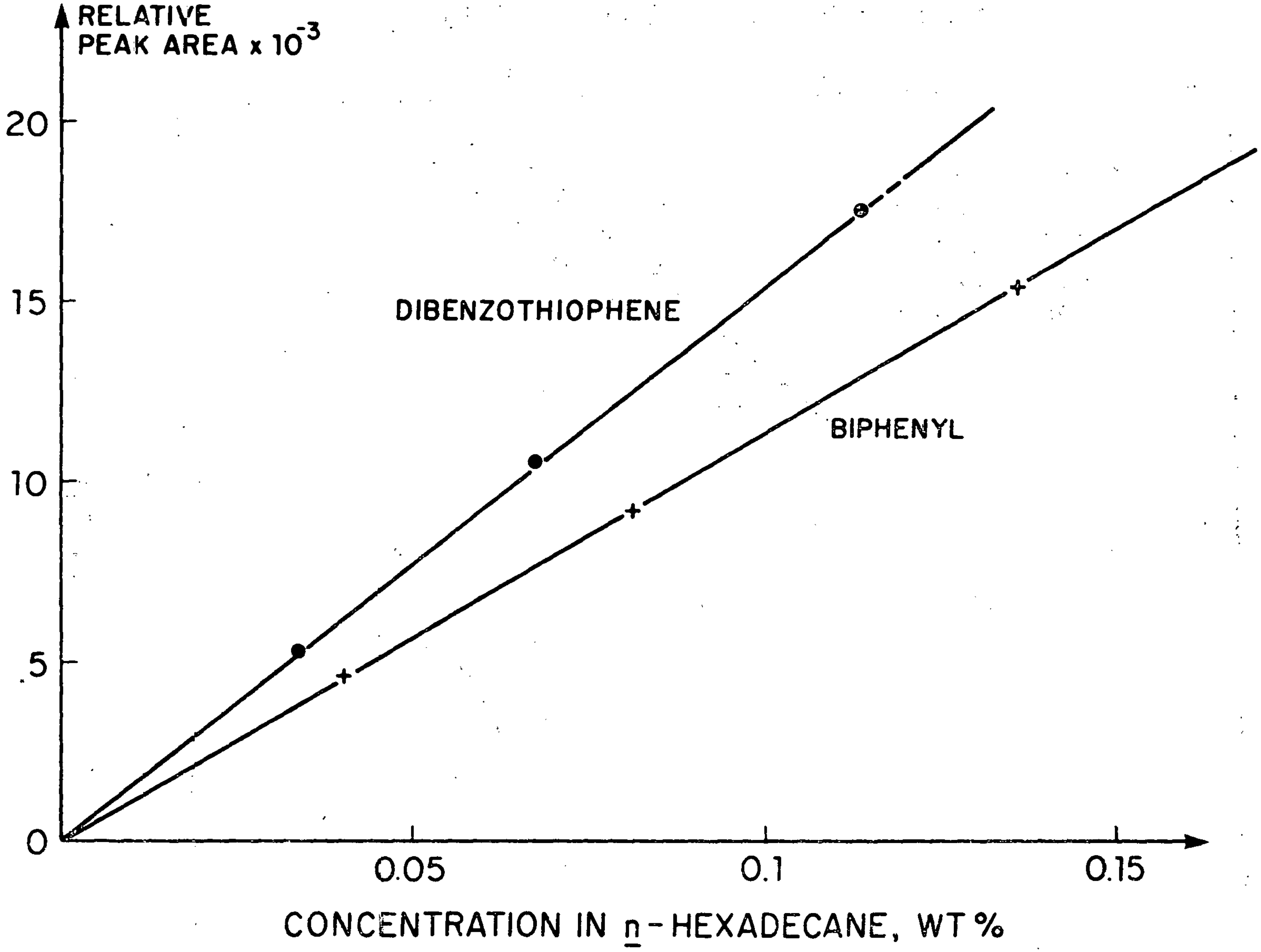


Figure A1. Calibration Data for Gas Chromatographic Analysis

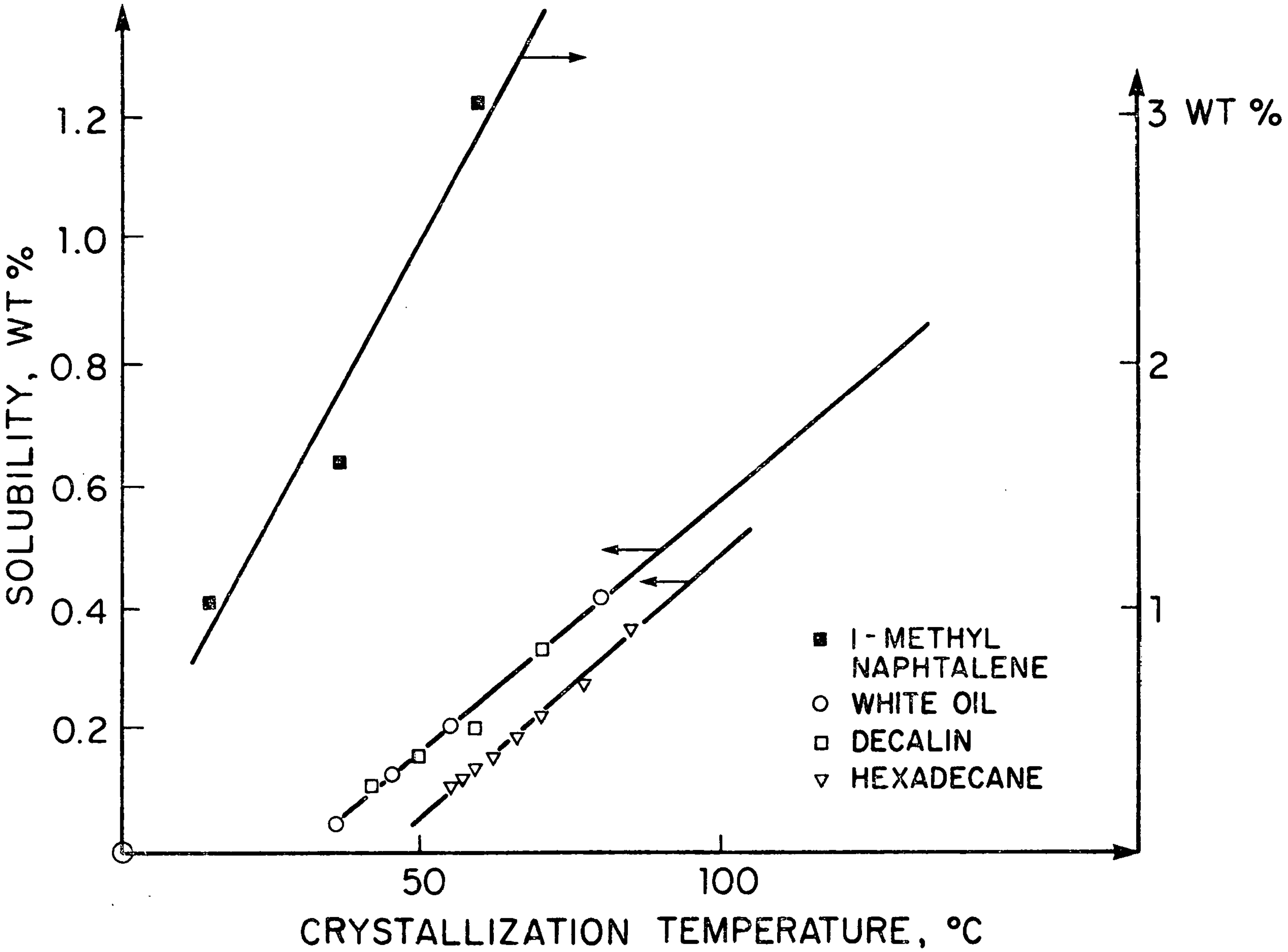


Figure A2. Solubility of Carbazole

APPENDIX B

1. Inventory of Sulfur and Nitrogen Containing Compounds
2. Priority List of Compounds to be Synthesized
3. Notes on Methods of Purification

TABLE B1

INVENTORY OF SULFUR-AND NITROGEN CONTAINING COMPOUNDS AS OF 9/20/76

COMPOUND	STRUCTURE (see accompanying key)	SUPPLY
Dihydrobenzothiophene	1	3g
3,7-Dimethylbenzothiophene	2	15g
2-Methylbenzothiophene	3	2g
3-Methylbenzothiophene	4	5g
7-Methylbenzothiophene	5	5g
2,3-Cyclohexylbenzothiophene	6	5g
2,8-Dimethyldibenzothiophene	7	0.05g
50-50 mixture of 4-Methyldibenzothiophene and 4,6-Dimethyldibenzothiophene		0.01g
3,7-Dimethyldibenzothiophene	8	
4-Methyldibenzothiophene	9	0.005g
o-Propylaniline	10	8g
Decahydroquinoline	11	CIS:None Trans:5g Mix:50g
2,8-Dimethylquinoline	12	10g
Sym-octahydroacridine	13	40g
4-Methylacridine	14	10g
1,8-Dimethylcarbazole	15	5g
cis-Hexahydrocarbazole	16	20g

TABLE B2

PRIORITY LIST OF COMPOUNDS TO BE SYNTHESIZED

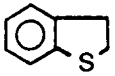
Priority		Structure (see accompanying key)	Amount
1	4,6-Dimethyldibenzothiophene	17	0.5g
1	2,8 Dimethyldibenzothiophene	8	0.5g
1	Purified quinoline	18	50g
1	1,2,3,4-Tetrahydroquinoline	19	50g
1	5,6,7,8-Tetrahydroquinoline	20	20g
2	Benzonaphthothiophene	21	5g

TABLE B2 (con't.)

2	2,8-Dimethyldibenzothiophene	7	2g
2	Perhydroacridine	22	5g
3	4-Methylbenzothiophene	23	0.5g
3	3-Methylbenzothiophene	4	0.5g
3	2-Methylbenzothiophene	3	0.5g
3	1-Methylcarbazole	29	
3	1,2-Benzocarbazole	25	

TABLE B2 (con't.)

3	4,5 Dimethylacridine	26



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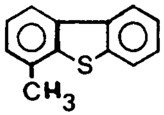

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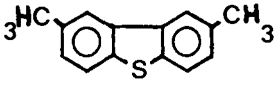

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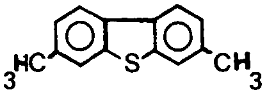

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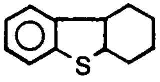

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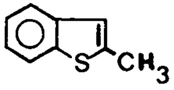

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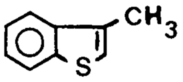

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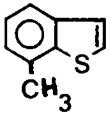

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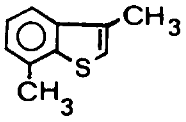

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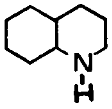

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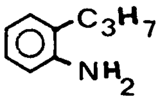

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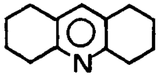

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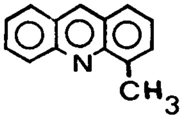

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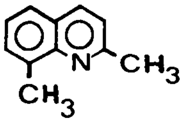

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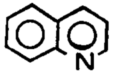

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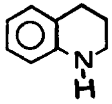

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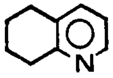

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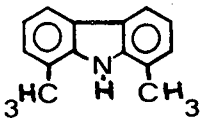

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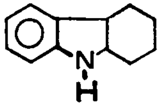

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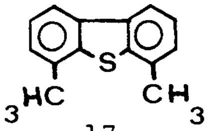

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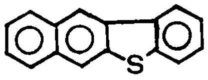

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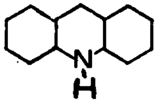

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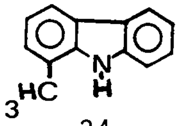

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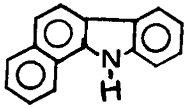

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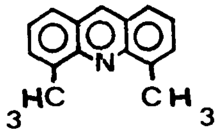
Key to Structures In Tables B1 and B2



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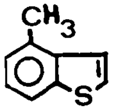

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Key to Structures In Tables B1 and B2 (con't.)

3. Methods of Purifications

A) The purification of hexadecane to levels where trace impurities which could interfere with the detection of reaction products in very small quantities is now being attempted. A 5 kg quantity of hexadecane containing small amounts of impurities detectable by glc techniques is now being subjected to distillation in a 100-plate column. This should require some 3 weeks of operation with constant monitoring of the fractions to see where the impurities emerge.

B) Many multistep syntheses usually end up with small impurities present to contaminate the desired product. Often removal of such impurities is costly in time and in yield of good material; often, too, such impurities cannot be removed by conventional methods of recrystallization. We have now undertaken studies directed toward purifying quantities as large as one to two grams via preparative-scale high-pressure liquid chromatography in the effort to solve this general problem in the synthesis of very pure materials on a relatively large scale.

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