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DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

First Quarterly Report for Period

September 15, 1978 to December 15, 1978

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I. ABSTRACT

Four experimental runs were made in this quarter. Two of them used decahydroquinoline as reactant and the other two runs were made using orthoethylaniline and quinoline-N-oxide respectively. The decahydroquinoline runs indicate that the carbon-nitrogen bond scission is not thermal but clearly catalytic. Important findings resulted from the run using o-ethylaniline and future runs will help define reaction pathways. Quinoline-N-oxide was rapidly deoxygenated to form quinoline under the conditions tested. Future runs will be conducted in the absence of hydrogen to avoid deoxidation of quinoline-N-oxide and to find out whether carbon-nitrogen bond scission can be promoted by the addition of oxygen to the quinoline molecule.

A review paper has been prepared that reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful direction to be followed in both catalyst and process development.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- To apply the reaction study and kinetic analysis techniques which we have developed in our past hydrodenitrogenation studies to the optimization of catalysts for hydrodenitrogenation of multi-ring nitrogen-containing compounds by balancing the hydrogenation and carbon-nitrogen bond scission functions, thereby developing improved catalysts for hydrodenitrogenation.

- To develop an improved understanding of the catalyst function required for carbon-nitrogen bond scission since this function is critical to hydrodenitrogenation but is not understood.

- To develop unique catalysts for hydrodenitrogenation of multi-ring nitrogen-containing compounds without first requiring hydrogenation of the surrounding aromatic rings.

- To determine the stability of the catalysts developing for processing coal-derived liquids.

Scope:

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. The carbon-nitrogen bond scission reaction needs to be better understood to facilitate development of new and improved catalysts. The nature of the catalytic function responsible for carbon-nitrogen bond scission is being determined by measuring the rates of carbon-nitrogen bond scission using mainly decahydroquinoline over a set of catalysts prepared specifically to evaluate the catalyst requirements for the carbon-nitrogen bond scission reaction. The catalysts being tested include Lewis and Brønsted acid catalysts without metal, alumina impregnated with Mo, Co, and Ni, promoted with halogens and various levels of sulfiding and in situ H_2S partial pressure and with and without Ni promotion to separate out the role of the support. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the carbon-nitrogen bond scission function) will be demonstrated, and promising catalysts will be tested for selectivity and activity maintenance for longer-term runs using highly aromatic synthetic feeds and coal-derived liquids if possible.

Another part of this research, and potentially the most beneficial part, involves the development of uniquely-new, highly-selective hydrodenitrogenation catalysts. This work is focusing on developing catalysts that can selectively coordinate nitrogen and remove it from multi-ring nitrogen-containing aromatic compounds with only limited or no hydrogenation of the aromatic rings, thus achieving major savings in hydrogen consumption. The catalysts formulated are being tested under high-pressure liquid-phase conditions using quinoline and possibly acridine in a carrier oil as a reactant. Since quinoline contains the requisite benzenoid ring and nitrogen-containing aromatic rings characteristic of nitrogen-containing compounds present in coal-derived liquids, it is considered to be a good compound for characterizing catalyst behavior.

The results of all of the above work are being evaluated utilizing our kinetic analysis schemes to give quantitative measures of the rates of carbon-nitrogen bond scission and the extents and rates of hydrogenation. These results are being interpreted in terms of the catalysts and their properties and recommendations will be made as to what further work needs to be done and the potentially most fruitful directions to be followed.

III. SUMMARY OF PROGRESS TO DATE

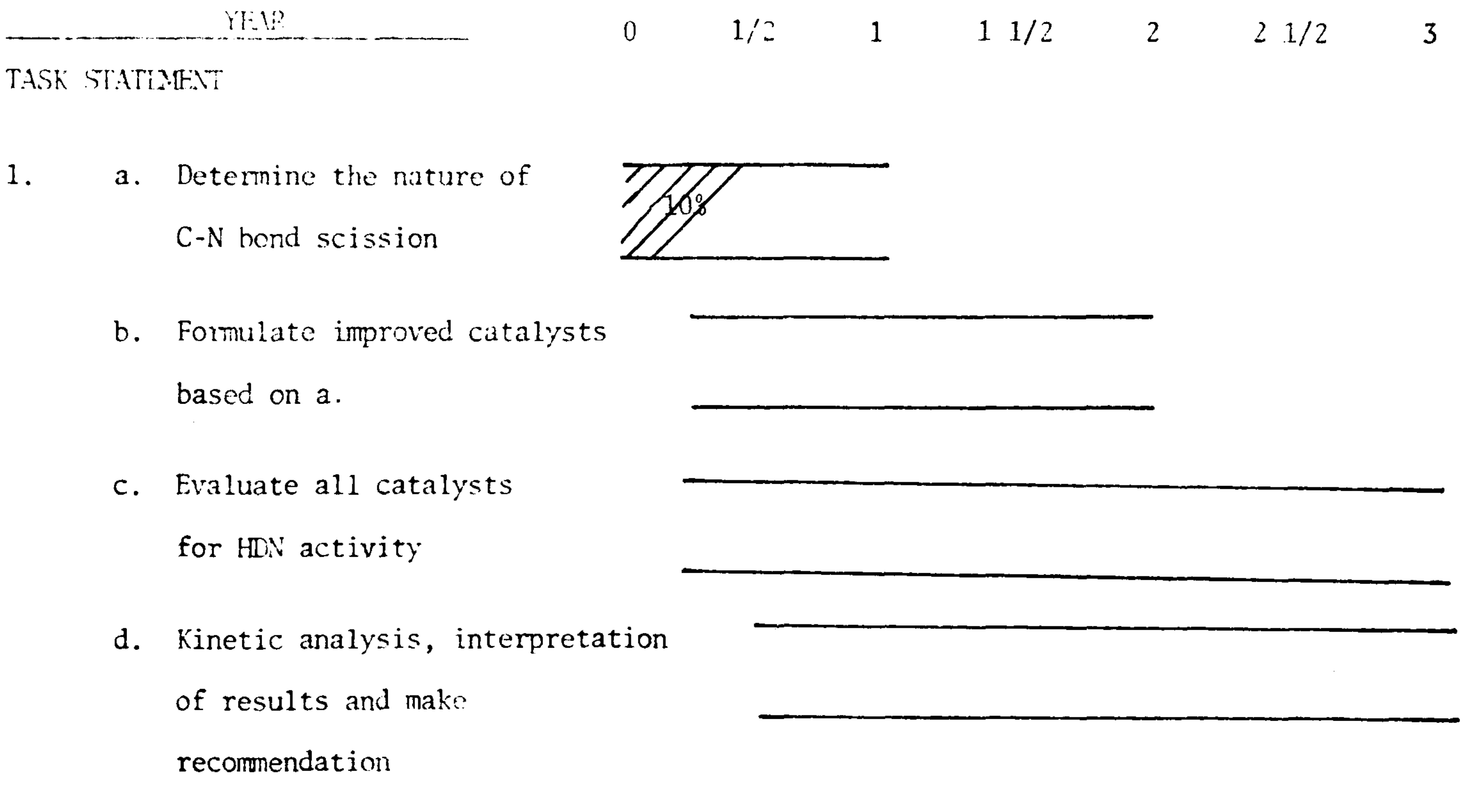
During the first quarter a Gas Chromotograph with a flame ionization detector and a nitrogen specific detector was purchased and analytical techniques were established. An integrator and a recorder were purchased and installed. Chemicals and catalytic materials, including catalyst supports, to be used in this research of this project were obtained.

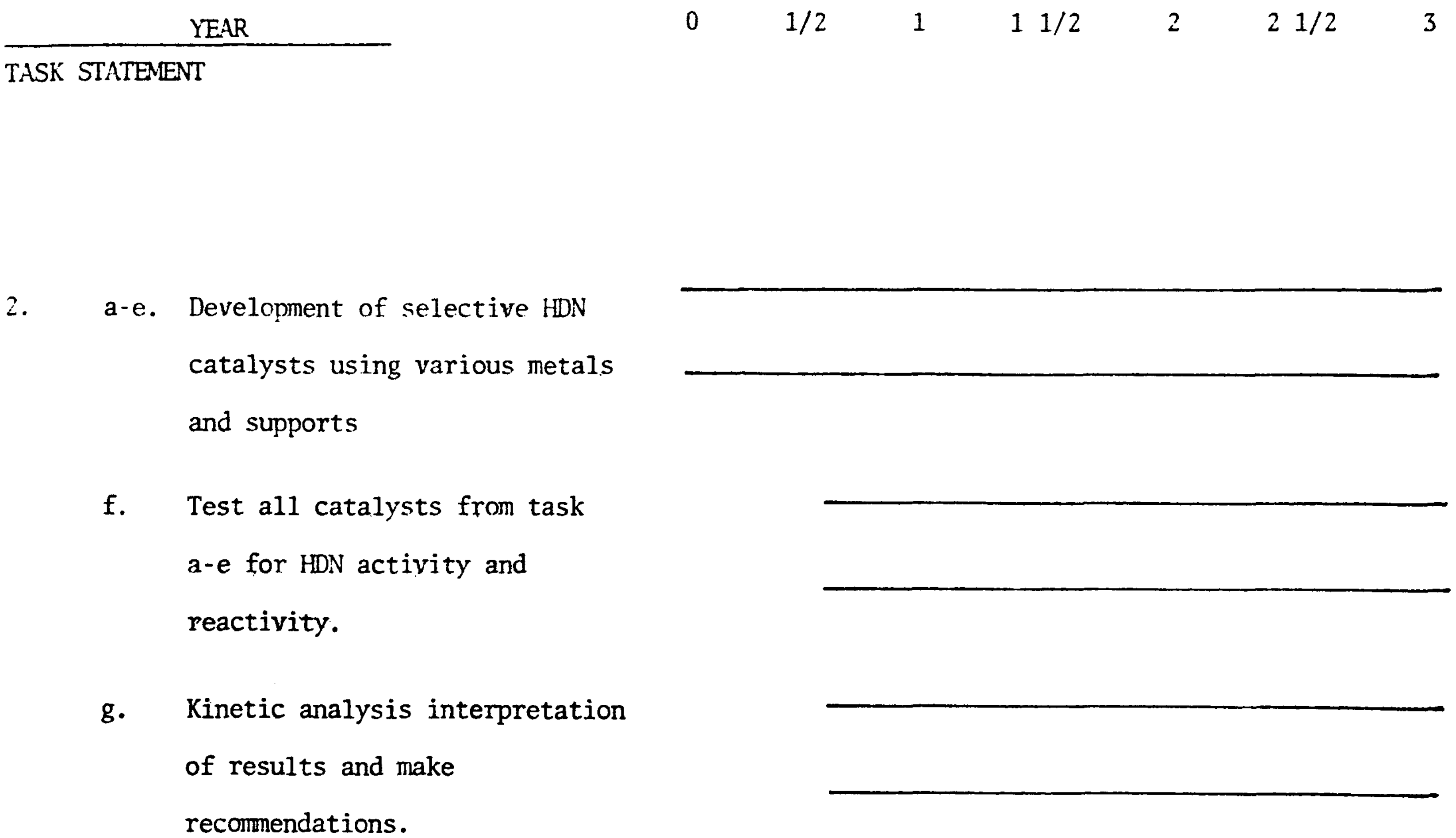
A high-temperature controlled-atmosphere furnace was purchased and set up. Samples of several catalysts have been prepared; these will be tested in the upcoming quarter.

Four experimental runs were made in this quarter. Two of them used decahydroquinoline as reactant and the other two runs were made using orthoethylaniline and quinoline-N-oxide, respectively. The decahydroquinoline runs were made to determine whether the carbon-nitrogen bond scission is non-ctalytic and also to determine whether the metal surface present in the autoclave reactor (wall and miscellaneous tubes) increase the hydrodenitrogenation activity. Preliminary results indicate that the autoclave walls do not increase the activity, and that carbon-nitrogen bond scission is not thermal but is clearly catalytic. In order to better understand the mechanism of hydrodenitrogenation of anilines and substituted anilines, a run was made using orthoethylaniline. Important findings resulted, and future runs will help define reaction pathways. A run was made using quinoline-N-oxide to determine whether the addition of oxygen to the quinoline molecule would reduce the aromaticity of the nitrogen-containing ring thereby making it easier to remove nitrogen directly. Results indicated that quinoline-N-oxide undergoes rapid deoxidation to form quinoline. Future runs will be conducted in the absence of hydrogen to determine the usefulness of this technique.

A paper has been prepared that reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and a more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful directions to be followed in both catalyst and process development. A draft of the paper submitted to "Catalysis Reviews" is given in Appendix B.

*TIME PLAN AND MILESTONE CHART





TASK STATEMENT

2. a-e. Development of selective HDN catalysts using various metals and supports

f. Test all catalysts from task a-e for HDN activity and reactivity.

g. Kinetic analysis interpretation of reasults and make recommendations.

☐ Scheduled

▨ Underway ■ Completed

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	FIRST QUARTER
PERSONNEL	5334
TRAVEL	0
SUPPLIES AND EXPENSES	212
OCCUPANCY AND MAINTENANCE	0
EQUIPMENT	585
OTHER EXPENSES	140
TRANSFERS (OVERHEAD)	2868
	9,139

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 - Development of Improved Hydrodenitrogenation Catalysts

Three experiments were conducted in a batch reactor during this quarter. The reactor used was a 300 cm^3 autoclave fitted with a magnetic drive stirrer. Two of the experiments used decahydroquinoline as reactant; orthoethylaniline was used as reactant in the third experiment.

Liquid samples were analyzed using a Perkin-Elmer gas chromotograph equipped with a flame ionization detector. A glass capillary column (75 m OV-101) was used for all reactant and product analysis.

a) Decahydroquinoline

The major objective of the runs using decahydroquinoline is to characterize the nature of the carbon-nitrogen bond scission. Since decahydroquinoline is a completely hydrogenated derivative of quinoline, it is an ideal reactant for studying the rates of carbon-nitrogen bond scission. Two experimental runs were conducted in this quarter to determine whether the carbon-nitrogen bond scission reaction is non-catalytic. These runs were conducted in the absence of a catalyst. In order to study the effects of metal surface (walls of the autoclave) present in the reactor, the first run was conducted using a glass liner and the second run was conducted without the glass liner. Reaction conditions were identical for both runs. They were:

- Temperature: 350 ± 2°C
- Total Pressure: 136 ± 2 atm
- Reactant Concentration: 0.5 weight percent decahydroquinoline in hexadecane
- CS_2 loading: 0.05 wt %
- Catalyst Concentration: 0.00

The results from the two runs are presented in Figures 1 and 2. These results indicate some minor differences between the two runs. The products from the run using the glass liner showed traces of quinoline, 1,2,3,4-tetrahydroquinoline, benzene, propylbenzene and normal propylcyclohexane with 5,6,7,8-tetrahydroquinoline and decahydroquinoline as major products. However, the products from the run without glass liner showed only decahydroquinoline, propylbenzene and propylcyclohexane. The dehydrogenation reaction between decahydroquinoline and 5,6,7,8-tetrahydroquinoline was absent in the second run. Also, material balance analysis indicated that all the decahydroquinoline that was placed in the catalyst loader was not injected into the autoclave. Due to experimental difficulties in the second run, the decahydroquinoline was left in the catalyst loader during the operation of the run without glass liner, under a pressure of 500 psig at a temperature of about 80°C for a period of 48 hours. This could have caused some of the differences between the two runs. The run without glass liner will be repeated.

However, preliminary conclusions can still be drawn from these two runs as to whether the carbon-nitrogen bond scission reaction is non-catalytic (thermal). The pseudo first-order rate constant for the carbon-nitrogen bond breaking step for decahydroquinoline can be obtained from earlier quinoline hydrodenitrogenation network studies. Using this value, and assuming that the rate constant will be the same if one starts with decahydroquinoline, the concentration of decahydroquinoline as a function of time can be predicted. Figure 3 presents the predicted curve. Comparison of Figures 1 and 3 indicate that the non-catalytic removal of nitrogen from decahydroquinoline is extremely small; this clearly shows that the C-N bond scission reaction requires a catalyst.

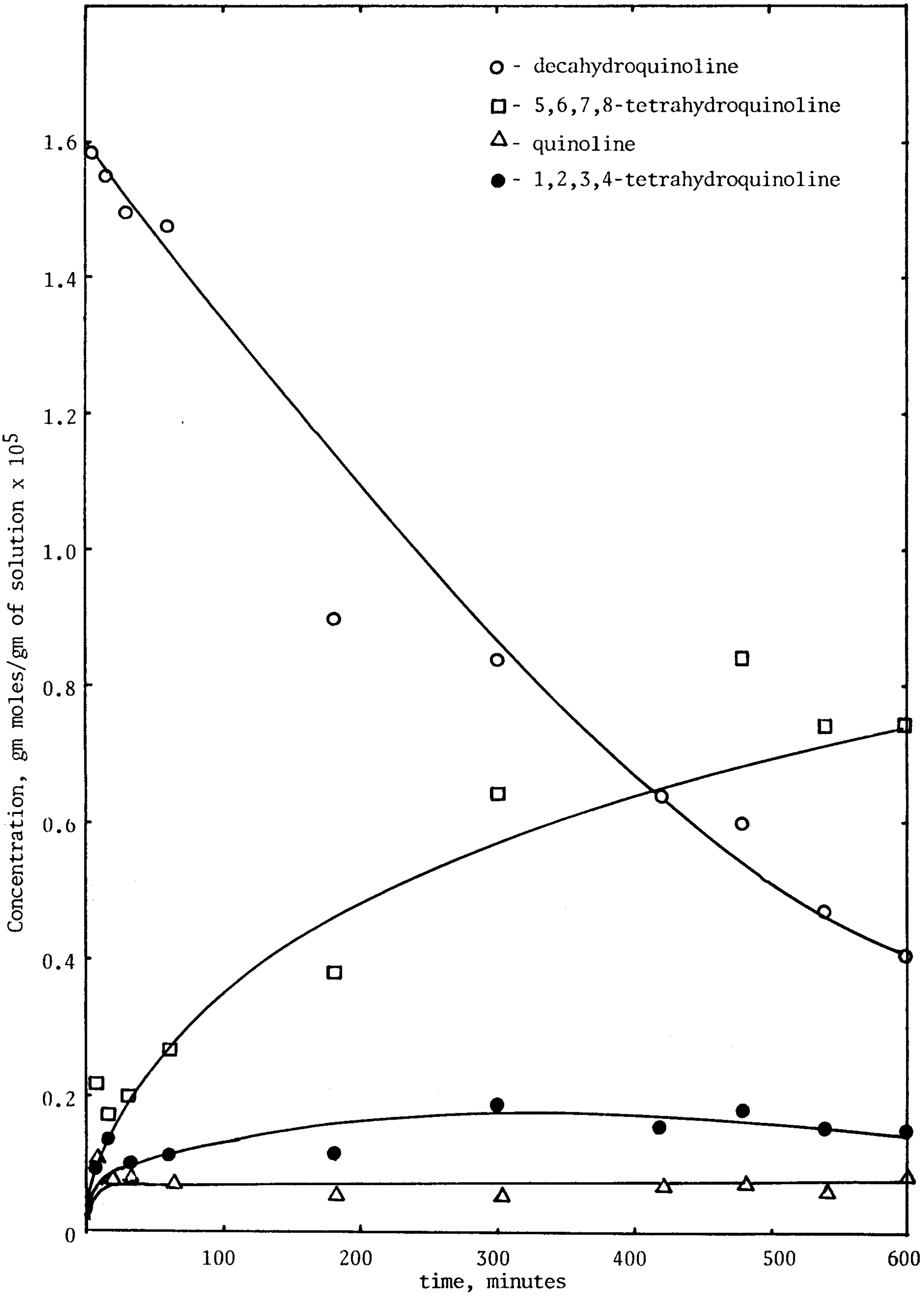


Figure 1. Concentration profiles for hydrodenitrogenation of decahydroquinoline using a glass liner in the reactor.

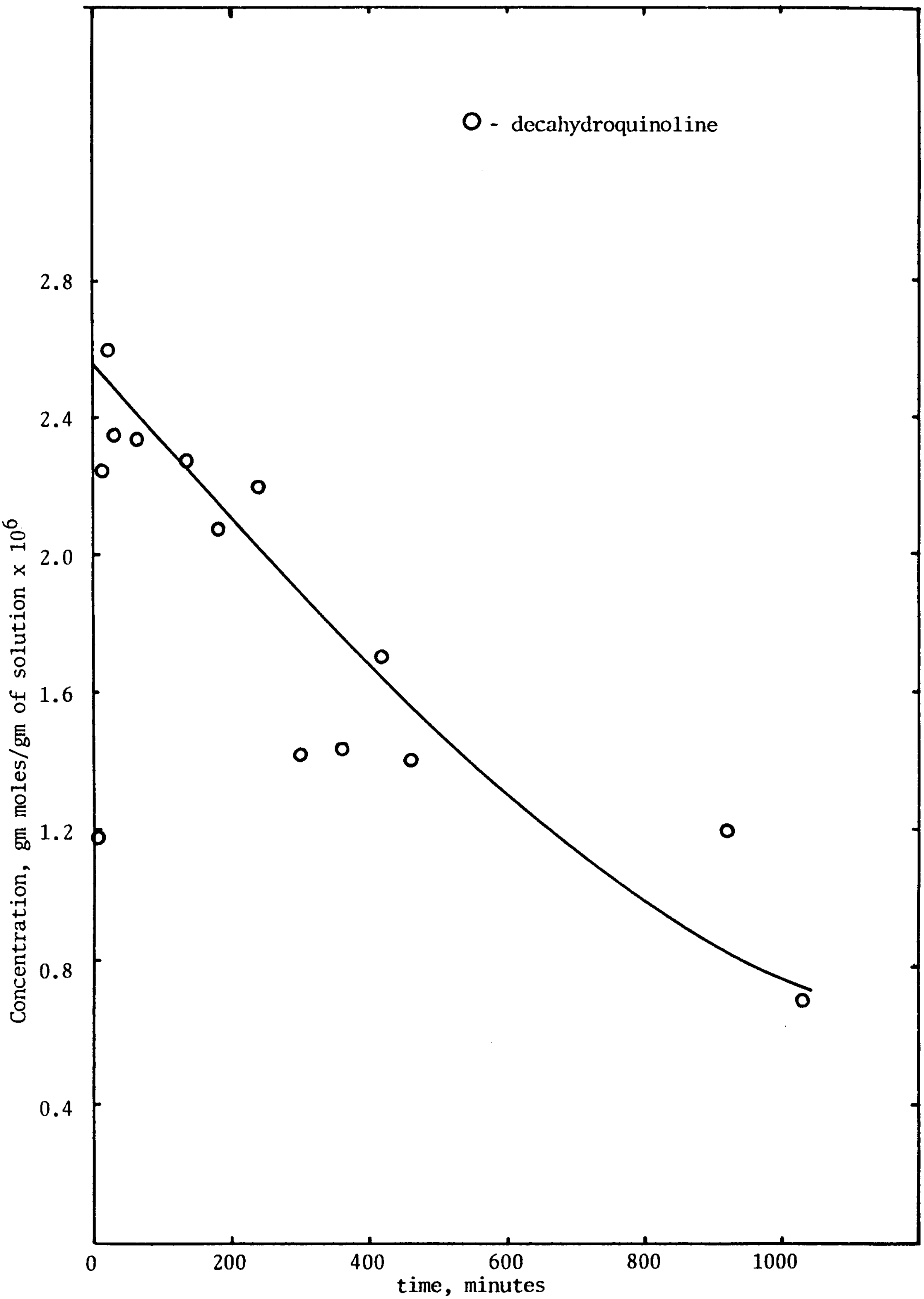


Figure 2. Concentration profile for hydrodenitrogenation of decahydroquinoline without a glass liner.

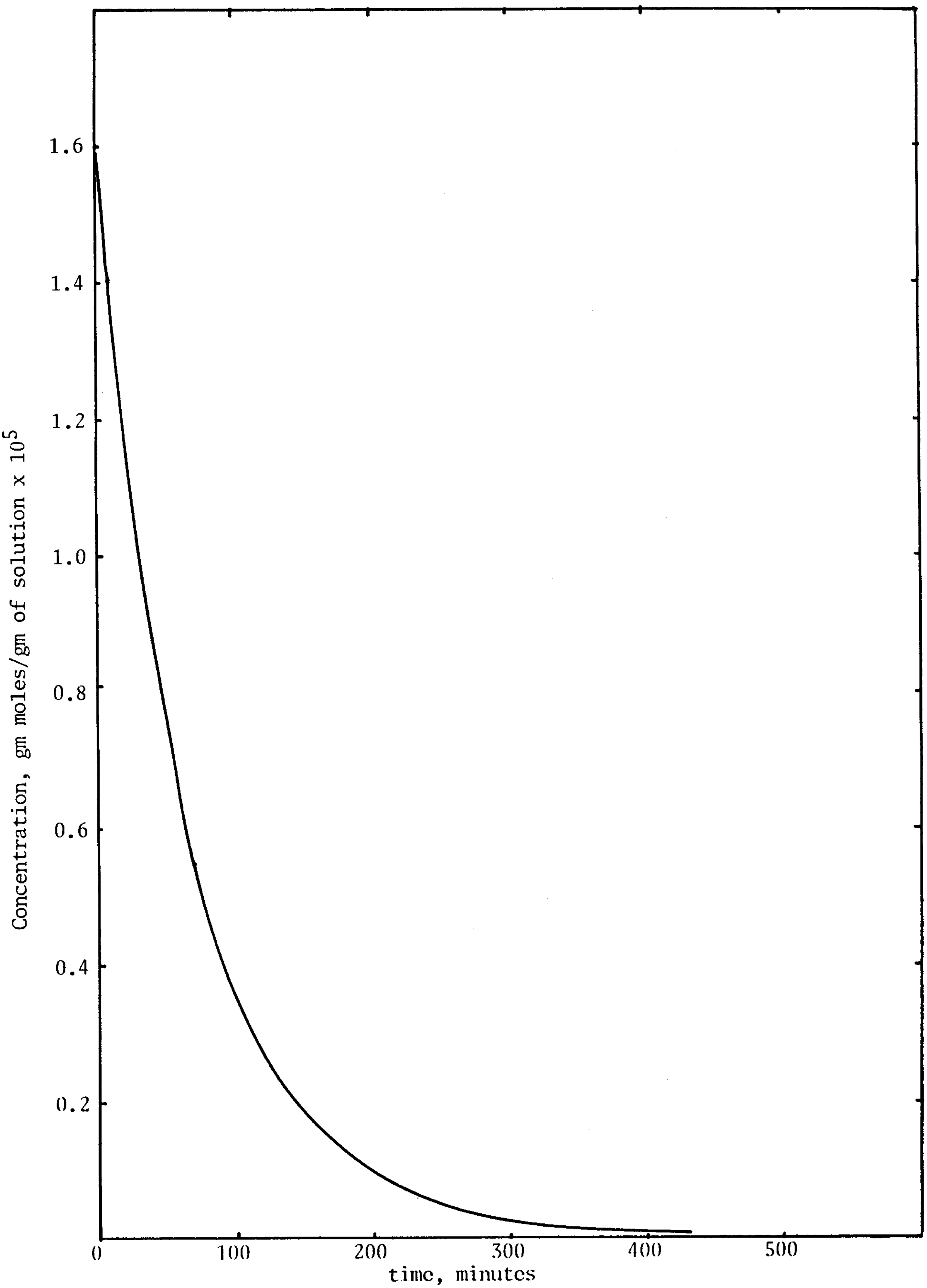


Figure 3. Predicted concentration of decahydroquinoline using pseudo first-order rate constants determined earlier using quinoline network

The pseudo first-order rate constants for the disappearance of decahydroquinoline were 0.0022 min^{-1} and 0.0012 min^{-1} for the runs with glass liner and without glass liner respectively. If these pseudo first-order rate constants are normalized to a weight of inert solid (non-catalytic) which is the same as the weight of catalyst, then the rate constants are 0.44 and 0.24 (g oil)/(gmol-min) respectively for the two runs. The rate constant for the disappearance of decahydroquinoline using a Ni-Mo/ Al_2O_3 at the same operating conditions calculated from quinoline hydrodenitrogenation is 3.2 (g oil)/g cat-min). Hence, the above results indicate that the increase in metal surface due to removal of glass liner did not appreciably increase the rate of reaction and that the carbon-nitrogen bond scission function is catalytic, i.e., its rate in the absence of catalyst is less than 1/10 that from the catalyst.

In the next quarter, runs will be made using supports with no active metals present and also using several catalysts. These runs should give us an insight into the catalyst requirements for the C-N bond scission.

b) Orthoethylaniline

Hydrodenitrogenation of anilines and substituted anilines have not been studied extensively. Our earlier work on quinoline hydrodenitrogenation indicated that orthopropylaniline may require hydrogenation of the benzene ring before nitrogen can be removed. Since anilines and substituted anilines are the end products from most nitrogen-containing compounds (quinoline, indole), the chemistry of nitrogen removal from these compounds is extremely important. Hence, an experimental run was conducted using orthoethylaniline as a reactant.

Experimental:

The catalyst used was a typical commercial Ni-Mo/γ-Al_2O_3 (HDS 9A, American Cyanamid; NiO 3.5%, MoO_3 18%, Na_2O 0.04%, Fe 0.05%, Al_2O_3 balance).

O-Ethylaniline was used as received (Aldrich Chemical Co., over 99% purity). Solvent n-hexadecane was supplied by Humphrey Chemical Company.

The detailed operating conditions are shown in Table 1. A 300 c.c. autoclave was used in batch mode. The reactor temperature was controlled to ±2°C. The catalyst was presulfided for two hours with a mixture of 10 vol % H_2S in H_2 at atmospheric pressure and 400°C. In order to maintain the catalyst in the sulfided form during the reaction, 0.05 wt % CS_2 solution in hexadecane was added to injection tubing together with catalyst and reactant. Under the operating conditions carbon disulfide rapidly converts to methane and hydrogen sulfide.

Reaction products were analyzed with a Perkin-Elmer Model 3920 gas chromotograph equipped with a flame ionization detector and an electronic integrator.

TABLE 1

EXPERIMENTAL CONDITIONS

Temperature:	350°C
Total Pressure:	500 psig
Catalyst:	Ni-Mo/Al_2O_3, 150-200 mesh sulfided for 2 hours at 400°C in the presence of 10% H_2S/H_2
Catalyst loading:	0.5 wt %
CS_2 conc. in feed:	0.05 wt %
Carrier oil (solvent):	n-hexadecane
Reactant Conc.: (OEA or QNO)	1 wt %
Autoclave Volume:	300 c.c.

Results and Discussion:

The results from o-ethylaniline hydrodenitrogenation runs are discussed below.

The results of a standard run are shown in Figure 4. O-ethylaniline was rapidly converted to ethylbenzene and ethylcyclohexane. Preliminary studies show that indoline was also present in the reaction products. There were no other nitrogen-containing compounds detected.

It can be seen from Figure 4 that formation of ethylbenzene and ethylcyclohexane was relatively rapid while the conversion of o-ethylaniline to indoline was relatively slow. Figure 4 shows that both ethylcyclohexane and ethylbenzene are the primary products of the reaction. As shown in Figure 5, the initial concentration of ethylbenzene is higher than the concentration of ethylcyclohexane (network I). While after initial 40 minutes the concentration of ethylcyclohexane increases very rapidly while the concentration of ethylbenzene remains approximately constant.

Based on the results presented in Figures 4 and 5, two different reaction networks can be defined as shown in Figure 6. In reaction network I, o-ethylaniline forms ethylbenzene by β-elimination process, which on hydrogenation gives ethylcyclohexane. In network II, o-ethylaniline forms intermediate 1-ethylcyclohexane,which on hydrogenation forms ethylcyclohexane. However, ethylbenzene can also be formed from this intermediate as shown in network II. In network II, the benzene ring of o-ethylaniline first must be hydrogenated to weaken the C-N bond (since aromatic C-N bond and o-ethylaniline is strong due to resonance with the benzene ring) sufficiently for hydrogenolysis to occur. Thus from networks I and II two

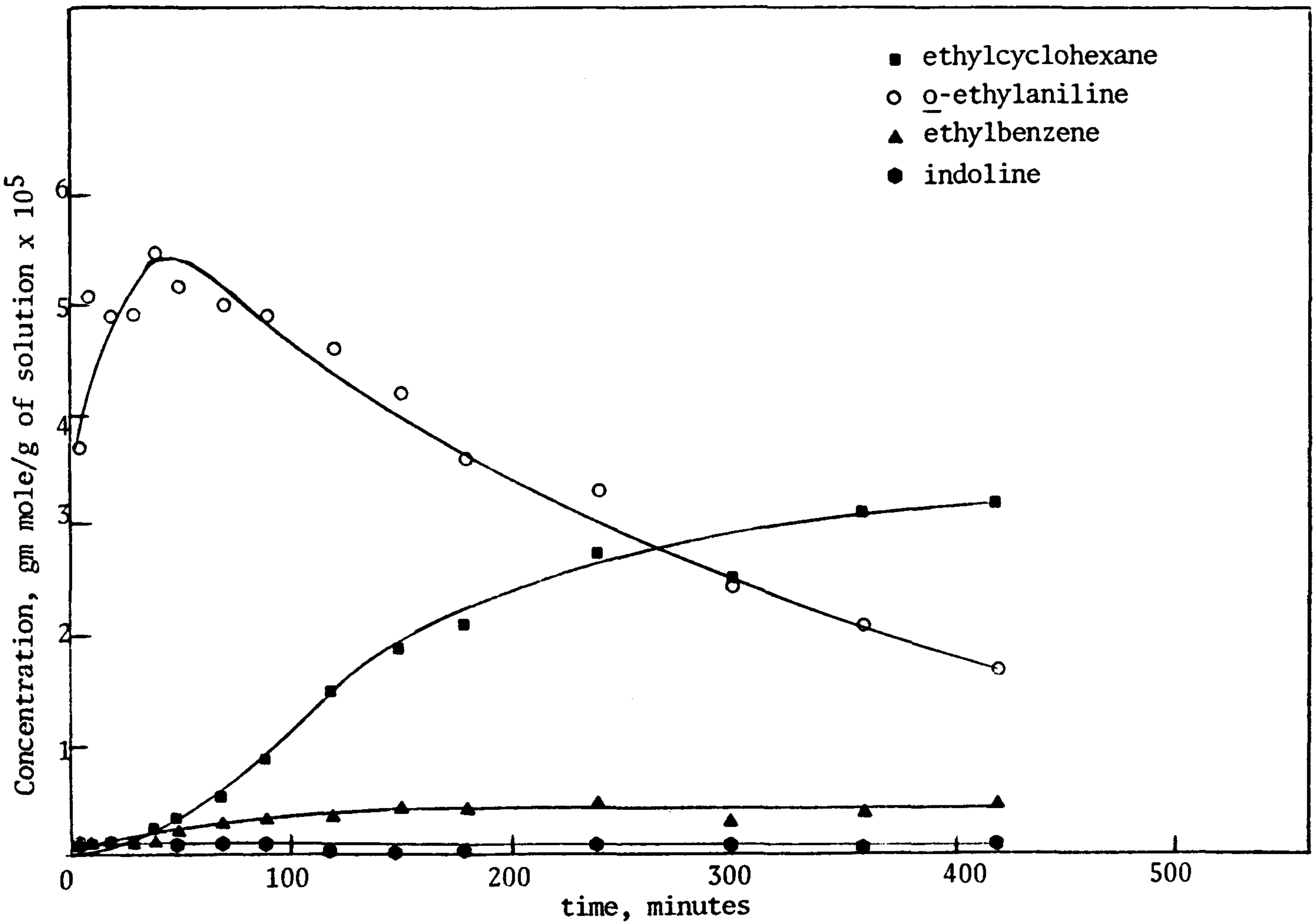


Figure 4. Concentration profiles of various hydrodenitrogenation products of orthoethylaniline.

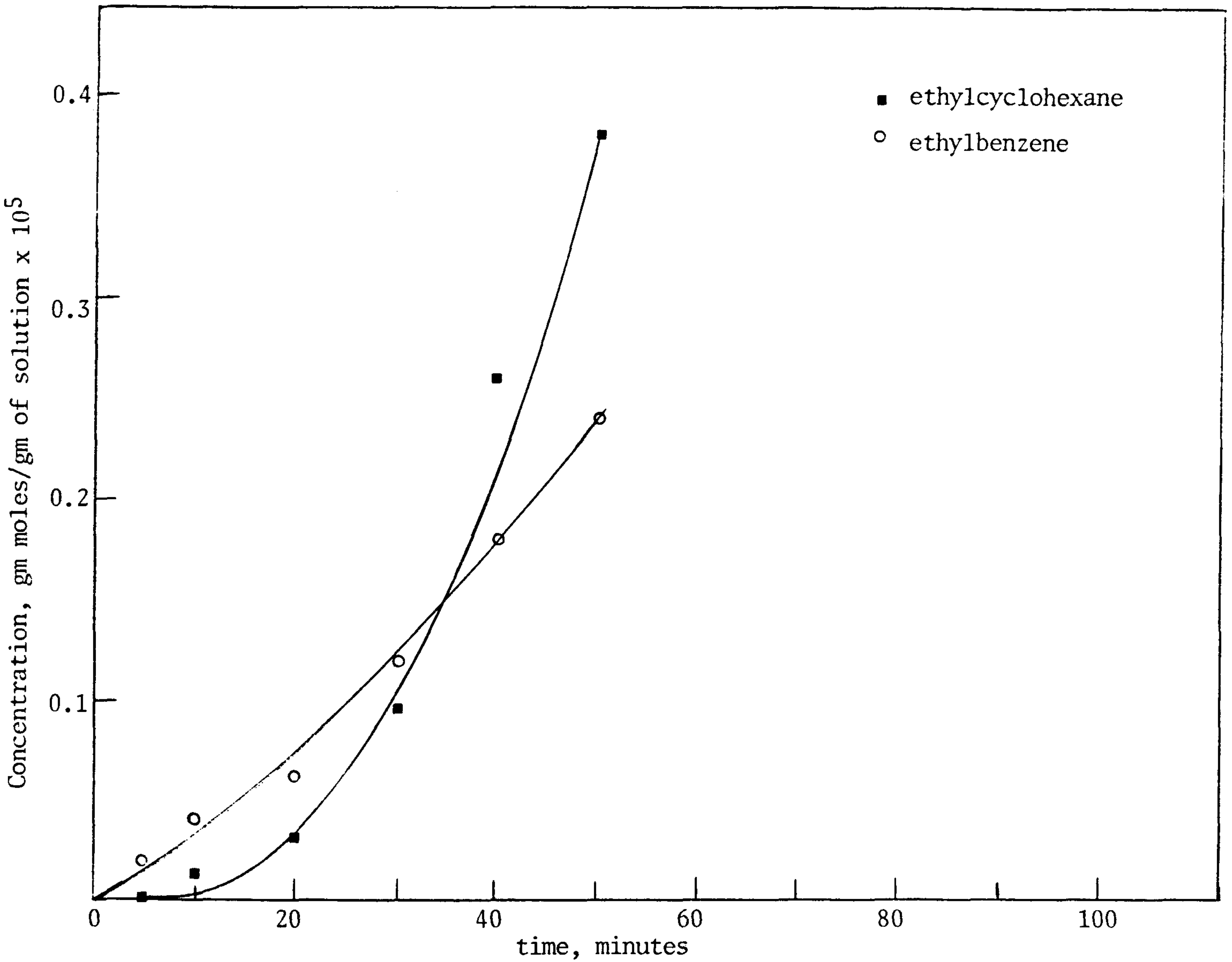
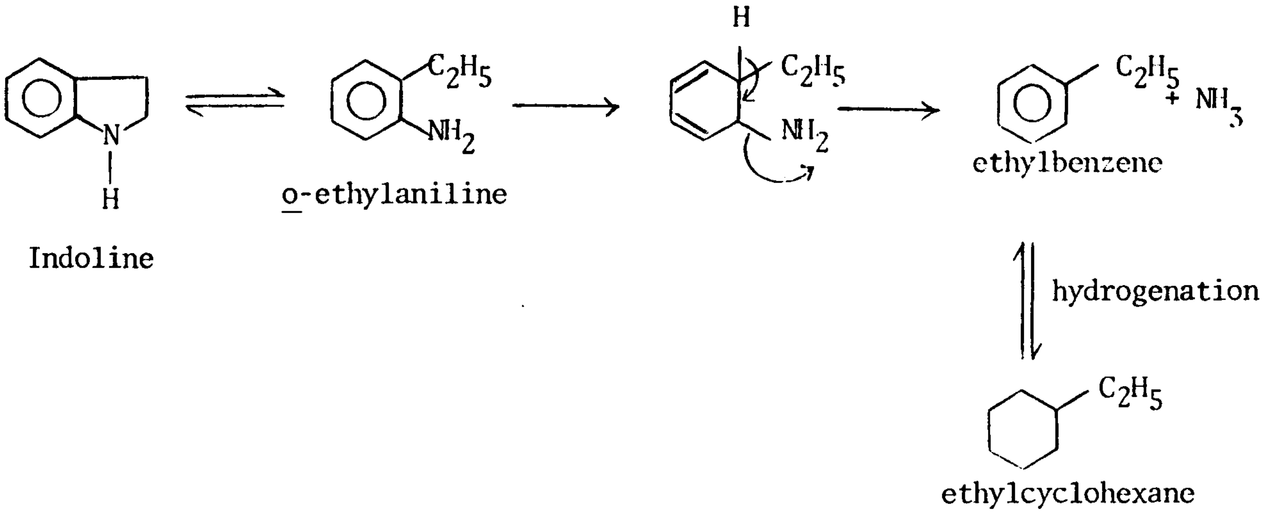


Figure 5. Concentration profiles of ethylcyclohexane and ethylbenzene during the initial period for hydrodenitrogenation of o-ethylaniline.

REACTION NETWORK I



REACTION NETWORK II

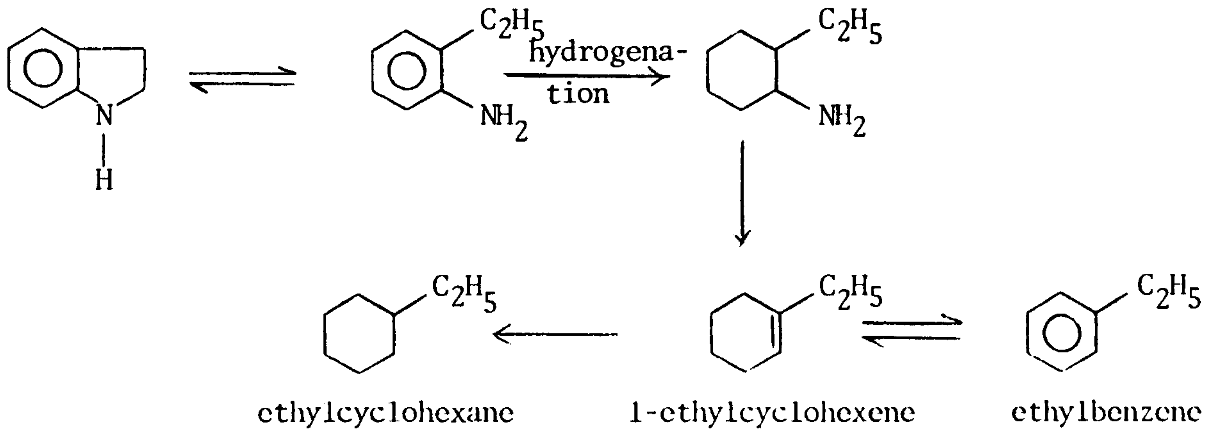


Figure 6. Preliminary networks for hydrodenitrogenation of o-ethylaniline.

different reaction paths are possible and from the present data it is not clear which one is the actual reaction path. There is no dealkylation of the o-ethylaniline as indicated by the fact that benzene and cyclohexane were not present in the reaction mixture.

Two runs will be made to further clarify and define the reaction network more fully for hydrodenitrogenation of o-ethylaniline and other anilines. The first run will be made with o-ethylaniline at a lower temperature (320°C) so that the initial concentration profiles for ethylbenzene and ethylcyclohexane can be studied more closely. In the second run the hydrodenitrogenation of aniline will be studied. This should also be helpful in identifying the intermediates and the reaction network.

Task 2. Development of catalysts which will effect hydrodenitrogenation with only limited or no hydrogenation of the heterocyclic rings present in the molecule.

The objective of this task is to develop uniquely new hydrodenitrogenation catalysts that will selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring thereby reducing hydrogen consumption. Hence, a run was made using a synthesized compound, quinoline-N-oxide to determine whether the addition of oxygen to the quinoline molecule would reduce the aromaticity of the nitrogen-containing ring thereby making it easier to remove nitrogen directly. The results are presented below.

Hydrodenitrogenation of Quinoline-N-Oxide

The work reported here was performed to study the reaction network of catalytic hydrodenitrogenation of quinoline-N-oxide. The main objective of the study was to remove nitrogen.*

Experimental conditions were the same as shown in Table 1. The quinoline-N-oxide was synthesized. The solvent n-hexadecane was supplied by Humphrey Chemical.

Results and Discussion

The quinoline-N-oxide conversion data show (Figures 7 and 8) the presence of propylcyclohexane and propylbenzene products and the intermediates quinoline, 1,2,3,4-tetrahydroquinoline, o-propylaniline, 5,6,7,8-tetrahydroquinoline and decahydroquinoline. The components mentioned above

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*from the quinoline-N-oxide as NO.

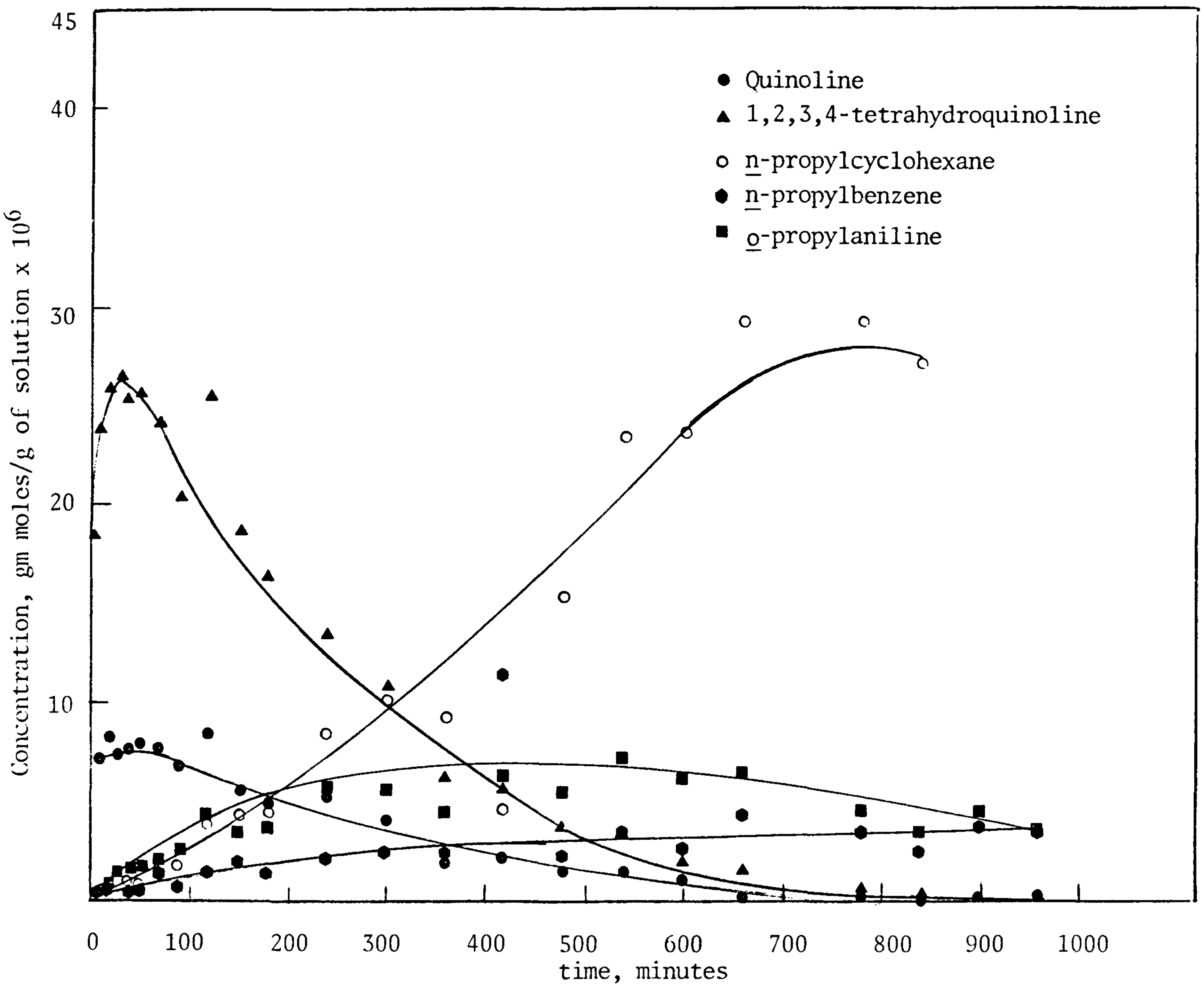


Figure 7. Concentration profiles of various hydrodenitrogenation products of quinoline-N-oxide.

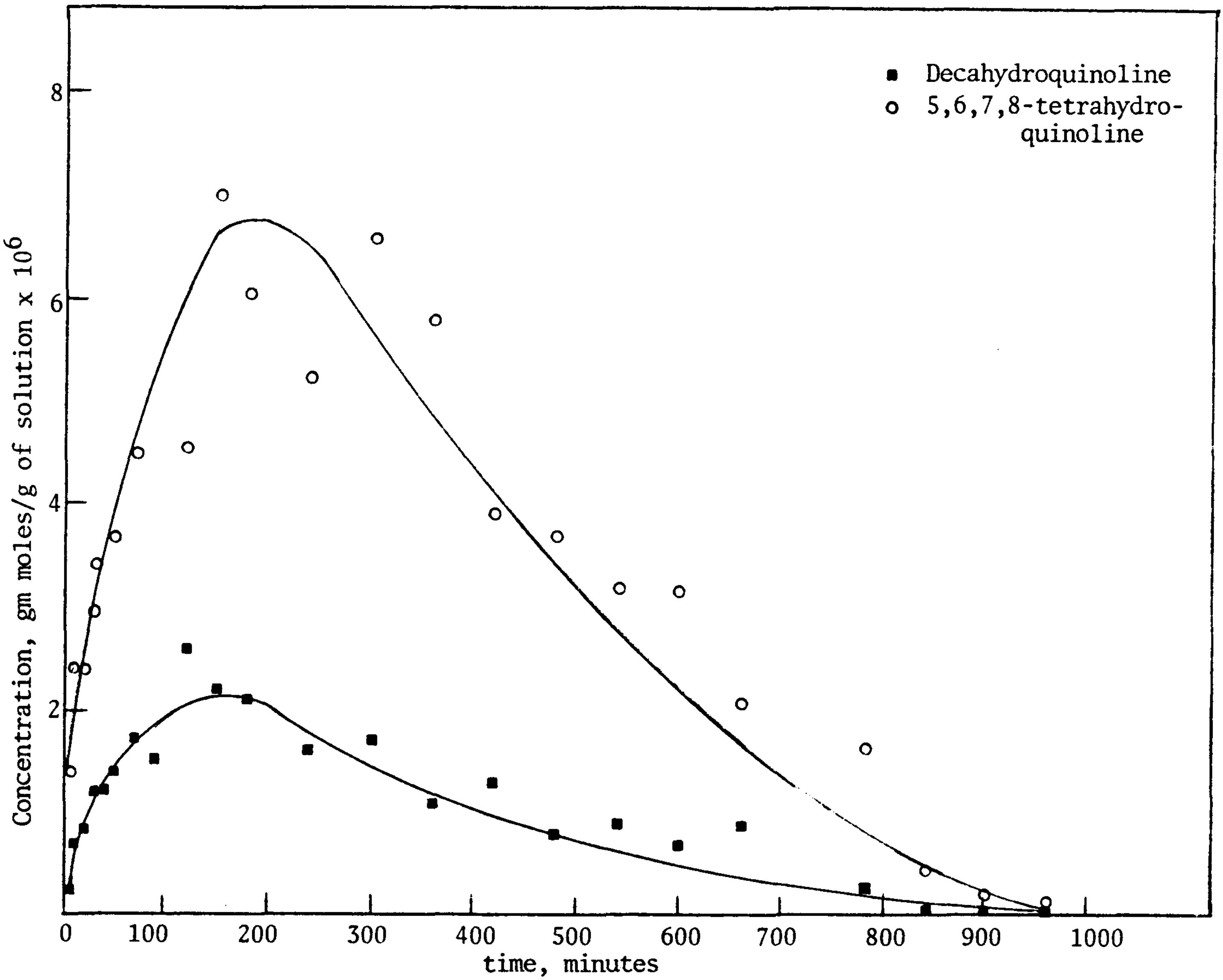


Figure 8. Concentration profiles of various hydrodenitrogenation products of quinoline-N-oxide.

are also present in hydrogenation of quinoline indicating that quinoline-N-oxide changes to quinoline very rapidly by deoxidation of the molecule. The C-N bond is very strong compared to NO bond, and in the presence of hydrogen the NO bond is broken easily resulting in the production of quinoline. The quinoline thus produced is subsequently converted into 1,2,3,4-tetrahydroquinoline, o-propylaniline, propylbenzene, 5,6,7,8-tetrahydroquinoline, decahydroquinoline and propylcyclohexane. A possible reaction network for quinoline-N-oxide hydrodenitrogenation is shown in Figure 9. The reaction network in Figure 9 shows that both benzene and pyridine rings are saturated before the C-N bond is broken.

An infrared analysis of the quinoline-N-oxide in hexadecane shows a -NO band in the stretching region (Figure 10). However, an IR analysis of the reaction product sample does not show -NO band. Disappearance of the NO band indicates that quinoline-N-oxide is rapidly converted to quinoline (Figure 11). To check this rapid conversion of quinoline-N-oxide to quinoline, an experiment has been made by replacing hydrogen with helium and the samples are being analyzed. It is expected that by substituting helium for hydrogen, quinoline-N-oxide may not deoxidize and therefore C-N bond scission may be promoted.

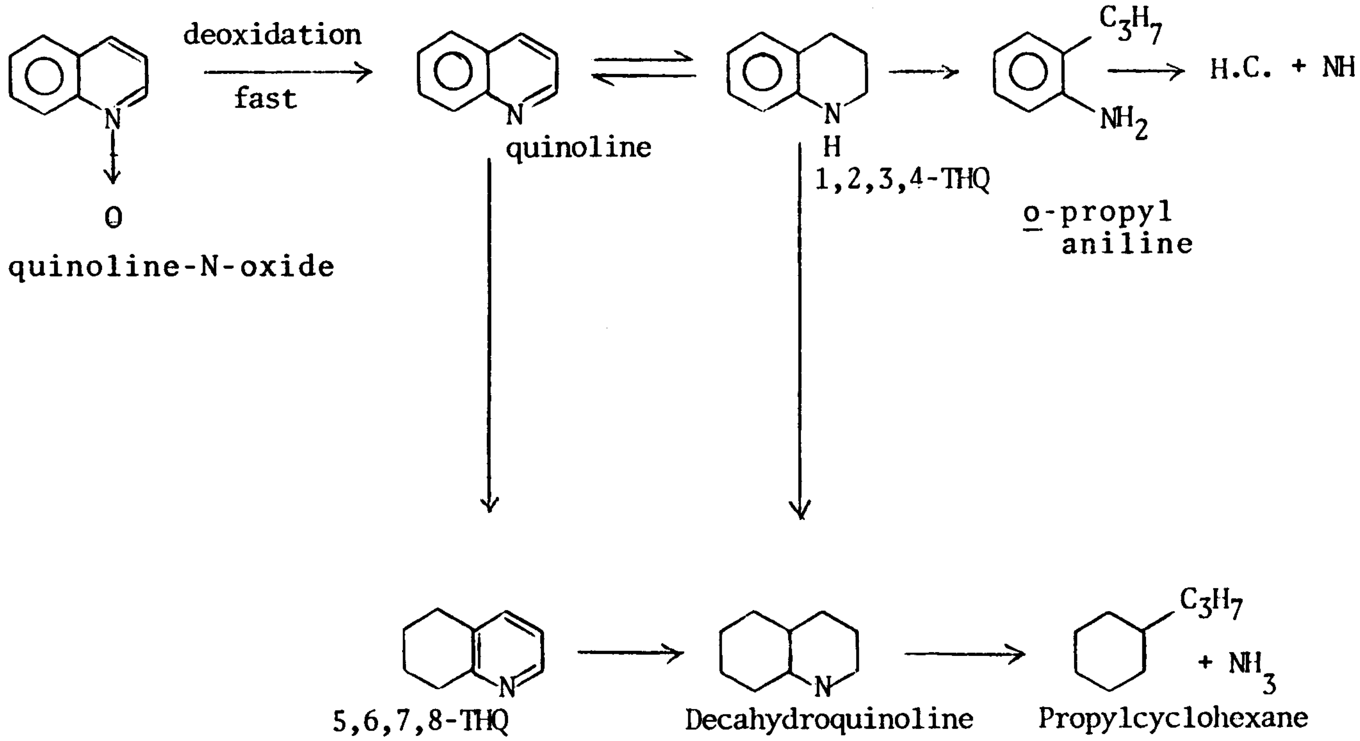
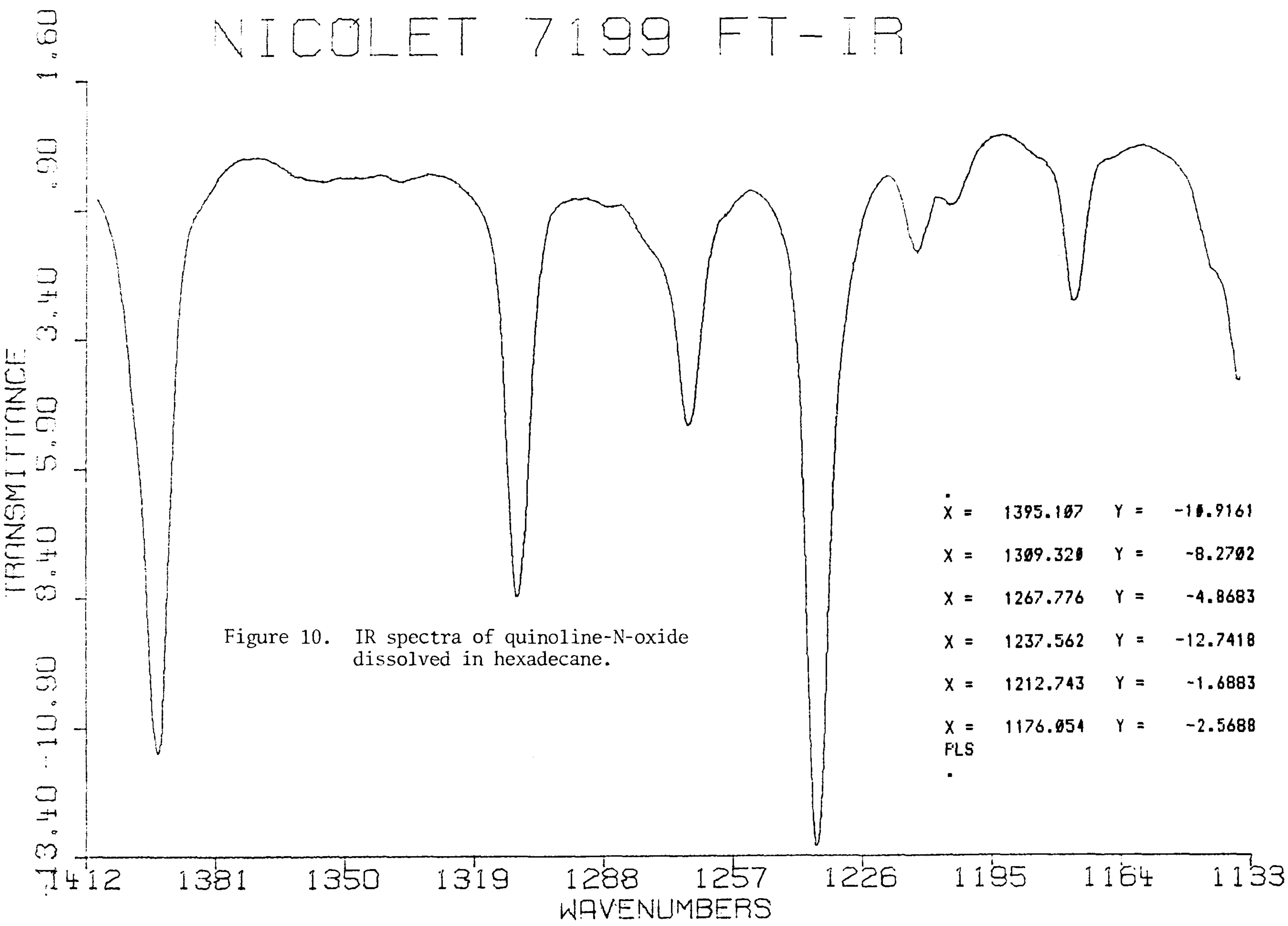


Figure 9. Reaction network for quinoline-N-oxide hydrodenitrogenation.



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.
X =   1395.107   Y =   -10.9161
X =   1309.320   Y =    -8.2702
X =   1267.776   Y =    -4.8683
X =   1237.562   Y =   -12.7418
X =   1212.743   Y =    -1.6883
X =   1176.054   Y =    -2.5688
FLS
.
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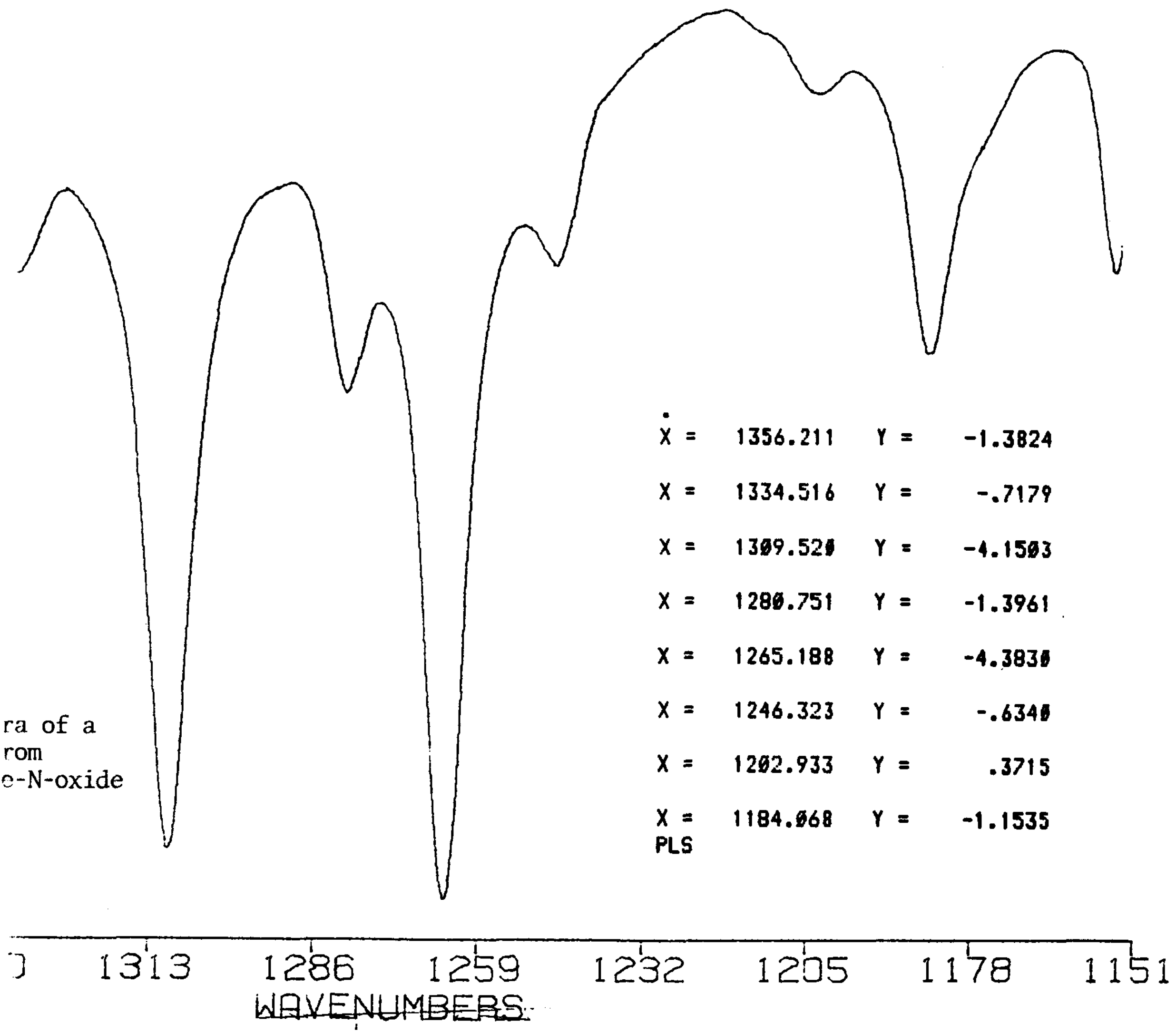
Figure 10. IR spectra of quinoline-N-oxide dissolved in hexadecane.

K-QNO-410-2

ILET 7199 FT-IR



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X =   1356.211   Y =    -1.3824
X =   1334.516   Y =     -.7179
X =   1309.520   Y =    -4.1503
X =   1280.751   Y =    -1.3961
X =   1265.188   Y =    -4.3830
X =   1246.323   Y =     -.6340
X =   1202.933   Y =      .3715
X =   1184.068   Y =    -1.1535
PLS
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1367

V. PERSONNEL

The project started on September 15, 1978. Dr. R. Sivasubramanian, a post doctoral fellow joined this project on October 16, 1978.

APPENDIX A

Tabulated Data for Hydrodenitrogenation Runs

TABLE II

Data From Decahydroquinoline Run Using Glass Liner

Concentration gm moles/gm x 10^5

Sample No.	Time Min.	Benzene	n-propyl cyclohexane	propyl benzene	decahydroquinoline	5,6,7,8-tetrahydroquinoline	quinoline	1,2,3,4-tetrahydro quinoline
1	5				1.585	0.217	0.106	0.096
2	15				1.547	0.173	0.076	0.140
3	30				1.493	0.205	0.080	0.098
4	60				1.474	0.261	0.076	0.111
5	180	0.063	0.037	0.028	0.897	0.380	0.041	0.115
6	300	0.071	0.056	0.009	0.843	0.645	0.060	0.188
7	420	0.085	0.055	0.047	0.643	0.632	0.062	0.156
8	480	0.108	0.060	0.045	0.601	0.844	0.068	0.180
9	540	0.103	0.056	0.048	0.468	0.774	0.059	0.159
10	600	0.087	0.048	0.043	0.405	0.774	0.081	0.154

Operating conditions are given on page 6.

TABLE III

Data From Decahydroquinoline Run Without Glass Liner

Concentration, gm moles/gm x 10^7

Sample Number	Time, Minutes	n-propyl cyclohexane	propyl benzene	decahydro-quinoline
1	5			11.775
2	10			22.486
3	20			25.966
4	30			23.564
5	60			23.397
6	132	1.446		22.773
7	133	2.602	1.609	20.800
8	240	1.798	--	22.072
9	303	4.827	1.699	15.273
10	360	4.815	2.099	15.393
11	420	5.105	1.895	17.237
12	462	3.177	--	15.091
13	923	3.708	1.568	12.05
14	1032	5.204	2.209	7.102

Operating conditions are given on page 6.

TABLE IV

Data From Orthoethylaniline Run

Concentration, gm moles/gm x 10^5

Sample Number	Time, minutes	Ethylcyclo hexane	Ethyl benzene	Orthoethyl aniline	Indoline	Indole
1	5	0.00	0.02	3.70	0.07	0.49
2	10	0.02	0.04	5.10	0.06	
3	20	0.03	0.06	4.90	0.06	
4	30	0.10	0.12	4.90	0.07	
5	40	0.26	0.18	5.50	0.11	
6	50	0.38	0.24	5.20	0.10	
7	70	0.55	0.30	5.00	0.12	
8	90	0.85	0.36	4.90	0.13	
9	120	1.48	0.39	4.60	--	
10	150	1.90	0.41	4.20	--	
11	180	2.10	0.40	3.60	--	
12	240	2.74	0.44	3.30	0.15	
13	300	2.54	0.36	2.50	0.12	
14	360	3.10	0.40	2.10	0.13	
15	420	3.20	0.48	1.70	0.15	

Operating conditions are given in Table I.

TABLE V

Data from Quinoline-N-Oxide Run

Concentration, gm moles/gm x 10^6

Sample Number	Time, Minutes	n-propyl cyclohexane	propyl benzene	deca-hydro quinoline	5,6,7,8-tetra-hydro quinoline	ortho-propyl-aniline	quinoline	1,2,3,4-tetra-hydro-quinoline
1	5	0.30	0.00	0.28	1.55	0.40	13.40	18.80
2	10	0.34	0.28	0.69	2.35	0.35	7.10	24.00
3	20	0.61	0.27	0.83	2.30	0.95	8.20	26.00
4	30	0.75	0.40	1.19	2.95	1.30	7.40	26.80
5	40	1.10	0.55	1.20	3.40	1.60	7.70	25.60
6	50	0.88	0.86	1.40	3.70	1.80	8.00	25.90
7	70	1.76	1.80	1.70	4.50	2.10	7.90	24.10
8	90	1.97	0.93	1.50	4.70	2.70	6.90	20.50
9	120	4.00	1.64	2.60	7.00	4.20	8.60	25.80
10	150	4.20	2.00	2.20	6.10	3.60	5.90	18.90
11	180	4.60	1.40	2.10	5.30	3.80	5.00	16.40
12	240	8.50	2.15	1.60	6.60	5.50	5.30	13.40
13	300	10.10	2.40	1.70	5.80	5.70	4.10	10.90
14	360	9.30	2.30	1.50	3.90	4.50	2.30	6.20
15	420	4.50	11.50	1.30	3.70	6.20	2.20	5.80
16	480	15.60	2.30	0.80	3.20	5.60	1.70	3.80
17	540	24.80	3.40	0.90	3.20	7.10	1.80	3.50
18	600	24.90	2.90	0.66	2.10	6.20	1.40	2.00
19	660	24.10	4.40	0.96	1.70	6.60	0.59	1.80
20	780	29.50	3.50	0.25	0.47	4.90	0.19	0.44
21	840	27.10	2.60	0.00	0.22	3.80	0.00	0.17
22	900	40.70	3.90	0.00	0.14	4.70	0.00	0.00
23	960	38.20	3.80	0.00	0.00	3.80	0.00	0.00

Operating conditions are given in Table I.

APPENDIX B

Review Paper Submitted to "Catalysis Reviews"

PROCESS AND CATALYST NEEDS FOR HYDRODENITROGENATION

SUBMITTED TO "CATALYSIS REVIEWS"

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Abstract

Current hydrodenitrogenation catalysts and processes are essentially an extension of the catalysts and processes used in the petroleum industry for hydrodesulfurization. Limitations exist in the application of the existing catalyst technology to hydrodenitrogenation of synthetic fuels and heavy petroleum feedstocks. This article reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and a more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful directions to be followed in both catalyst and process development.

INTRODUCTION

During the last decade there has been increased interest in the production of synthetic fuels and chemicals feedstocks from coal and oil shale due to declining petroleum reserves. Table I gives the projected gasoline to mid-distillate ratio through the year 2000 and beyond; the shift is away from high-octane fuels requiring a relatively high aromatics content and a relatively low hydrogen content to highly paraffin-based fuels having a high hydrogen content. Figure 1 shows the projected United States energy supply and demand through the year 1990 (2). Current petroleum production in the contiguous United States is about 9 million bbl/day and has declined at a rate of about 0.5 million bbl/day per year for a number of years. Alaskan oil will arrest this decline in production briefly but will not make up for even the loss in the rate of petroleum production incurred in the contiguous 48 states during the last five years. In all probability declining production from current oil fields will not be offset by further new discoveries, and thus the United States will become increasingly dependent on foreign oil. Further, petroleum feedstocks are becoming harder to process as crude quality decreases, and as it becomes more and more necessary to process the bottom of the barrel. Declining oil supply in the face of increasing demand will ultimately require that some of the projected gap be made up with synthetics made from coal and oil shale. Such synthetic feedstocks and heavier petroleum fractions contain higher concentrations of nitrogen than light petroleum stocks, and decidedly more difficult to process, and will place increasing demands on hydroprocessing catalysts and processes.

Table II gives the analysis of several coals and of oil shale. Coal is very aromatic, very low in hydrogen content, and requires addition of considerable hydrogen for its conversion to a liquid. Hydrogen consumption in coal liquefaction and also in hydrotreating coal-derived liquids is high and represents a major cost. Table III presents elemental analyses of two petroleum crudes and of liquids derived from coal and oil shale. The hydrogen content of liquids derived from coal is particularly low in comparison with that for petroleum liquids. Thus without large amounts of hydrogen addition, liquids derived from coal do not fit readily into the changing fuel demands of the future (Table I). Oil shale has a hydrogen content more similar to that of petroleum crude.

Both coal-derived liquids and shale oil contain high nitrogen contents because coal and oil shale contain high concentrations of organic nitrogen. Nitrogen removal from these liquids is necessary because:

- these fuels cannot otherwise be burned without exceeding NO_x emission restrictions;
- nitrogen-containing compounds severely reduce the activity of cracking, reforming, hydrocracking, hydrodesulfurization, hydrogenation and isomerization catalysts (the catalysts used in these processes are acidic and are thus poisoned by nitrogen-containing compounds, which are strongly basic);
- high nitrogen concentrations are detrimental to product quality and properties, including stability;
- heavy petroleum fractions and particularly coal-derived liquids and shale oil that have high aromatic nitrogen contents can be quite carcinogenic and require hydrodenitrogenation to reduce the nitrogen content and the carcinogenicity.

The nitrogen contents typically found in coal-derived liquids and shale oil make hydrodenitrogenation imperative if the liquids are to be refined into the range of products produced from petroleum crude.

The need for more active and more selective hydrodenitrogenation catalysts to process heavier petroleum-based feedstocks and to process future synthetic feedstocks is becoming progressively more imperative. Much research has been directed toward hydrodesulfurization of petroleum feedstocks to reduce sulfur levels to those required for catalytic processing by supported-metal catalysts and to meet SO_x emission levels when the liquid is burned, whereas considerably less research has been directed toward hydrodenitrogenation of heavy petroleum and synthetic feedstocks. Hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, hydrocracking, and hydrogenation all occur simultaneously in hydrotreating petroleum or synthetic liquids. However, hydrotreating catalysts are usually optimized to selectively catalyze one of the above reactions (typically hydrodesulfurization) relative to the others. Since nitrogen-containing compounds are considerably different in their chemistry than sulfur-containing compounds, catalysts that are optimized for hydrodesulfurization are not optimum for hydrodenitrogenation. Hydrodesulfurization catalysts typically remove sulfur quite selectively without excessive consumption of hydrogen, excessive meaning greatly in excess of stoichiometric requirements. Catalysts currently used for hydrodenitrogenation are not selective and require very high hydrogen consumptions to achieve nitrogen removal. Because hydrogen consumption represents a large fraction of the cost of coal liquefaction and of hydrotreating heavy liquids, reduction in the hydrogen requirement in these processes, particularly in hydrodenitrogenation, are highly desirable and must come through improved catalyst technology.

Limitations exist in the application of the existing catalyst technology to hydrodenitrogenation of heavy liquids. New and improved catalysts and process concepts are required to allow more efficient and less costly hydrodenitrogenation of heavy feeds. A breakthrough, similar to the introduction of zeolite cracking catalysts in the late fifties, is needed in the development of hydrodenitrogenation catalysts. This article briefly reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and a more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful directions to be followed in both catalyst and process development.

REACTION CHEMISTRY

Nitrogen-Containing Compounds

Knowledge of the types, quantities, and chemical behavior of the nitrogen-containing compounds present in petroleum fractions and synthetic liquids is important for the development of improved catalysts and processing techniques for their removal. A brief review of the nitrogen-containing compounds present in petroleum crudes and in synthetic liquids is presented in this section.

Most of the nitrogen present in these liquids is found in heterocyclic compounds which are resistant to hydrodenitrogenation (Table IV). Non-heterocyclic nitrogen-containing compounds are present in liquid fuels in small concentrations and include aliphatic amines, and nitriles. These non-heterocyclic nitrogen-containing compounds are relatively more reactive for hydrodenitrogenation than are heterocyclic nitrogen-containing compounds. The low concentrations and relatively high reactivity of non-heterocyclic nitrogen-containing compounds means that they are of little engineering significance in hydrodenitrogenation. The heterocyclic nitrogen-containing compounds in petroleum and synthetic liquids derived from coal and oil shale can be subdivided into basic or non-basic fractions (Table IV).

Several studies of the nature of the nitrogen-containing compounds in petroleum have been made. Snyder (6) found indoles, pyridines and their higher benzologs in a California petroleum and found that the nitrogen concentration increased with increasing boiling point of the petroleum fractions. One and two ring heterocyclic nitrogen-containing compounds (pyridines, quinolines, pyrroles and indoles) predominated in the lighter fractions, whereas large multi-ring nitrogen-containing compounds were concentrated in the heavier fractions. Pyridines and quinolines have been identified in a cracked gasoline (7), quinolines, pyridines and anilines were found in a catalytically cracked jet fuel (8), and quinolines, benzoquinolines, hydroxybenzo-quinolines have been identified in a straight-run heavy-gas oil (9). Brandenburg and Latham (10) characterized the classes of nitrogen-containing compounds in the 130 to 350°C distillate fraction of a Wilmington petroleum.

By comparison, less information is available on the nitrogen-containing compounds in synthetic liquids; nitrogen concentrations are typically two to five times those in petroleum. Quader _et_ _al_. (11) reported that pyridines, quinolines, pyrroles, indoles and carbazoles are the principal heterocyclic nitrogen-containing compounds present in low-temperature coal tars. Anderson and Wu (12) compiled the physical properties for many nitrogen-containing compounds found in coal carbonization liquids. McNeil (13) listed compounds boiling above 300°C which have been identified in high-temperature coal tars or pitches. Characterization of coal-derived liquids carried out in several laboratories indicate that similar types of nitrogen-containing compounds are present in petroleum liquids, coal-derived liquids, and shale oil (14-16).

Wolk _et_ _al_. (17) found that there was a steady increase in the nitrogen content of coal-derived liquids as the average boiling point increased, in agreement with the behavior found by Snyder (6) for petroleum fractions. Dinneen _et_ _al_. (18) determined the types of nitrogen-containing compounds present in the gas oil fractions of a shale oil and presented the data in terms of the number of aromatic rings in the molecule. On this basis, single-ring nitrogen-containing compounds comprised about 35% of the nitrogen present in the gas oil, indoles and quinolines made up 25%, and the remaining 40% was found in multi-ring nitrogen-containing compounds, many of which contain both oxygen and nitrogen. Dinneen _et_ _al_. (18) found only small quantities of pyrroles.

The above studies indicate that most of the nitrogen-containing compounds in petroleum are also found in synthetic liquids and are heterocyclic in nature. The nitrogen-containing compounds are generally divided into basic and non-basic compounds; non-basic compounds are converted into basic compounds upon hydrogenation. High molecular weight compounds frequently contain sulfur and oxygen in addition to nitrogen. Since most of the nitrogen-containing compounds are common in both petroleum and synthetic feedstocks, generally the principles of hydrodenitrogenation of petroleum liquids will apply for hydrodenitrogenation of coal-derived liquids and shale oil. However, the synthetic liquids because of their higher nitrogen content, their high aromaticity and low hydrogen content are difficult to hydroprocess and require special considerations.

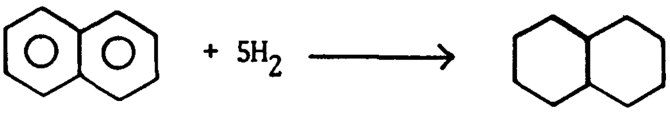
Reactions and Reaction Networks

Hydrodenitrogenation involves hydrogenolysis of the carbon-nitrogen bonds in nitrogen-containing compounds to give ammonia and the corresponding hydrocarbon. The overall reaction can be represented by

$$\underset{\text{compound}}{\text{Nitrogen-containing}} + H_2 \xrightarrow{\text{catalyst}} NH_3 + \text{denitrogenated organic compound} \qquad ($$

Under industrial conditions hydrodenitrogenation is always accompanied by other hydrotreating reactions such as hydrogenation, hydrocracking, hydrodeoxidation, demetallization and hydrodesulfurization, in addition to coking. A summary of these reactions is given below.

Hydrogenation of unsaturated compounds, particularly polynuclear aromatic compounds, e.g.,



(2)

Hydrocracking involves scission of C-C bonds with hydrogen addition, e.g.,

$$RCH_2CH_2R' + H_2 \rightarrow RCH_3 + R'CH_3. \qquad (3)$$

Hydrogenation and hydrocracking consume large quantities of hydrogen and are exothermic.

Demetallization reactions, e.g.,

$$\text{Organo-Ni} + H_2 \xrightarrow{\text{catalyst}} \text{organic compound} + \text{Ni} \qquad (4)$$

also accompany hydrodenitrogenation since heavy feedstocks frequently contain significant concentration of organometallic compounds. The metals in the presence of sulfur such as H_2S are converted to metal sulfides

$$2Ni + 3H_2S \longrightarrow Ni_2S_3 + 3H_2 \qquad (5)$$

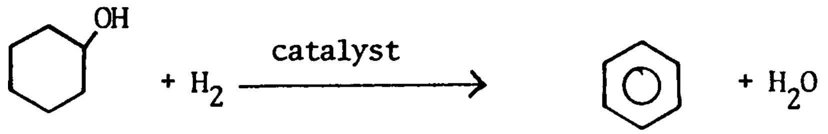
These metal sulfides plug the pores of the catalyst, thereby leading to catalyst deactivation. Coking reactions also occur during hydrodenitrogenation.

Since most petroleum and synthetic liquids always contain sulfur-containing compounds, hydrodesulfurization also takes place, e.g.,

$$+ 4H_2 \longrightarrow H_2S + C_4H_{10} \qquad (6)$$

The reaction network for hydrodesulfurization of dibenzothiophene under high-pressure liquid-phase conditions is shown in Figure 2 (19). Numbers on the arrows are pseudo-first-order rate constants for each reaction at the indicated reaction conditions; the reaction involves direct sulfur extrusion to give biphenyl with greater than 95% selectivity, and further hydrogenation of the hydrocarbon products is considerably slower. For a Ni-Mo/Al_2O_3 catalyst at more severe reaction conditions the fraction of the reaction involving the ring hydrogenation prior to sulfur removal increases.

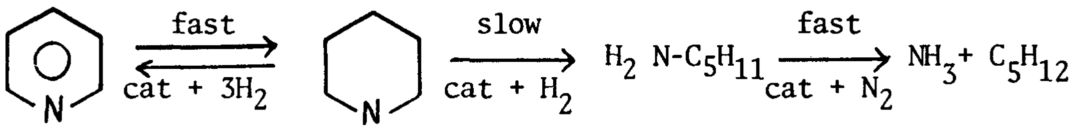
Hydrodeoxygenation involves hydrogenation to form although the details of the reaction network is not known, e.g.,



(7)

Hydrodenitrogenation of aromatic nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings followed by carbon-nitrogen bond scission, in contrast to hydrodesulfurization which involves mainly direct scission of carbon-sulfur bonds. Although it is generally accepted that nitrogen removal from aromatic-ring compounds takes place through an initial saturation of the ring (hydrogenation) followed by breaking of the carbon-nitrogen bonds (hydrogenolysis), the kinetics of the reaction network are not established, particularly for complex nitrogen-containing compounds under industrial hydrotreating conditions. To understand how the catalyst affects the relative rates of hydrogenation and of carbon-nitrogen bond scission in the complex nitrogen removal network, it is necessary to quantitatively define the reaction network and the kinetics of the individual reactions within the network. Knowledge of the reaction networks and reaction kinetics involved in the hydrodenitrogenation of nitrogen-containing compounds present in synthetic liquids and heavy petroleum fractions is essential to the rational design of improved hydrodenitrogenation catalysts.

The reaction network for pyridine-hydrodenitrogenation as demonstrated by McIlvried (20) on sulfided Co-Ni-Mo/Al_2O_3 and by Sonnemans et al. (21) on unsulfided supported Mo/Al_2O_3 is



(8)

Sonnemans et al. (21) found that piperidine can undergo disproportionation reactions that can be quite important in the overall reaction scheme.

Reaction networks become more complex as the nitrogen-containing compound becomes more complex. Shih et al. (22) and Zawadzki et al. (23) defined the reaction networks and associated reaction kinetics for quinoline and acridine hydrodenitrogenation respectively. Figures 3 and 4 present the reaction networks for quinoline and acridine hydrodenitrogenation; the pseudo first-order rate constants for each individual reaction in the network is given on the arrows for the reaction conditions indicated. These results show that hydrodenitrogenation of quinoline and of acridine involves first hydrogenation of the aromatic rings, with hydrogenation of the nitrogen-containing ring being favored kinetically, which is followed by carbon-nitrogen bond scission. Carbon-nitrogen bond scission occurs only in saturated rings. The carbon-nitrogen bond associated with an aniline-type species is stabilized by resonance with the aromatic ring, and thus the aromatic ring may require hydrogenation prior to carbon-nitrogen bond scission. Under representative commercial reaction conditions both hydrogenation and carbon-nitrogen bond scission are kinetically important, and hydrodenitrogenation is not characterized by a rate limiting step. These results clearly show that hydrodenitrogenation involves two distinct reaction types, hydrogenation and carbon-nitrogen bond scission. Because of the bifunctional nature of hydrodenitrogenation reactions, catalysts having both hydrogenation and bond breaking functions are required. The most effective evaluation and development of new and improved catalysts for hydrodenitrogenation requires quantitative determination of the rate of each of the reactions within the reaction network or at least of the hydrogenation as compared with the hydrogenolysis reactions.

The reaction network data for hydrodenitrogenation of aromatic nitrogen-containing compounds clearly show how <u>non-selective</u> current hydrotreating catalysts are for hydrodenitrogenation, in contrast with the high selectivity of these catalysts for hydrodesulfurization (Figures 3 and 4 vs. Figure 2). These data also clearly show the reason for high hydrogen consumption in hydrodenitrogenation; in addition to having to saturate the aromatic rings associated with the nitrogen-containing compounds other aromatic species in the oil are simultaneously being hydrogenated. Thus the highly aromatic nature of coal-derived liquids results in excessive hydrogen consumption and in processing costs. Because of the complexity of the hydrodenitrogenation reaction networks, involving hydrogenation and carbon-nitrogen bond scission as distinct reactions, the evaluation and further development of hydrodenitrogenation catalysts can be greatly aided by knowledge of the kinetics of the various intermediate reactions in the network. Further it is extremely important that the nature of the active sites involved in hydrogenation and in carbon-nitrogen bond scission and the mechanism of these reactions be adequately defined and understood; this is not the situation now.

PROCESSES

Processes designed for hydrodenitrogenation of heavy petroleum fractions and synthetic liquids are essentially an extension of the processes used in the petroleum industry for hydrodesulfurization. The liquid feedstock is mixed with hydrogen and passed over a catalyst, typically in a trickle-bed reactor, at high temperature and pressure. The extent of nitrogen removal depends on the nature of the feedstock, the severity of reaction conditions, and the type of catalyst. Operating conditions for hydrodenitrogenation of petroleum feedstocks typically include: reaction temperatures from 300 to 400°C, pressures from 30 to 200 atm, hydrogen flow rates from 300 to 10,000 scf/bbl of oil and space velocities from 0.2 to 10 hr^{-1} (Table V). However, synthetic liquids and heavy petroleum fractions require more severe operating conditions than those required for lighter petroleum liquids and consume more hydrogen. Table V presents typical operating conditions used in hydrotreating petroleum and synthetic liquids.

A simplified flow diagram of a hydrodenitrogenation process is shown in Figure 5. Hydrogen separated from the product stream is scrubbed to remove H_2S, NH_3, and light hydrocarbons and is recycled to the process, with added make-up hydrogen. The individual components of the process include: preheat furnace, reactor, hydrogen recycle facilities and product separation train. Reactors are typically of the trickle-bed type with oil "trickling" down over the catalyst and high-pressure hydrogen flowing cocurrent with the oil. The catalyst bed is fixed, the flow pattern of liquid and gas is essentially plug flow, and the liquid hold up is low. The heat effect due to reaction for light petroleum feeds in a single-stage reaction is typically not a major problem, and the trickle-bed reactor is preferred because of its simplicity and because a plug-flow reactor is smaller than a stirred-tank (ebullated-bed) reactor for a given conversion. At high operating pressure reactor size is important to process capital investment.

For the more severe operating conditions which are required to achieve high degrees of nitrogen removal from coal-derived liquids, shale oils and heavy petroleum residua, multiple-bed reactors may be required to limit the temperature rise in a given reactor (Figure 6). Cold hydrogen is injected between the beds to reduce the temperature of the reactant stream. In multiple-bed reactors, the amount of catalyst in each bed may be the same, or the downstream bed may contain more catalyst. The quantity of hydrogen injected between beds is adjusted to achieve the desired axial temperature profile. For "dirty" feeds a guard bed containing a cheap, disposable material to take out metals, particulate matter and rapid-coking components may be desirable to extend the life of the catalyst in the reactor. Two guard beds may be included so that one can be used alternately while the catalyst in the other is replaced.

When the feed is particularly heavy and high in nitrogen and sulfur contents, two separate recycle stages, one for each reactor, may be required for more efficient process operation (Figure 7). Scrubbing the light gases out of the hydrogen between stages increase the partial pressure of hydrogen in the second reactor for a given total operating pressure and removes NH_3 and H_2S which inhabit the rates of heteroatom (S and N) removal.

An alternative reactor type is the ebullated-bed reactor; the H-oil process utilizes an ebullated-bed reactor to hydrotreat petroleum residua. However, this type of reactor has received limited application to date. For heavier liquids such as coal-derived liquids and heavy petroleum residua the ebullated-bed reactor may be the reactor of choice because of rapid catalyst deactivation caused by these liquids. The ebullated-bed reactor allows catalyst to be removed continuously and regenerated, if possible, or replaced with fresh catalyst. An ebullated-bed reactor, being essentially a continuous-flow stirred-tank reactor with respect to the liquid, requires a larger reactor volume for a given conversion than a plug-flow trickle-bed reactor; for high conversion this size difference is quite large. Thus, for high conversions ebullated-bed reactors may be staged. Further, the larger reactor volume required for the ebullated-bed reactor can be partially offset by increased operating temperature, but this leads to increased hydrocracking and increased rates of catalyst deactivation. Also, smaller particles (<0.8 mm) of catalyst can be used in an ebullated-bed reactor than are feasible in a trickle-bed reactor, reducing intraparticle mass-transfer limitations, which frequently exist with heavier feeds. The design of both reactor types is straightforward based on much experience in the petroleum industry. The required data are rather complete "lumped" analysis of the feed, kinetic rate constants for the feed or pilot plant data over the desired conversion range, and catalyst deactivation rates for the feedstock.

In operation, the temperature of the trickle-bed reactor is increased with time to compensate for catalyst deactivation and to maintain constant conversion. However, there is an upper limit on the temperature since the rate of hydrocracking and of coking increases strongly (possibly exponentially) with increasing temperature leading to high heat release rates and hot spots, to rapid catalyst deactivation, and ultimately to plugging of the reactor. It is most desirable to start the reactor with a freshly regenerated catalyst or with fresh catalyst at the lowest possible temperature because this should result in the lowest initial rate of catalyst deactivation and the longest run time between catalyst regeneration or replacement. Thus high catalyst activity is equally as important as high catalyst selectivity. If the deactivation is due predominantly to coking, the catalyst can be regenerated by controlled combustion of the coke off the catalyst; satisfactory regeneration techniques have not been developed if deactivation is due to metals or mineral matter deposition.

CATALYSTS

Catalysts consisting of Mo(W) and Ni(Co) supported on gamma alumina or gamma alumina stabilized with minor amounts of silica are commonly used for hydrodenitrogenation. Table VI summarizes the chemical composition and physical properties of commercial hydrotreating catalysts, emphasizing the wide range of critical physical and chemical properties (28). The most frequently used metal combinations are Co-Mo, Ni-Mo, Ni-Co-Mo and Ni-W. Co and Mo, commonly referred to as cobalt molybdate is normally used for hydrodesulfurization. Ni with W or Mo are frequently the choice for hydrodenitrogenation. Typically as the concentration of active metals is increased, the catalyst activity increases, through a maximum and then decreases. However, as the active metals concentration increases, the catalyst cost increases.

Hence, the optimum concentration of active metals involves a balance between obtainable activity and cost. The preferred industrial catalysts for hydrodesulfurization contain 2 to 4 wt % Co as CoO and 8 to 17 wt % Mo and MoO_3. Beuther et al. (29) reported that commercial preparations consist of cobalt and molybdenum in atomic ratios of 0.1:1.0 to 1.0:1.0; maximum activity was observed for ratios around 0.3:1.0. In the case of Ni-Mo catalysts they observed a maximum activity for an atomic ratio of 0.6:1.0. Ahuja et al. (30) studied the activity and selectivity of presulfided hydrotreating catalysts and evaluated many combinations of metals and supports. They concluded that nickel-promoted catalysts are better for hydrodenitrogenation than cobalt-promoted catalysts since nickel promotes hydrogenation.

Industrial catalysts are typically extrudates with dimensions of 1.5-3 mm. The particle size is usually chosen to be as small as possible so as to minimize intraparticle mass transfer, particularly for heavy feedstocks with the lower limit on particle size being set by pressure drop through the catalyst bed.

The effect of physical properties of the catalyst support on catalyst activity has recently been the subject of many investigations. Livingston (31) showed that support properties can have a significant effect on hydrotreating catalyst performance. On the other hand, Van Zoonen and Douwes (32) showed that volume average pore radius in the range of 33 to 232 Å had a negligible effect on hydrodenitrogenation of a Middle East gas oil. Similar results were obtained by Satehell (33) for hydrodenitrogenation of raw anthracene oil and by Kovach et al. (34) for hydrogenation over coal liquefaction catalysts. Sooter and Crynes (35) found that reducing the average pore radius from 35 Å to 25 Å for a Co-Mo/Al_2O_3 catalyst resulted in a reduction of the hydrodesulfurization activity for raw anthracene oil. Chiou and Olson (36) simulated the catalytic behavior in the H-coal process. They showed that under certain conditions improvement in catalyst life and activity could be obtained by proper selection of the pore-size distribution. Kang and Gendler (37) found that for hydrodenitrogenation of heavy coal-derived liquids, increasing the amount of macropore volume for a Ni-Mo/Al_2O_3 resulted in increased activity on a weight basis. Sivasubramanian and Crynes (38) found for the hydrodenitrogenation of raw anthracene oil with essentially no ash content that changes in pore-size distribution did not affect nitrogen removal and that a bimodal pore-size distribution did not offer aky obvious advantages over a monodispersed pore-size distribution. However, they found that a reduction in surface area resulted in a reduction in nitrogen removal.

The literature contains conflicting data on the effect of pore size and surface area on the activity of hydrotreating catalysts. Decreasing pore size could increase the pore diffusion resistance and also restrict larger molecules from reaching the active catalyst surface. In the case of hydrodesulfurization, for which the effectiveness factor is frequently somewhat less than 1.0, diffusion resistance may cause the observed catalyst activity to decrease with decreasing pore size. Whereas, hydrodenitrogenation, being slower than hydrodesulfurization, may not be affected by diffusional limitations, and thus within a reasonable range variations in pore size will not affect the observed catalyst activity. Thus the catalytic activity will be proportional to the available active surface area. However, with higher molecular weight nitrogen-containing compounds, decreasing pore size may result in the appearance of diffusional limitations. For liquids containing large amounts of mineral matter large pores are frequently desirable because they can tolerate more mineral matter deposition before being plugged and thus promote increased catalyst life.

HYDRODENITROGENATION DIFFICULTY

Hydrodenitrogenation is typically more difficult than hydrodesulfurization as shown in Table VII. For all three coal-derived liquids the same Co-Mo/Al_2O_3 catalyst was used. Typically as the boiling point and complexity of the feedstock increases, nitrogen removal becomes more difficult.

The differences in difficulty of hydrodesulfurization and hydrodenitrogenation and the need to hydrogenate aromatic ring systems in the case of hydrodenitrogenation before carbon-nitrogen bond scission can occur are partially explained by the relative carbon-carbon, carbon-nitrogen, and carbon-sulfur bond strengths in aromatic and saturated systems (Table VIII). Carbon-nitrogen bonds are always stronger than carbon-sulfur bonds. Carbon-nitrogen bonds are slightly stronger than carbon-carbon bonds in aromatic systems; the relative bond strengths (carbon-nitrogen vs. carbon-carbon) are reversed upon hydrogenation.

The difficulty of hydrodenitrogenation typically increases with increasing boiling point of the feedstock; hydrogen pressure also plays a major role in the rate of nitrogen removal. For heavy vacuum gas oils and residua, substantially complete nitrogen removal was difficult even at

409 atm (42). Haensel et al. (42) found that progressively lower nitrogen concentrations in the product could be attained with increasing hydrogen partial pressure to 1600 atm.

Flinn et al. (43) postulated that the difficulty of nitrogen removal increases with increasing boiling point of the fraction because the increasing size of the non-nitrogen-containing part of the molecule reduces the accessibility to the catalytic surface. However, Sarbak et al. (44) have shown that the pseudo first-order rate constants and relative reactivities of important polynuclear aromatic nitrogen-containing compounds found in coal-derived liquids decrease to four ring nitrogen-containing compounds and then increase for larger molecules (Table IX). These data question the conclusion that one of the reasons hydrodenitrogenation becomes more difficult with increasing boiling range is increasing size of the nitrogen-containing molecule. Since these data were obtained with single compounds dissolved in white oil, other factors may cause decreasing reactivity for hydrodenitrogenation with increasing boiling point for real feedstocks. These factors include:

- formation of nitrogen-containing secondary products during hydrodenitrogenation which are more resistant to nitrogen removal than the original ones.
- competitive adsorption by the higher molecular weight highly-aromatic molecules in the feedstock
- self-inhibition by the high concentration of nitrogen-containing compounds
- more severe catalyst deactivation caused by the higher-molecular weight highly-aromatic compounds in the feedstock.

Recent studies in our laboratory show that aromatic compounds compete only very weakly with nitrogen-containing compounds for adsorption on the catalyst surface and thus do not strongly inhibit the rate of hydrodenitrogenation (45). However, nitrogen-containing compounds strongly inhibit the rates of other hydroprocessing reactions and also inhibit their own rates of reaction by competitive adsorption. Since higher boiling feedstocks typically contain higher concentrations of nitrogen, this self-inhibiting effect results in the requirement of more severe operating conditions to achieve the same extent of nitrogen removal. In view of our results we infer that this is one of the main reasons that hydrodenitrogenation becomes progressively more difficult with increasing boiling point. The increased severity of catalyst deactivation which results from increasing boiling point and decreasing hydrogen content of the feedstock requires severe operating conditions and is another major reason for the difficulty of hydrodenitrogenation or higher boiling feedstocks.

Higher boiling feedstocks typically require higher hydrogen pressures to reduce catalyst deactivation. Catalyst deactivation can be extremely severe with coal-derived liquids because of their high aromatic content and their high coke-forming tendencies. The high aromaticity and high operating pressures required to reduce deactivation and to achieve the desired conversion leads to high hydrogen consumption for synthetic feedstocks.

HYDROGEN CONSUMPTION

High hydrogen consumption is one of the major costs of hydroprocessing heavy petroleum feeds and synthetic liquids. In a balanced petroleum refinery sufficient hydrogen is available from catalytic reforming to meet the needs of hydrotreatment, and therefore the cost of hydrogen is not as important in considering hydrotreating economics. However, when it becomes necessary to generate hydrogen separately as in the case of coal liquefaction or hydrotreating synthetic feedstocks, hydrogen consumption can become a large fraction of the cost of processing, particularly for low quality liquids, such as coal-derived liquids.

Hydrogen consumption data for hydrodesulfurization of Kuwait residuum show that a significant portion of the hydrogen is used to saturate aromatic rings rather than to remove sulfur (Figures 8 and 9). The fraction of hydrogen consumed by reactions other than hydrodesulfurization increases with increasing degree of hydrodesulfurization (Figure 8) and with increasing hydrogen pressure (Figure 9).

Nelson (48) summarizes hydrogen consumption data for hydrodesulfurization of residua (Figure 10). He estimated that in producing fuel oils containing from 0.3 to 1.0 wt % sulfur from atmospheric bottoms 345 to 775 scf/bbl of hydrogen is required, whereas vacuum bottoms require about 870 to 1150 scf/bbl. Nelson also estimated the stoichiometric amount of hydrogen consumed in removing the sulfur and nitrogen-containing compounds and compared this with the average hydrogen consumption. A one percent reduction in sulfur content requires an average hydrogen consumption of about 73 scf/bbl whereas a one percent reduction in nitrogen would require a hydrogen consumption of about 300 scf/bbl. Hydrodenitrogenation consumes more hydrogen than hydrodesulfurization since hydrodenitrogenation apparently requires full ring hydrogenation to destroy the aromaticity of the heterocyclic nitrogen compounds prior to nitrogen-atom removal. Hydrogen requirements for heteroatom removal is considerably below (at least several fold) that observed.

Figure 11 shows hydrogen consumption as a function of the amount of nitrogen remaining in the processed shale oil (27). Hydrogen consumption increases as the concentration of nitrogen in the product shale oil is decreased. By the time the nitrogen content had been reduced to 500 to 1000 ppm, the hydrogen consumption was around 2000 scf/bbl. However, the differential amount of hydrogen consumed per unit nitrogen removed is largest at low degrees of nitrogen removal and is markedly less at high degrees of nitrogen removal (Figure 11). This behavior is just opposite to that observed for hydrodesulfurization in which the differential hydrogen consumption increases with the degree of sulfur removal; the difference is due to the fact that in hydrodenitrogenation the heterocyclic ring structures require hydrogenation before carbon-nitrogen bond scission can occur. Thus high hydrogen consumption occurs at low degrees of nitrogen removal, and at high degrees of nitrogen removal differential hydrogen consumption is low because most of the aromatic structures have already been saturated. Figure 12 shows the effect of reactor pressure on hydrogen consumption in hydrotreating an oil derived from a Pittsburgh No. 8 seam coal. The hydrogen consumption increases with increase in pressure and with decrease in space velocity.

Table X summarizes the hydrogen consumptions for hydroprocessing several coal-derived liquids and a shale oil. Hydrogen consumption ranges from 65 to 3740 scf/bbl. Heck and Stein (26) reported that 700-800 scf/bbl of hydrogen was consumed without significant oxygen or nitrogen removal from an SRC recycle solvent. However, for H-coal distillate which is much more saturated than SRC recycle solvent, substantial heteroatom removal was accomplished with lower hydrogen consumption. Heck and Stein speculated that the higher hydrogen consumption for the SRC recycle solvent was due to the hydrogen required in saturating aromatic compounds as a first step in heteroatom removal. This is verified by our results on reaction networks associated with hydrodenitrogenation.

Bertolacini _et_ _al_. (28) measured the hydrogen consumption for coal liquefaction from a single run in an H-Coal pilot plant (Table XI). About 80 percent of the hydrogen consumed ended up in the liquefied coal oil with a major fraction of the hydrogen going to hydrogenate the raw anthracene oil. Oxygen removal consumed about 11 percent of the total hydrogen consumption, whereas hydrodesulfurization and hydrodenitrogenation each consumed about 4 to 5 percent. However, for the run, sulfur removal was 84 percent, but nitrogen and oxygen removal were 33 and 34 percent respectively.

Dabkowski _et_ _al_. (49) estimated the cost of upgrading various coal-derived liquids to turbine fuels; the estimates are presented in Table XII. The hydrogen cost in these cases varied from 26 to 71 percent of the total operating costs depending on the initial quality of the coal-derived liquid and on the extent of upgrading desired. Dabkowski _et_ _al_. also estimated the sensitivity of total upgrading cost to hydrogen cost and found that increasing the cost of hydrogen by \$0.50/MSCF (base H_2 cost assumed to be \$2/MSCF) increases the upgrading costs by \$0.06 to 0.40/MMBTU. The low-end values reported are for a high quality light liquid which is not characteristic of typical coal-derived liquids and shale oils.

Large amounts of hydrogen are consumed even for low extents of nitrogen removal, but incremental hydrogen consumption decreases with increase in nitrogen removal (Figure 11). This is opposite to the behavior observed in hydrodesulfurization and is clearly explained in terms of the reaction networks for hydrodenitrogenation. Simultaneous saturation of aromatics not containing heteroatoms also contributes to high hydrogen consumption and is highly undesirable. Hydrogen consumption typically increases with increased hydrogen pressure and with increased conversion. Since nitrogen removal from petroleum residua and synthetic feedstocks requires severe operating conditions, hydrogen consumption will be higher than for lighter liquids. The hydrogen consumption problem is further complicated by the fact that projected future fuel needs will require an increasing fraction of high hydrogen content fuels (Table I); this is just opposite to the trend in fuel availability. To reduce hydrogen consumption, catalysts are required that can selectively remove nitrogen from aromatic nitrogen-containing compounds without first requiring hydrogenation of the entire ring system. Process requirements combined with catalyst requirements must meet the need for highly selective hydrogen consumption involving only the hydrogen requirement for heteroatom removal and for fuel quality upgrading to achieve the needed product requirements. Small reductions in hydrogen consumption are worth millions of dollars per year at the scale of our fuel consumption.

CATALYST DEACTIVATION

Long catalyst life is essential to hydrotreating processes; catalyst deactivation rates often determine the commercial viability of a process.

Most of the research on hydrotreating catalysts has dealt with their activity for petroleum feedstocks. Catalyst deactivation rates in petroleum hydroprocessing vary from low for light feeds to high for heavier feeds. Petroleum residue hydrotreating has advanced in the last fifteen to twenty years with respect to catalyst activity and stability and is practiced commercially. However, synthetic liquids, particularly coal-derived liquids, are much harder to hydroprocess, cause more rapid catalyst deactivation, and represent another step upward in terms of difficulty of hydrotreating.

The rate of catalyst deactivation can be significantly reduced by increasing the hydrogen pressure, and therefore heavier feedstocks require higher hydrogen pressures. Lighter feeds cause deactivation predominantly by coke laydown. These catalysts are easily and almost completely regenerated by burning the coke off at intervals of 6-12 months and may last up to 10 years. Heavier petroleum fractions may contain high concentrations of Ni and V, e.g., in excess of 300 ppm in many Venezuelan crudes. These metals are deposited on the catalyst causing deactivation by covering the active surface and plugging the pores, frequently at the pore mouths thereby reducing mass transfer into the catalyst. For deactivation caused by metals deposition on the catalyst, regeneration techniques have not been developed, and thus for residue processing, catalyst life may be as short as six months. Hence, deactivation caused by metals deposition is more serious than deactivation due to coke deposition if coke deposition is not excessively rapid.

Synthetic liquids contain predominantly different metals than petroleum liquids. Table XIII gives trace metals analysis for three coal-derived liquids, and for El Palito No. 6 fuel oil. The table shows that the three coal-derived liquids have high iron and titanium contents, whereas the petroleum liquid contains significantly higher levels of vanadium and nickel. The No. 6 fuel oil has a higher than typical Ti concentration. In petroleum liquids, the metals are mostly present as organometallic compounds; however, for coal-derived liquids the nature of the metal-containing species has not been clearly defined.

Table XIV shows the fate of metal components from hydrotreating runs involving Synthoil and an SRC liquid. The table suggests that iron and calcium entered the reactor as particulates, and the majority did not deposit on the catalyst. Titanium, on the other hand, is probably organically complexed, and the majority was reactively deposited on the catalyst.

Kovach et al. (34) investigated the effect of mineral matter on the poisoning of hydrodesulfurization catalysts under coal liquefaction conditions in batch autoclave studies and measured the loss of hydrogenation activity due to the carbonaceous deposits. They found that severe deactivation of catalysts occurs within the first few hours of on-stream coal processing. However, this deactivation is due to carbonaceous deposits, and the catalysts can be regenerated. They also found that K, Na, Mg, Ca, P, Ti, Fe and Si permanently poison the catalyst, but deposition of carbonaceous matter within the catalyst pores suppressed the deposition of metals insoluble in coal-derived liquids. However, organometallics, like titanium, are soluble in coal-derived liquids and hence gain access to the interior catalyst surface and are deposited there in high concentrations.

Catalyst deactivation in processes which directly contact dissolving coal with particulate catalyst has always been found to be very severe. For instance the activity of a Co-Mo/Al_2O_3 catalyst used in the Synthoil process was essentially zero after less than 300 hr on stream; such short catalyst life is not commercially viable in a fixed-bed process.

The results of deRosset et al. ( ) for the hydrotreating of synthoil liquid and solvent refined coal are presented in Figures 13 and 14. One objective of the work using the Synthoil liquid was to reduce the heptane insolubles to below 3.5%. The catalyst activity decreased by about 60% over the first 80 hr on-stream time and remained constant for the remainder of the run (Figure 13). One objective of the work involving the solvent refined coal was to reduce the heptane insoludes to a minimum value. However, as Figure 14 indicates, the percent of heptane insoludes increased continuously with time because of rapid continual deactivation of the catalyst. These results illustrate the difficulty of hydrotreating coal-derived liquids and show that for low quality coal-derived liquids, especially solvent refined coal, hydroprocessing is not commercially feasible.

Estimates of catalyst requirements based on measured deactivation indicate that the H-Coal process would require 1 pound of fresh catalyst per ton of coal processed, whereas the Synthoil process would require 4 pounds of catalyst per ton of coal processed (51). The above estimates were for coal liquefaction. Dabkowski et al. (49) recently estimated the average catalyst requirements for hydrotreating 400^oF^+ fuel oil from the H-Coal process is 0.21 pounds per barrel of feed and that for hydrotreating solvent refined coal is 0.8 pounds per barrel of feed. Therefore the total catalyst requirement for producing an environmentally acceptable fuel oil by the H-Coal process is about 0.5 lb fresh catalyst per bbl. At a commercial level of operation of 2 million barrels per day (~10% of oil consumption) the projected catalyst requirements range from 1.0 (H-Coal) to 1.6 (SRC) million pounds per day. These large projected catalyst requirements represent rates of production for in excess of current levels and would require metals (Co and Mo) production several times the current total world production. These numbers underscore the serious need for process configuration that do not entail such severe catalyst deactivation and for catalysts that are less susceptible to deactivation and that are regenerable.

Ahmed (52) hydrotreated Synthoil liquid dissolved in raw anthracene oil and determined surface area and pore structure changes between fresh and spent catalysts. He found that there is more accumulation of carbonaceous deposits on the Co-Mo/Al_2O_3 catalysts relative to Ni-Mo/Al_2O_3 catalysts and Co-Mo/Al_2O_3 lost more surface area than Ni-Mo/Al_2O_3 (Table XV).

Holloway (53) postulated one primary and three secondary mechanisms for the deactivation of Co-Mo/Al_2O_3 catalysts in the Synthoil process. Coking was considered to be the primary deactivation mechanism. The secondary mechanisms were Fe deposition and Ti deposition on the interior catalyst surface, and the adsorption of nitrogen-containing compounds. Deposition of Fe and Ti did not cause significant activity decay in short-term experiments (<120 wt coal/wt catalyst), but undoubtedly causes marked activity reduction as more metals are deposited with longer on-stream times.

Stanulonis <u>et al</u>. (54) used a scanning electron microscope and an electron microprobe to analyze Co-Mo/SiO_2-Al_2O_3 catalyst aged in the Synthoil process. The electron microscope results showed that catalyst pellets removed from the upstream portion of the reactor had a thin inorganic crust covering the external surface of the pellets; this inorganic crust was covered by a thick layer of coke. In addition to these deposits on the external surface, coke and metals were also deposited within the pores of the catalyst resulting in a 70% reduction in catalyst surface area and pore volume. Figure 12 presents electron microprobe concentration profiles of a catalyst particle from the upstream end of the reactor. The aluminum profile identifies the external boundary of the catalyst particle. The iron concentration is approximately proportional to the sulfur concentration in the exterior surface (crust); the sulfur/iron ratio is higher in the interior of the catalyst because of the presence of Co-Mo sulfides. Titanium was deposited primarily in the interior of the catalyst; the irregular silicon profile suggests the incorporation of mineral constituents of the coal within cracks or macropores. The cobalt and molybdenum profiles show large radial variations across the catalyst. These results indicate that mineral matter and coke deposition in coal hydroprocessing reactors could lead to bed plugging and pore mouth blocking.

Chiou and Olson (55) analyzed aged catalyst from the H-Coal process by scanning electron microscopy and electron microprobe. In contrast to the aged catalyst from the Synthoil process, there was no external crust on the catalyst aged in the H-Coal process. This is inferred to be due to the abrasion that occurs in the ebullated bed used in the H-Coal process, as opposed to the fixed bed of the Synthoil process. Mineral matter deposition within the catalyst pores, particularly at the pore mouths, appeared to be more severe for the catalyst aged in the H-Coal process; however, the coal-catalyst contact time was probably longer for the catalyst from the H-Coal process. An ebullated-bed reactor would therefore appear to have an advantage over a fixed-bed reactor in reducing blinding of the external catalyst surface by attrition of surface crusts as they form.

In another study, Chiou and Olson (55) regenerated spent catalyst used in a fixed-bed proprietary coal liquefaction process by burning the carbon off the catalyst and resulfiding it, and the activities of the spent and regenerated catalysts for quinoline hydrodenitrogenation were compared with that of the fresh catalyst. The rates of each of the reactions in the quinoline hydrodenitrogenation reaction network were calculated using techniques developed by Shih _et_ _al_. (22); Table XVI lists the relative rate constants (referred to the fresh catalyst) for the individual reactions in the quinoline reaction network for spent and regenerated catalysts. Deactivation affects the specific reactions in the hydrodenitrogenation network differently. The hydrogenation activity of the spent catalyst is markedly reduced, whereas carbon-nitrogen bond scission activity for decahydroquinoline, as represented by k_8^* is apparently less affected.

In another study, Ni-Mo/Al_2O_3 (Nalco M502) catalyst aged in the hydroprocessing of an equal volume mixture of Synthoil liquid and raw anthracene oil was examined for its simultaneous nitrogen and sulfur removal activities (56). Pseudo first-order rate constants for each of the reactions in the quinoline reaction network and the pseudo first-order rate constant for total nitrogen and sulfur removal from quinoline and dibenzothiophene respectively were determined for fresh, spent, and regenerated (carbon burnt off) catalyst (Table XVII). Total nitrogen removal (hydrodenitrogenatio over the spent catalyst was essentially zero at standard operating conditions, whereas sulfur removal over the spent catalyst was about 4 percent of that for the fresh catalyst. After burning off the carbon and resulfiding, the hydrodenitrogenation, activity was 61% of that of the fresh catalyst, and the hydrodesulfurization activity was 48 percent of that of the fresh catalyst. For the spent catalyst, the pseudo first-order rate constants for hydrogenation in the quinoline reaction network are more severely reduced than observed by Chiou and Olson (53). The observed reduction in the pseudo first-order rate constants for carbon-nitrogen bond scission were also markedly reduced. This is in contrast to the observation of Chiou and Olson, for k_8. Regeneration of the catalyst resulted in marked activity increases for all of the reactions, to levels similar to those reported by Chiou and Olson (54).

Catalyst deactivation depends to a large extent on the environment of the working catalyst and is particularly severe for hydrotreating synthetic liquids. The deactivation of hydrotreating catalysts used in petroleum processing has been well characterized and many advances in improved catalyst durability have been made in the last two decades. Much of this improvement has come from modification and control of surface area and pore size distribution to maximize catalyst life. Sufficient quantitative data on catalyst deactivation during hydroprocessing of synthetic liquids is not available. The metallic constituents of synthetic liquids differ significantly from those of petroleum and the effect of these metals on catalyst deactivation is not well quantified. Generally, if deactivation is due to metals deposition, regeneration of the catalyst is not possible at present, whereas deactivated catalysts due to coke laydown can be regenerated by controlled combustion.

Currently hydrotreating catalysts are deactivated so rapidly in an environment with dissolving coal that it is not possible to see how such a process configuration can be considered acceptable as a commercial coal-liquefaction process. The quality of the liquids produced by most coal-liquefaction technologies are quite low, and these liquids cause rapid deactivation of hydrotreating catalysts. Coal liquids of higher quality can be hydroprocessed including hydrodenitrogenation, but even these liquids require high hydrogen pressures to prevent catalyst deactivation, thereby resulting in high consumption of hydrogen. Since environmentally acceptable synthetic fuels (coal-derived liquids and shale oil) cannot be produced in a single-step process, future developments need to focus on the interplay between the production of these fuels (liquefaction) and their upgrading. Processes need to be developed that can produce liquids of better quality so that they may be upgraded with acceptable rates of catalyst deactivation and acceptable amounts of hydrogen consumption. The interplay between catalyst activity, selectivity, and resistance to deactivation and process configuration and operation must remain a dynamic one as improved catalysts are developed to assure that the ultimate process-catalyst combination produces the products desired at a minimum of hydrogen consumption and cost.

HEAVY LIQUIDS TOXICITY

Many of the nitrogen-containing compounds found in heavy petroleum fractions, coal-derived liquids, and shale oil are carcinogenic, and in the presence of polynuclear aromatics their carcinogenicity is frequently increased many fold. Benzo(a)pyrene, benzo(a)anthracene and benzo(c)phenanthrene are established carcinogins in coal-derived liquids (57-60), aromatic petroleum fractions (61,62), and shale oils (63). These materials boil at temperatures in excess of 315°C; lower-boiling fractions are less carcinogenic. Because of the high concentration of both nitrogen-containing compounds and polynuclear aromatics, coal-derived liquids are particularly toxic. This is illustrated by the observation that oils from the Bergius (coal hydrogenation) process were potent in generating cancer in mice (63). The extent of toxicity was more fully illustrated during the seven-year operating program of a 300-ton-per-day coal hydrogenation plant at Institute, West Virginia, during the 1950's. There was an 11% incidence of skin carcinnoma among the workers in this plant (57-60). More recent experience demonstrates, however, that coal can be liquefied safely, and that the coal-derived liquids can be handled safely with proper hygiene measures and periodic medical examinations just as carcinoginic streams in current petroleum refinery operations, such as "cat recycle" oil, can be handled safely. The carcinoginic nature of synthetic liquids, particularly coal-derived liquids, will severely restrict their applications to major combustion facilities where strict hygienic measures can be maintained and enforced unless they are effectively detoxified by hydrotreatment, particularly by hydrodenitrogenation. Thus the broad distribution and utilization of coal-derived liquids will require extensive hydrodenitrogenation to remove the carcinoginic nitrogen-containing compounds and reduce somewhat the concentration of polynuclear aromatic hydrocarbons. Again these needs require catalysts and processes that can selectively remove nitrogen heteroatoms with minimum hydrogen consumption and perform no more than the desired amount of hydrogenation to achieve required product properties. If these highly toxic synthetic liquids cannot be selectively detoxified, then extensive hydrocracking and hydrogenation will be required producing substantially light fuels at a high cost.

CATALYST AND PROCESS NEEDS

Existing catalysts which have been developed largely for petroleum hydrodesulfurization are clearly not optimum for hydrodenitrogenation, and similarly-based catalysts that have been developed for hydrodenitrogenation achieve nitrogen removal by first hydrogenating the aromatic rings in the nitrogen-containing molecule, particularly the ring containing the nitrogen atom, followed by carbon-nitrogen bond scission. The reaction networks are complex and therefore difficult to analyze kinetically. Although it is often speculated that either hydrogenation or carbon-nitrogen bond scission are rate limiting, recent studies show that both hydrogenation and carbon-nitrogen bond scission are kinetically important under industrially important reaction conditions (22). Because hydrodenitrogenation involves both hydrogenation and carbon-nitrogen bond scission (hydrogenolysis) on current catalysts, these catalysts must be bifunctional, having both hydrogenation sites and hydrogenolysis sites. Therefore improved catalysts can be developed by carefully optimizing the hydrogenation activity and the cracking activity of the catalyst. This optimization is typically carried out empirically by determining the total rate of nitrogen removal as a function of catalyst preparation and composition. However, quantitative knowledge of the reaction networks and reaction kinetics for each step in the reaction network provides a firm basis for the rational design and optimization of improved hydrodenitrogenation catalysts. In this way it is possible to determine how catalyst modifications affect the rate of hydrogenation and that of hydrogenolysis. Process optimization can also utilize this type of information because processing conditions affect the two reaction types differently.

It is also critical to determine the nature of the catalyst sites which catalyze these two reaction types (hydrogenation and carbon-nitrogen bond scission) to rationally develop new and improved catalysts. The metal sulfide provides the hydrogenation function in typical commercial hydrotreating catalysts although a detailed understanding of the nature of the active site and of the reaction mechanism is still lacking. The origin of the carbon-nitrogen bond scission (hydrogenolysis) function is not clear. The presence of halogens in Co-Mo/Al_2O_3, Ni-Mo/Al_2O_3, or Ni-W/Al_2O_3 catalysts seems to improve the activity of catalysts for catalytic hydrodenitrogenation (64,65). The role of acidity in hydrodenitrogenation catalysts needs to be investigated. We speculate that the hydrogenolysis site may involve an $OH^{\delta+}$ group adjacent to a transition metal ion in the surface of the Al_2O_3, that both the proton and the transition metal ion are involved, and that the reaction occurs by a Hoffman E-2, β-elimination reaction. A better understanding of the nature of the site that catalyzes the carbon-nitrogen bond scission reaction would help considerably in developing catalysts which had a more-active carbon-nitrogen bond cracking function; improved catalysts will require a more active carbon-nitrogen bond cracking function because carbon-nitrogen bond scission is probably always kinetically important.

Hydrodenitrogenation of multi-ring nitrogen-containing compounds requires complete hydrogenation of the ring system before nitrogen removal occurs as indicated by the reaction networks. This results in high hydrogen consumption both in hydrogenation of the nitrogen-containing compounds and in hydrogenation of other aromatics present at the same time. Hydrogen consumption typically increases with increasing pressure and increasing heteroatom removal. Since nitrogen removal from petroleum residua and synthetic feedstocks requires relatively severe operating conditions, hydrogen consumption is higher than for lighter liquids.

Both coal liquefaction and the further hydroprocessing of coal-derived liquids currently consume hydrogen in excess of stoichiometric requirements for conversion to a liquid of the desired quality and for sulfur and nitrogen removal. Since it is extremely unlikely that both the coal liquefaction and the hydroprocessing can be done simultaneously in the same process, it is extremely important that the liquefaction process and the hydrotreating process be developed to optimally interface with each other. Optimum hydroprocessing, including hydrodenitrogenation, processes and catalysts cannot be developed without a firm knowledge of the coal liquefaction process and product properties and will undoubtedly dictate numerous factors concerning the liquefaction process and vice versa. Two major concerns in this development are how to minimize the hydrogen consumption consistent with product quality requirements and how much hydrogen is put in in the liquefaction step and how much in the hydroprocessing step. Even a 20 percent reduction in hydrogen consumption would result in enormous savings. Based on Table IX, we can assume an average consumption of 2500 scf/bbl for the hydroprocessing step alone. At a commercial level of operation of 2 million barrels of oil per day, which is only 10% of our projected 1985 oil consumption, a 20 percent reduction in hydrogen consumption would result in a reduction of a billion standard cubic feet of hydrogen per day. Table XVIII presents economics of hydrogen generation. Based on 1980 dollars and the economics of hydrogen production given in Table XVIII, this reduction would result in a savings of 265 to 318 million dollars per day in the cost of hydrogen required to produce the desired product, using coal as the source for hydrogen.

A very pressing need is the development of hydrodenitrogenation catalysts that can selectively coordinate the nitrogen atom and promote its removal without first requiring ring hydrogenation and thus be able to limit expensive hydrogen consumption. Catalysts must be designed that can selectively coordinate and catalyze the carbon-nitrogen bond scission reaction without first requiring full hydrogenation of the aromatic ring, and the catalyst must be stable under industrial operating conditions. The selectivity of hydrodesulfurization catalysts may be related to the fact that they are metal sulfides; thus sulfur atom vacancies on their surfaces are natural locations for the sulfur atom of the sulfur-containing molecule to interact, promoting its removal from the hydrocarbon molecule. Nitrogen having a very considerably different chemistry from that of sulfur can be expected to require a different type of catalyst site. The literature provides little specific information on the directions in catalyst properties and composition that could be most fruitful; major new developments and chemical routes remain to be developed in this area. For instance a Ni-W/zeolite catalyst has been developed which catalyzes hydrodenitrogenation with our catalyzing hydrodesulfurization (66). We can only speculate on directions but one guiding principle should be to evaluate materials involving elements that coordinate nitrogen (or nitrogen and carbon) or which can form vacancies into which the nitrogen atom can be coordinated as with sulfur. Because the sulfur level may be lower than the nitrogen level in some coal-derived liquids a number of materials not normally stable in higher concentration H_2S environments may now be possible candidates. Materials of particular interest are transition metal nitrides possibly promoted by other metals. Fe, Ru, Mo and W are particularly good candidates both as the major components and/or as promoters. Mixed transition metal oxides and oxysulfides in addition to materials such as borides and carbides or mixed systems such as Mo_2BC, and $M_2Mo_3O_8$ where M can be Mg, Zn, Co, Mn and other transition metals may show potential (67,68). Boudart, Cumumano, and Levy (69) have reviewed some of the properties of new materials that could be applicable to new catalytic chemistry. Important criteria are thermal stability, chemical stability and particularly stability in the presence of H_2S and coke-forming species. However thermodynamic information on bulk compounds frequently is of little value when considering highly dispersed materials on a support. Thus a combination of empiricism and enlightened chemical intuition will serve best the development of new catalytic materials. This work should always be coupled with careful network and kinetic analysis to define uniquely the chemical behavior of these new materials in catalytic hydrodenitrogenation.

Catalyst deactivation problems can be extremely severe with coal-derived liquids because of their high aromatic content and coke-forming tendencies. The rate of deactivation can be reduced by increasing the hydrogen partial pressure which, however, may result in excessive hydrogen consumption.

The metallic constituents of synthetic liquids differ significantly from those of petroleum and the effect of these metals on catalyst deactivation is not well quantified. Permanent loss of activity results from metal deposition on hydrotreating catalysts. The development of regeneration procedures for hydrotreating catalysts poisoned by alkali metals, iron, vanadium, titanium, and other materials is needed, and the tolerance of the catalyst materials to such metals should be increased. Catalysts with built in activity maintenance must be developed. Current methods of increasing the tolerance of hydrotreating catalysts to metal deposition involve modification of the pore-size distribution of the catalyst. A more quantitative understanding of the role of the pore structure in activity maintenance is needed, prediction of the optimum pore structure and pore size distribution is required, and development of techniques to produce desired pore structure and pore size distributions in commercial catalysts is needed.

The effect of catalyst support properties such as surface area, pore volume, and pore size distribution on hydrodenitrogenation activity needs to be better understood. Detailed characterization of the synthetic liquids from coal and oil shale is desirable to better quantify the type and concentration of nitrogen-containing compounds present in these liquids. These studies should also provide the information needed for lumping and process modeling under industrial operating conditions.

Industrial hydrodenitrogenation processes almost invariably use trickle-bed reactors. The fluid dynamics and model description of trickle-bed reactors are complex and have not been adequately characterized. Uncertainties exist as to degree of vaporization of the feed, the number of phases present, the distribution of components between phases at reaction conditions, and the degree of catalyst wetting. Quantitative information on these uncertainties would markedly help in modeling trickle-bed reactors and hydrotreating processe:

The products obtained from most current coal liquefaction processes are very low in quality and cause rapid deactivation of hydroprocessing catalysts. For these feeds, it may be desirable to use an ebullated-bed reactor since the ebullated-bed reactor allows catalysts to be removed continuously and regenerated, if possible, or replaced with fresh catalyst.

However, an ebullated-bed reactor requires a larger volume than a trickle-bed reactor to achieve a given conversion. The larger volume required for an ebullated-bed reactor can be partially offset by increased operating temperature which leads to increased rates of catalyst deactivation and increased hydrogen consumption. The ebullated-bed reactor typically achieves the desired conversion at a lower selectivity. Thus the optimum processes for hydrotreating low-quality liquids will probably involve an ebullated-bed reactor to give partial upgrading followed by a higher-selectivity trickle-bed reactor designed to give the desired heteroatom removal and product quality. Therefore,it is essential that the interface between the synthetic liquid formation process and the hydrotreating process remain a dynamic one to achieve the best balance between the two with respect to hydrogen consumption and product quality.

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TABLE I

PROJECTED GASOLINE-MID-DISTILLATE RATIO (1)

Year	Gasoline/Mid-distillate
1975	1.7
1980	1.5
1990	1.2
2000	1.0
>2000	0.5 - 1.0

TABLE II

PROPERTIES OF REPRESENTATIVE COALS AND OIL SHALE

	Oil Shale[a]	Lignite[b] (Glenhowold Mines)	Sub-Bituminous[b] (Big Horn)	Bituminous[b] (Kentucky #9 & #11)	Bituminous[b] (Pittsburgh Seam)	High Volatility Bituminous[b] (Illinois #6)	Anthracite[b] (Black Mountain, Pa)
Elemental Analysis							
Carbon	80.52	65.44	69.34	68.53	76.84	68.92	78.18
Hydrogen	10.30	4.49	4.60	4.60	5.06	5.01	2.25
Nitrogen	2.39	1.01	1.23	1.42	1.61	1.01	0.66
Sulfur	1.04	0.77	0.54	4.63	1.49	6.66	0.55
Oxygen	5.75	17.39	19.10	5.82	6.72	7.57	4.42
Proximate Analysis[c]							
Moisture		32.1	22.0	7.2	2.9	12.1	2.5
Volatile Matter		43.0	33.2	32.3	33.1	40.7	5.8
Fixed Carbon		17.5	41.4	44.3	55.9	48.4	80.3
Ash		7.4	3.4	16.2	8.1	10.8	13.9
Agglomerating Character		non-agglomerating		agglomerating			non-agglomerating
Density					increases		

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[a] Ref. 3, an average of 10 samples, moisture- and ash-free (maf) basis.

[b] The elemental analysis for coals has been gathered from several sources and is on a moisture-free basis.

[c] analysis based on heating in a standard manner, followed by oxidation of the remainder.

TABLE III

ELEMENTAL ANALYSES OF SYNTHETIC LIQUIDS AND PETROLEUM CRUDES

Element	SRCI[a]	H-Coal[a]	Synthoil[a]	Colorado[b] Shale Oil	El Palito[a] No. 6 fuel oil	1000 F+[a] West Texas residuum
C, wt %	87.93	89.00	87.62	83.92	86.40	83.88
H, wt %	5.72	7.94	7.97	11.36	11.20	9.97
O, wt %	3.50	2.12	2.08	.67	0.30	0.48
N, wt %	1.71	0.77	0.97	2.14	0.41	0.40
S, wt %	0.57	0.42	0.43	0.70	1.96	4.19

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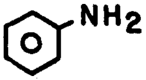
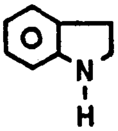
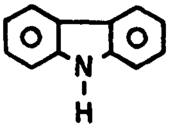
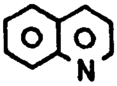
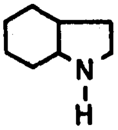
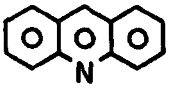
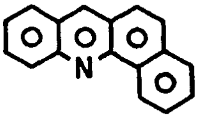
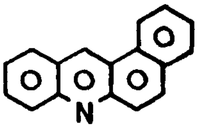
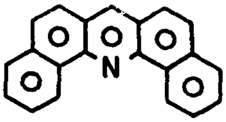
[a] Ref. 4.

[b] Ref. 5.

TABLE IV

REPRESENTATIVE NITROGEN-CONTAINING COMPOUNDS FOUND IN PETROLEUM CRUDE, SHALE OIL AND COAL-DERIVED LIQUIDS

Compound	Formula	Structure
Non-heterocyclic compounds:		
Aniline	$C_6H_5NH_2$	
Pentylamine	$C_5H_{11}NH_2$	
Non Basic Heterocyclic compounds:		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Basic Heterocyclic Compounds:		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Acridine	$C_{13}H_9N$	
Benz(a)acridine	$C_{17}H_{11}N$	
Benz(c)acridine	$C_{17}H_{11}N$	
Dibenz(c,h)acridine	$C_2H_{13}N$	

Note: Coal-derived liquids also contain methyl and alkyl substitution on most of the aromatic compounds.

TABLE V

OPERATING CONDITIONS FOR HYDROTREATING PETROLEUM AND SYNTHETIC FEEDSTOCKS

	Light[a] Petroleum (distillates)	Heavy[a] Petroleum (residua)	COED Liquid[b]	H-Coal[c] Distillate	Shale Oil[d]
Temperature, °C	300-400	340-425	343-454	356-414	406-418
Pressure, atm	35-70	54-170	136-306	54-170	160
Space Velocity, hr^{-1}	2-10	0.2-1	0.3-3.0	0.44-4.09	0.60
H_2 Recycle, scf/bbl	300-2000	2000-10,000			4906-10308

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[a] Ref. 24.

[b] Ref. 25.

[c] Ref. 26.

[d] Ref. 27.

TABLE VI

PROPERTIES OF TYPICAL COMMERCIAL HYDROTREATING CATALYSTS (28)

	$Co\text{-}Mo/Al_2O_3$			$Ni\text{-}Mo/Al_2O_3$			$Ni\text{-}W/SiO_2\text{-}Al_2O_3$		$Co\text{-}Ni\text{-}Mo/Al_2O_3$
Catalyst Source	Cyanamid	Filtrol	Nalco	Filtrol	Harshaw	Shell	Harshaw	Ketjen	Filtrol
Designation	HDS-20A	HPC-5	474	HPC-30	HT-500E	514	4401E	HC-5	HPC-45
Composition, wt%									
CoO	4.9	3.1	3.5						4.2
NiO				2.8	4.1	2.4	6.2	7.6	1.2
MoO_3	16.2	15.0	13.8	14.7	14.2	8.2			17.8
WO_3							ND	ND	
Physical Properties									
Surface area m^2/g	229	181	284	190	213	269	117	228	178
Average Pore Diameter, Å	72	125	79	122	96	49	48	147	116
Pore Volume, cc/g in pores									
35-100 Å dia	.992	.239	.558	.224	.351	.360	.139	.212	.225
100-200 Å dia	.037	.312	.015	.323	.172	.021	.004	.173	.278
200-400 Å dia	.011	.003	.014	.006	.002	.005	.008	.174	.003
400-600 Å dia	.004	.002	.012	.003	0	.003	.005	.035	.002
>600 Å dia	0	.004	.014	0	0	.003	.016	0	.001

TABLE VII

COMPARISON OF SULFUR AND NITROGEN REMOVAL FROM DIFFERENT PETROLEUM AND COAL-DERIVED LIQUIDS

Coal-derived Liquids[a] (39)

Feedstock	% Removal	
	S	N
Raw anthracene oil	96	63
Hydrocarbonization liquid	70	38
Synthoil liquid	33	15

Three Different Petroleum Distillates[b] (40)

	wt % Sulfur			wt % Nitrogen		
	Original	Product	% Removal	Original	Product	% Removal
I	0.8	0.05	94	0.015	0.007	53
II	1.19	0.07	94	0.056	0.041	27
III	1.58	0.14	91	0.012	0.007	42

[a] Operating Conditions: 371°C, 102 atm, and 1.5 hours liquid volume hourly space time LHSV = 0.7 hr^{-1}.

[b] Operating conditions unknown.

TABLE VIII

BOND ENERGIES BETWEEN CARBON AND HETEROATOMS IN POLYATOMIC MOLECULES (41)

Bond	Energy kcal/mole	Bond	Energy kcal/mole
C-H	99	C-N	73
C-C	83	C=N	147
C=C	146	C≡N	213
C≡C	200	C-S	65
N-H	93	C=S	128
		S-H	83

TABLE IX

RELATIVE REACTIVITIES OF NITROGEN-CONTAINING COMPOUNDS[a] (44)

Compound	Pseudo-first Order Rate Constant, k, $(\mathrm{min})^{-1}$
Quinoline	2.52
Carbazole	2.43
Acridine	1.62
Benz(a)acridine	1.08
Benz(c)acridine	1.54
Dibenzacridine	3.79

Standard Conditions: 367°C, 136 atm, presulfided Ni-Mo/Al_2O_3, carrier oil white oil, H_2S present during reaction in batch autoclave.

TABLE X

HYDROGEN CONSUMPTION IN HYDROTREATING SYNTHETIC LIQUIDS

Feedstock	Hydrogen consumption scf/bbl	Temp,°C	Pressure, atm	Feedrate or LHSV, hr^{-1}	S	N	O	Ref.
Oil from Western Kentucky Coal	2597-2894	454-469	115-125	150-174 lb/hr	91-96	67-87	84-94	25
SRC Recycle Solvent (various boiling point cuts)	973-3410	400-479	80-170	0.45-2.11 LHSV	88-98	37-98	36-98	26
H-Coal Distillate (various boiling point cuts)	65-1698	400-471	55-170	0.46-4.09 LHSV	64-98	26-98	25-92	26
Oil from Pittsburgh Seam	2096-3735	440-457	120-130	127-153 lb/hr	95-96	62-85	76-85	25
SRC (60/40 Blend)[a]	2530-3230	486	190	0.5 LHSV	95	63-79	64-85	37
Synthoil	1840	not available		0.98 LHSV	96	58	80	28
Shale Oil	1616-2175	443-460	147	0.60 LHSV	99	99	--	27

TABLE XI

HYDROGEN CONSUMPTION FOR COAL LIQUEFACTION BY H-COAL PROCESS (28)

Reaction Type	Hydrogen Consumption Based on Slurry Feed wt %	Hydrogen Consumption Based on Slurry Feed liters/kg	% of total Hydrogen Consumption
liquid hydrogenation	1.059	118.6	80.3
hydrodesulfurization	0.056	6.3	4.3
hydrodenitrogenation	0.058	6.5	4.4
hydrodeoxygenation	0.146	16.3	11.0
Total	1.319	147.7	100.0

TABLE XII

COST OF UPGRADING COAL LIQUIDS TO TURBINE FUELS (49)

	H-Coal Distillate			SRC Recycle Solvent				H-Coal, 400°F$^+$ Fuel Oil			SRC		
Feed													
Hydrogen in C_5^+ Product, wt %	10.7	11.4	12.0	9	10	11	12	9	10	11	8	9	10
Capital Investment $ Million, 1980	69	94	113	87	108	131	171	104	136	193	132	182	308
Upgrading Cost, $/MMBTU													
Hydrogen (Net)	0.21	0.40	0.60	0.46	0.76	1.05	1.31	0.62	1.06	1.46	0.83	1.24	1.67
Operating	0.22	0.28	0.33	0.27	0.33	0.38	0.47	0.25	0.35	0.45	0.35	0.54	0.85
Capital Recovery	0.21	0.28	0.33	0.26	0.31	0.36	0.46	0.28	0.36	0.51	0.34	0.47	0.77
By-Product Credit	(0.02)	(0.03)	(0.05)	(0.02)	(0.04)	(0.05)	(0.08)	(0.11)	(0.24)	(0.47)	(0.09)	(0.23)	(0.42)
Net Cost, 1980 $	0.61	0.93	1.21	0.97	1.36	1.74	2.16	1.04	1.53	1.95	1.43	2.02	2.87
Net Cost, 1976 $	0.50	0.77	1.00	0.80	1.12	1.43	1.78	0.86	1.26	1.60	1.18	1.66	2.36
Net Cost Levelized	0.89	1.36	1.77	1.42	1.99	2.54	3.15	1.52	2.23	2.85	2.09	2.95	4.19
Sensitivites, Δ$/MMBTU H_2 Cost ± 50¢/MSCF	±0.06	±0.10	±0.15	±0.12	±0.19	±0.26	±0.32	±0.15	±0.26	±0.35	±0.20	±0.30	±0.40

Equity Financing, 5%/yr. Inflation, 1980 Initial Year Cost

TABLE XIII

TRACE METALS ANALYSES OF COAL-DERIVED LIQUIDS AND PETROLEUM (26)

Element, ppm	SRC Recycle Solvent	SRC	H-Coal	Synthoil	El Palito No. 6 Fuel Oil
Si	0.0	30.0	2.0	1348.0	3.0
Mg	0.2	4.0	1.0	33.0	4.0
Pb	0.3	1.0	0.0	5.0	2.0
Fe	4.4	140.0	20.0	375.0	6.4
Al	1.5	31.0	11.0	886.0	5.0
Ni	0.3	2.1	1.0	1.0	59.0
Ti	11.0	130.0	80.0	150.0	78.0
Ca	0.4	49.0	8.0	27.0	14.0
Na	1.6	100.0	0.8	79.0	19.0
K	0.4	8.0	0.4	116.0	(a)
V	0.0	6.8	2.6	1.8	275.0

(a) Analysis not determined.

TABLE XIV

FATE OF INORGANIC COMPONENTS IN COAL-DERIVED LIQUIDS DURING HYDROPROCESSING (50)

	Ti	Ca	Fe
Feedstock: Synthoil Liquid			
Charged, g of metal	1.41	1.58	1.49
Deposited on Catalyst, g	1.46	0.16	0.59
% deposited	104	10	40
Feedstock: SRC Product			
Charged, g of metal	3.87	3.41	6.85
Deposited on Catalyst, g	2.81	0.54	2.21
% deposited	73	16	32

TABLE XV

CARBON DEPOSITION AND SURFACE AREA LOSS FROM HYDROTREATING OF COAL-DERIVED LIQUIDS (52)

Catalyst	Run Duration, hr	Reactor Zone	Carbon Deposited, wt %	Catalyst Surface Area[a]		% of Surface Area Lost[b]
				Spent, m^2/g	Regenerated m^2/g	
Ni-Mo/Al_2O_3 (Nalco NM502)	674	Top	22	99	172	23
		Middle	23	111	194	12
		Bottom	21	118	184	17
Co-Mo/Al_2O_3 (Nalco 474)	372	Top	33	26	205	15
		Bottom	28	52	178	26

Reaction Conditions: 371°C, 102 atm, 0.8 hr^{-} LHSV, 50/50 mixture of Synthoil liquid in raw anthracene oil

[a] Surface area of fresh Ni-Mo/Al_2O_3 = 221 m^2/g
Surface area of fresh Co-Mo/Al_2O_3 = 240 m^2/g

[b] % surface area lost = $\dfrac{\text{surface area fresh - surface area regenerated}}{\text{surface area fresh}}$

TABLE XVI

RELATIVE RATE CONSTANTS IN THE QUINOLINE REACTION NETWORK (55)

	k_1^*	k_2^*	k_3^*	k_4^*	k_5^*	k_6^*	k_7^*	k_8^*
Spent Catalyst	19	19	23	48	47	16	16	84
Regenerated Catalyst	67	78	77	48	77	42	50	84
Rate Constants for Fresh Catalyst	(92.0)	(20.0)	(0.67)	(0.14)	(0.84)	(0.11)	(0.10)	(3.47)

g of oil/ g of cat)/minute

Reaction Conditions: 350°C, 36 atmos., presulfided Ni-Mo/Al_2O_3,
0.5 wt % quinoline.

Values in parentheses for fresh catalyst are actual values of the rate constants defined by $\frac{Mo}{Mc}\frac{dCi}{dt} = k_{ij}C_i$

$$k_i^* = \frac{k_i}{k_{i\ \text{fresh}}} \times 100$$

Quinoline Network:

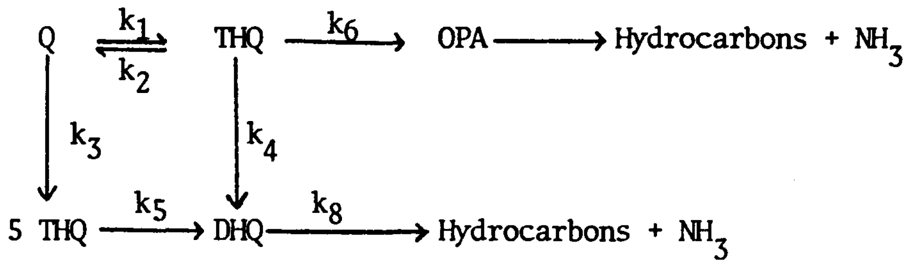


TABLE XVII

ACTIVITY OF CATALYSTS AGED IN HYDROTREATING COAL DERIVED LIQUIDS (56)

First-Order Rate Constants,[a] min^{-1}

	Fresh Catalyst	Spent Catalyst	Regenerated Catalyst
Total Nitrogen Removal from Quinoline First-order rate constant for total nitrogen removal	0.20	<0.01	0.12
Total sulfur removal from dibenzothiophene of First-order rate constant for sulfur removal	0.33	0.012	0.15

Rate Constants in the Quinoline Network Relative to Fresh Catalyst, %

	k_1^*	k_2^*	k_3^*	k_4^*	k_5^*	k_6^*	k_7^*	k_8^*
Spent Catalyst	9	8	12	11	12	11	--	8
Fresh Catalyst	58	82	59	88	42	62	--	41

Reaction Conditions: 350°C, 36 atm

Spent catalyst was used to hydrotreat a 50/50 mixture of synthoil and raw anthracene oil at 102 atm and 1.25 hrs LVHST for 674 hours of oil contact on catalyst. The catalyst was regenerated by controlled combustion in a furnace at 450°C with a 2% mixture of O_2 in Helium flowing through.

[a] The first order rate constant is defined as

$$\frac{M_o}{M_c}\,\frac{dC_i}{dt} = k_i C_i$$

where M_o = mass of oil, g
M_c = mass of catalyst, g.
C_i = concentration, g moles i/g oil
t = time, minutes
k_i = pseudo first order rate constant for reaction i, $(\text{go oil})(\text{g cat}\cdot\text{min})^{-}$ $= (\text{min})^{-1}$

$$k_1^* = \frac{k_i}{k_i \text{ fresh}} \quad \text{X } 100$$

TABLE XVIII

ECONOMICS OF HYDROGEN GENERATION

	Reforming of CH_4	Partial Oxidation of Residua	Coal Gasification Koppers-Totzek (K-T)	Coal Gasification Improved K-T
Capital Investment, $ Millions	63	159	246	200
On-site facilities	41	94	146	122
Off-site facilities	22	65	100	78
Cost of Feedstock, $/MMBtu	3.15	2.35	0.96	0.96
Costs and Charges, $/1000 SCF hydrogen				
Feedstock	1.33	0.92	0.52	0.49
Other operating costs	0.02	0.10	0.17	0.14
Capital related charges	0.64	1.62	2.49	2.02
Total cost including 20% before tax return	1.99	2.64	3.18	2.65

Cost estimation is for a 100 million SCF/day plant located at a mid-continent site with startup in 1980 and with 1980 dollars. This table is adapted from Ref. 1.

LIST OF FIGURES

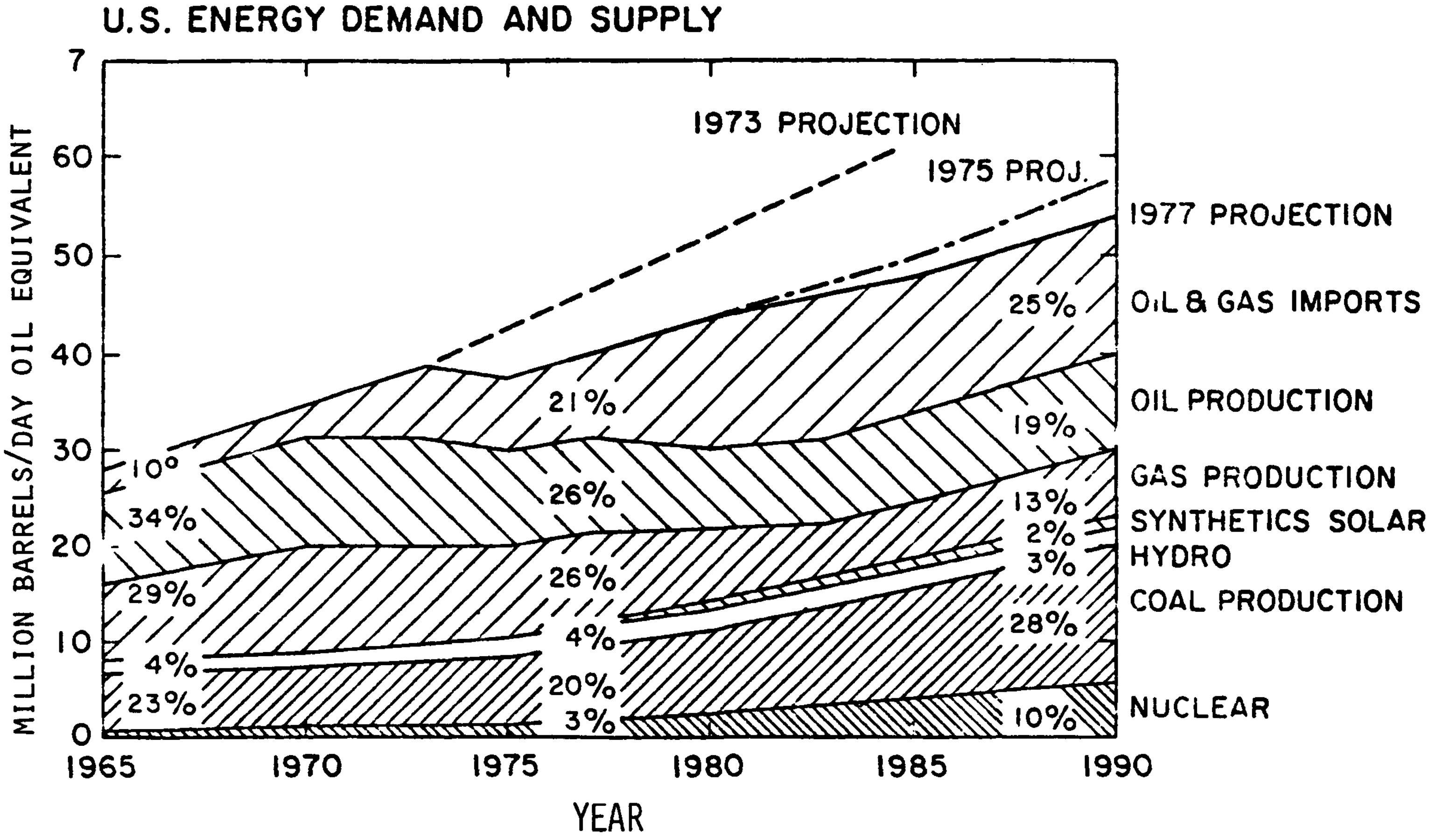

U.S. ENERGY DEMAND AND SUPPLY
MILLION BARRELS/DAY OIL EQUIVALENT
7
60
50
40
30
20
10
0
1965
1970
1975
1980
1985
1990
YEAR
1973 PROJECTION
1975 PROJ.
1977 PROJECTION
OiL & GAS IMPORTS
OIL PRODUCTION
GAS PRODUCTION
SYNTHETICS SOLAR
HYDRO
COAL PRODUCTION
NUCLEAR
10°
34%
29%
4%
23%
21%
26%
26%
4%
20%
3%
25%
19%
13%
2%
3%
28%
10%

Figure 1

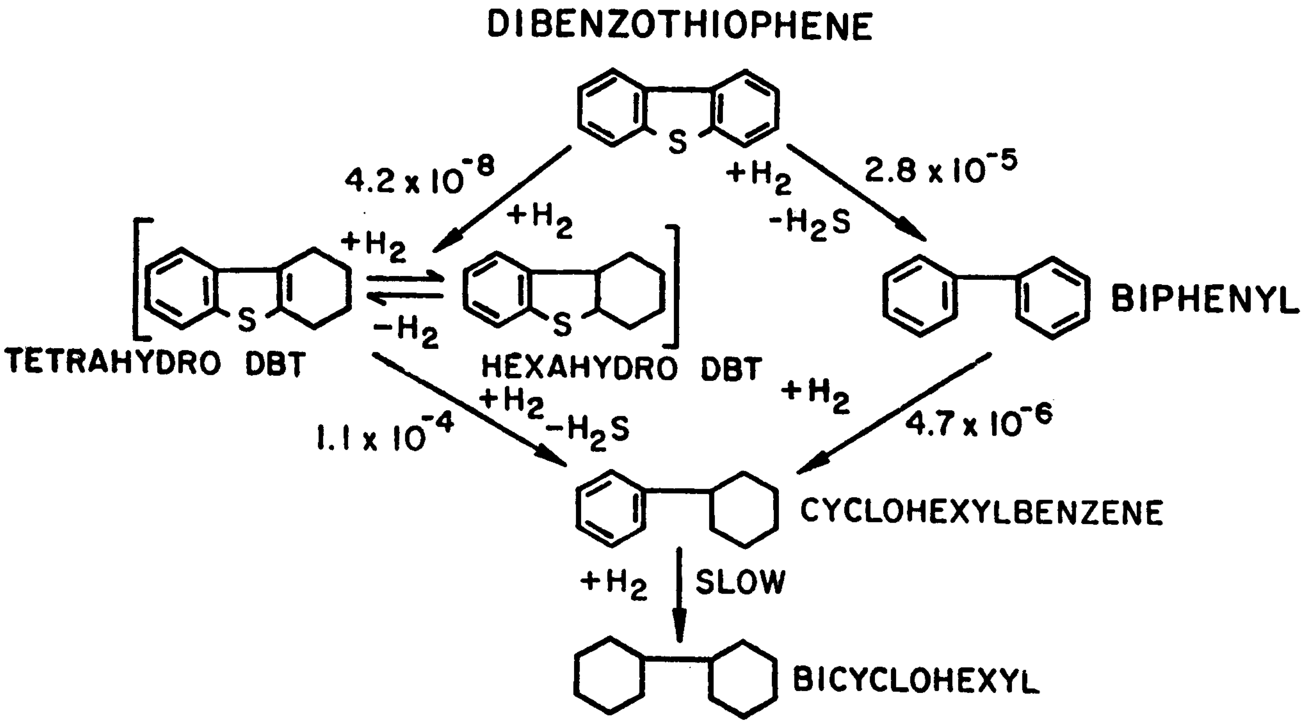

DIBENZOTHIOPHENE
S
4.2 x 10-8
+H2
2.8 x 10-5
+H2
-H2S
+H2
-H2
TETRAHYDRO DBT
HEXAHYDRO DBT
BIPHENYL
+H2
-H2S
1.1 x 10-4
+H2
4.7 x 10-6
CYCLOHEXYLBENZENE
+H2
SLOW
BICYCLOHEXYL

Figure 2

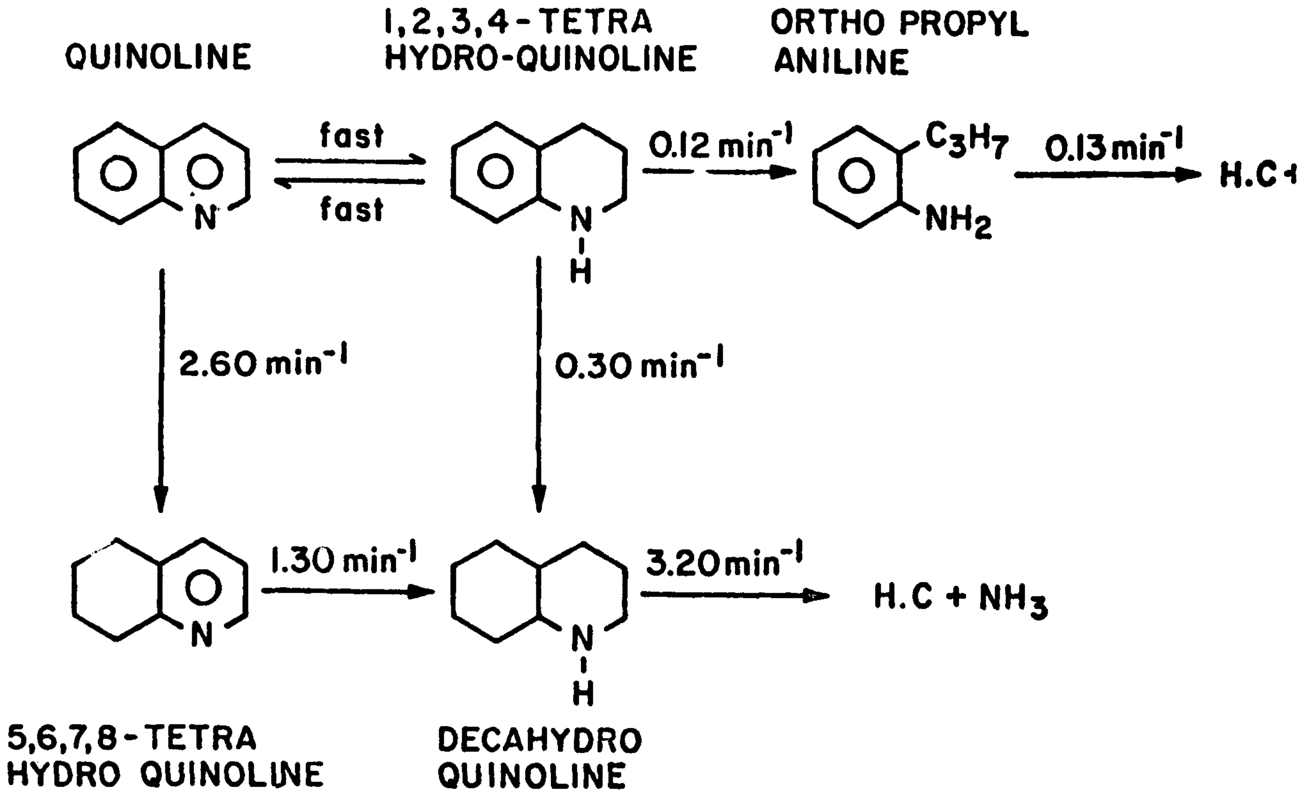

QUINOLINE
1,2,3,4-TETRA HYDRO-QUINOLINE
ORTHO PROPYL ANILINE
fast
fast
0.12 min-1
C_3H_7
NH_2
0.13 min-1
H.C
2.60 min-1
0.30 min-1
1.30 min-1
3.20 min-1
H.C + NH_3
5,6,7,8-TETRA HYDRO QUINOLINE
DECAHYDRO QUINOLINE

Figure 3

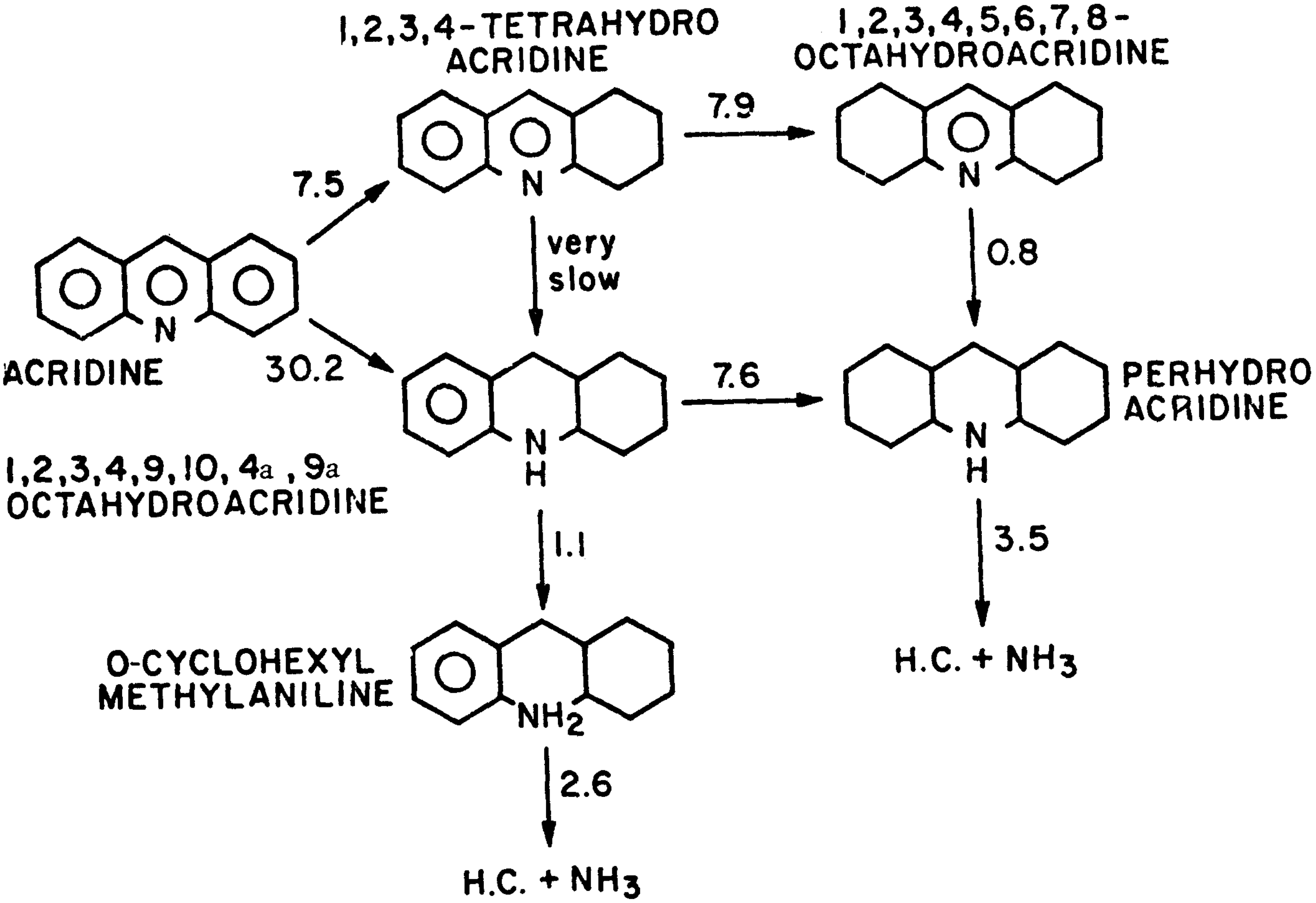

1,2,3,4-TETRAHYDRO ACRIDINE
1,2,3,4,5,6,7,8-OCTAHYDROACRIDINE
7.9
7.5
very slow
0.8
ACRIDINE
30.2
7.6
PERHYDRO ACRIDINE
1,2,3,4,9,10,4a,9a OCTAHYDROACRIDINE
1.1
3.5
O-CYCLOHEXYL METHYLANILINE
H.C. + NH3
2.6
H.C. + NH3
N
NH
NH2

Figure 4

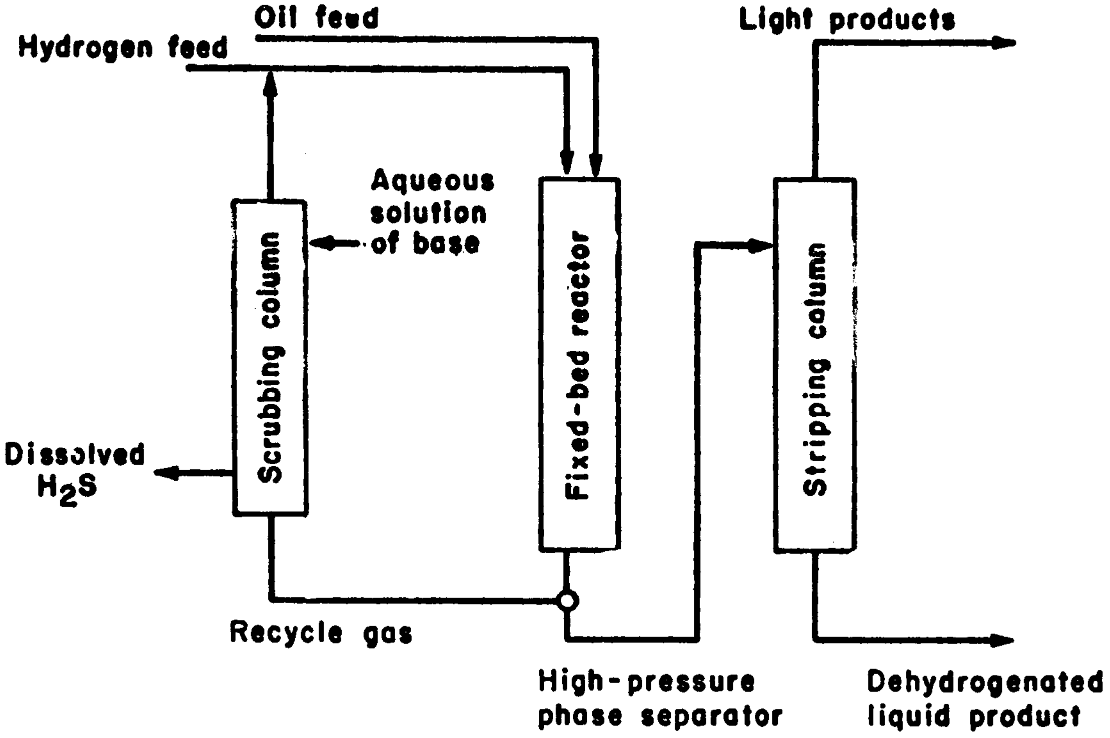
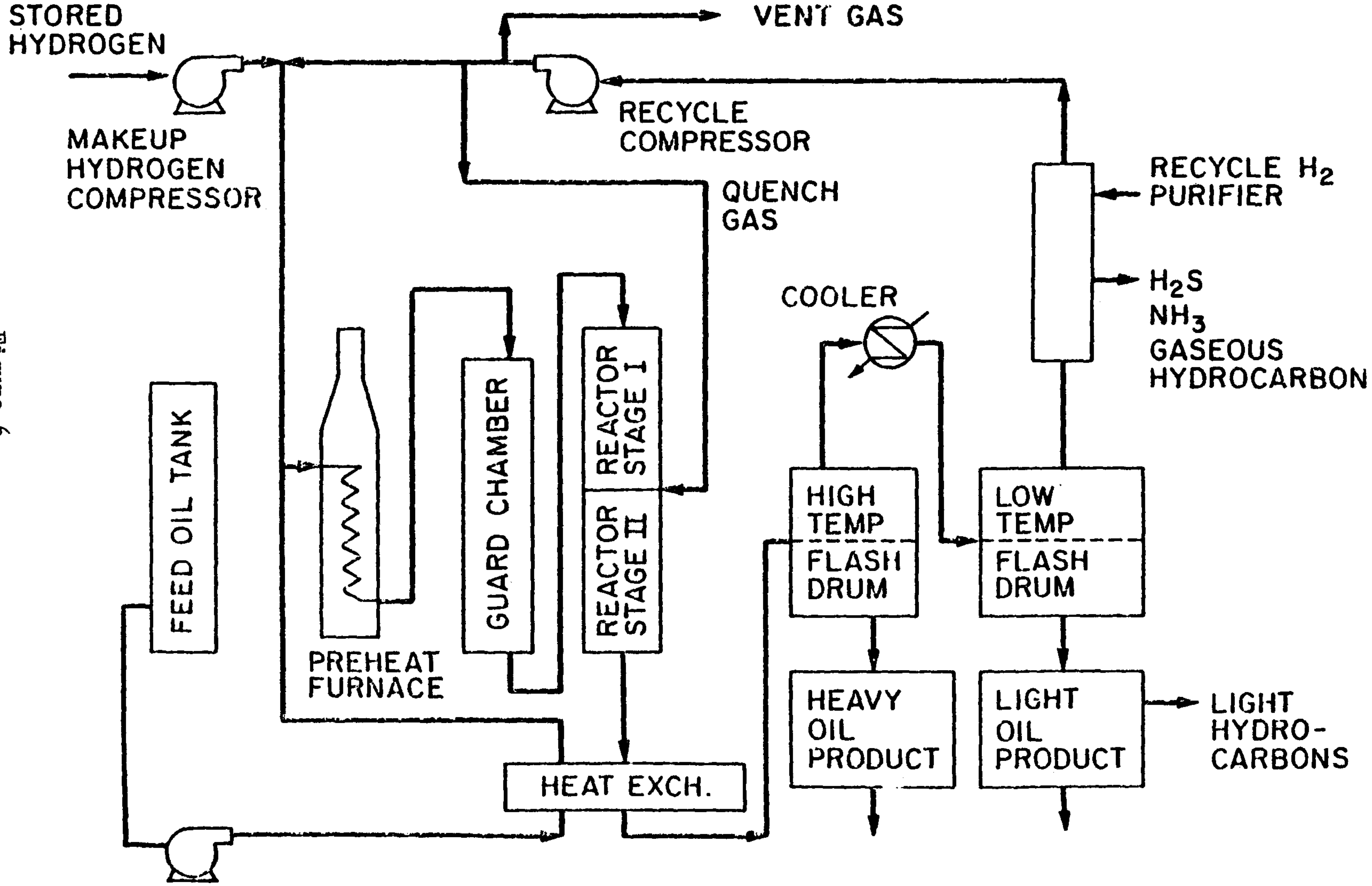

Oil feed
Hydrogen feed
Light products
Aqueous solution of base
Scrubbing column
Fixed-bed reactor
Stripping column
Dissolved H_2S
Recycle gas
High-pressure phase separator
Dehydrogenated liquid product

Figure 5

Figure 6


STORED HYDROGEN
VENT GAS
MAKEUP HYDROGEN COMPRESSOR
RECYCLE COMPRESSOR
QUENCH GAS
RECYCLE H_2 PURIFIER
H_2S
NH_3
GASEOUS HYDROCARBON
COOLER
FEED OIL TANK
PREHEAT FURNACE
GUARD CHAMBER
REACTOR STAGE I
REACTOR STAGE II
HIGH TEMP FLASH DRUM
LOW TEMP FLASH DRUM
HEAVY OIL PRODUCT
LIGHT OIL PRODUCT
LIGHT HYDRO-CARBONS
HEAT EXCH.

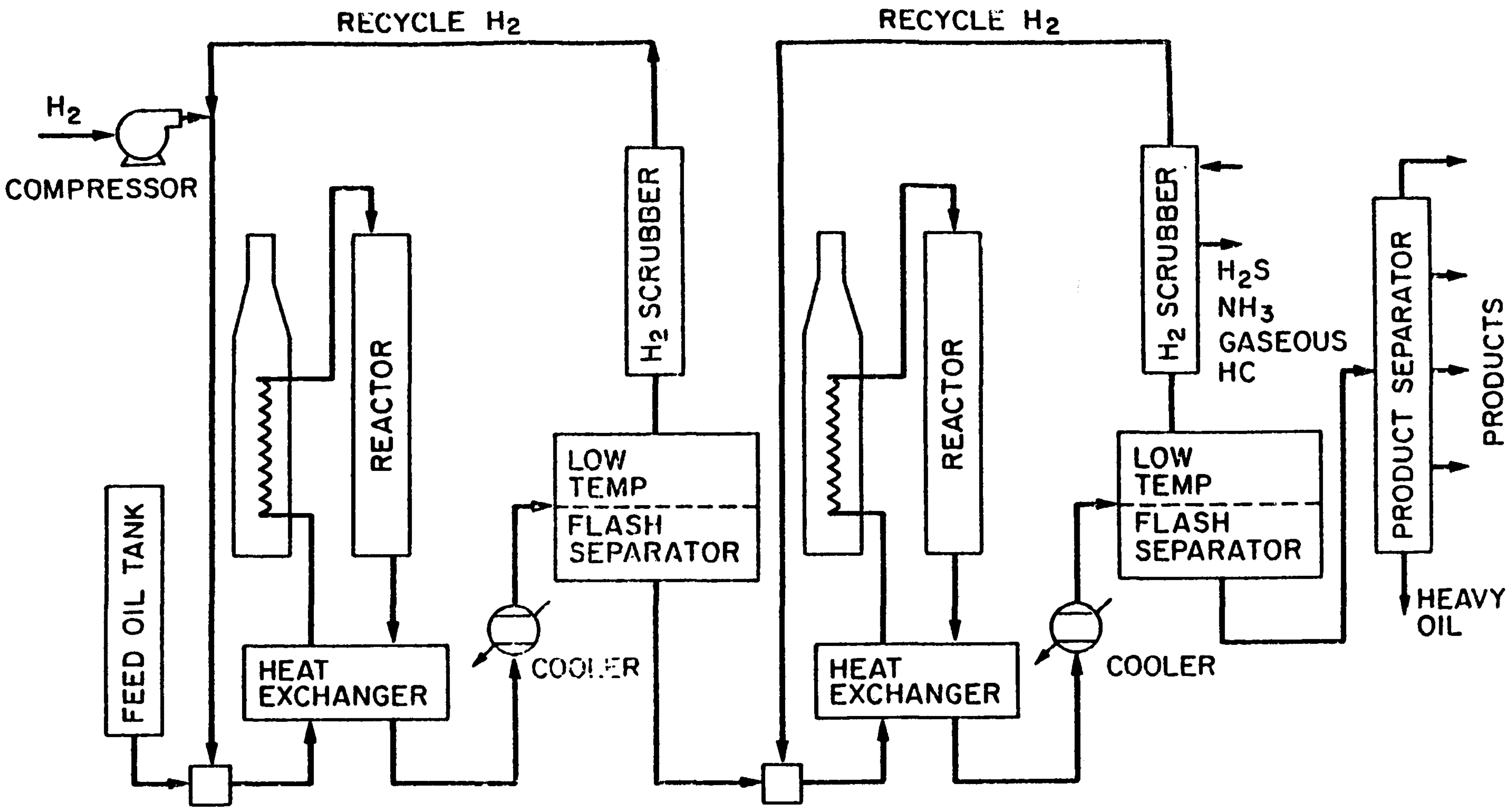

RECYCLE H_2
RECYCLE H_2
H_2
COMPRESSOR
FEED OIL TANK
REACTOR
HEAT EXCHANGER
H_2 SCRUBBER
LOW TEMP
FLASH SEPARATOR
COOLER
REACTOR
HEAT EXCHANGER
H_2 SCRUBBER
H_2S
NH_3
GASEOUS HC
LOW TEMP
FLASH SEPARATOR
COOLER
PRODUCT SEPARATOR
PRODUCTS
HEAVY OIL

Figure 7

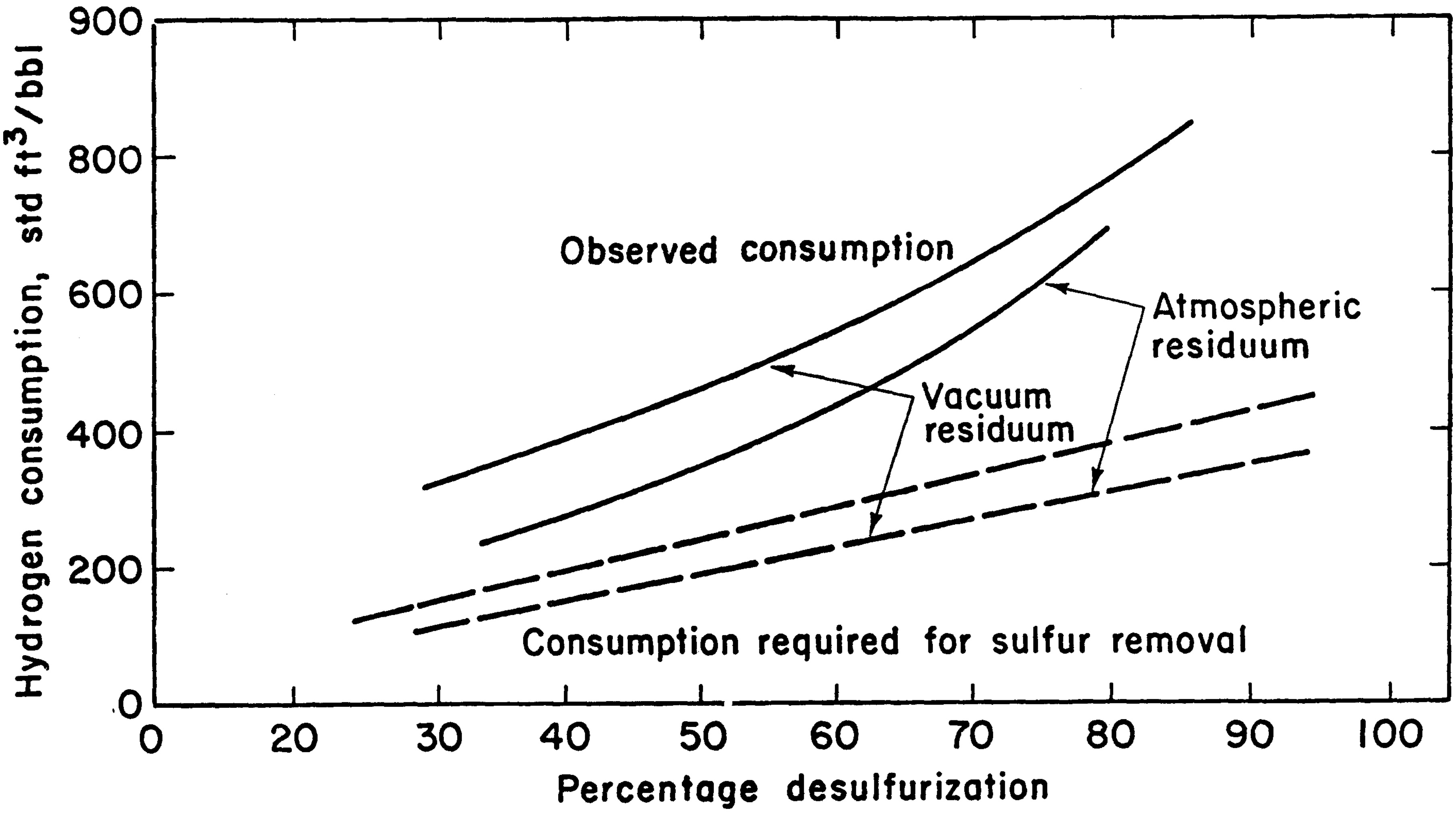

Hydrogen consumption, std ft^3/bbl
900
800
600
400
200
0
0
20
30
40
50
60
70
80
90
100
Percentage desulfurization
Observed consumption
Atmospheric residuum
Vacuum residuum
Consumption required for sulfur removal

Figure 8

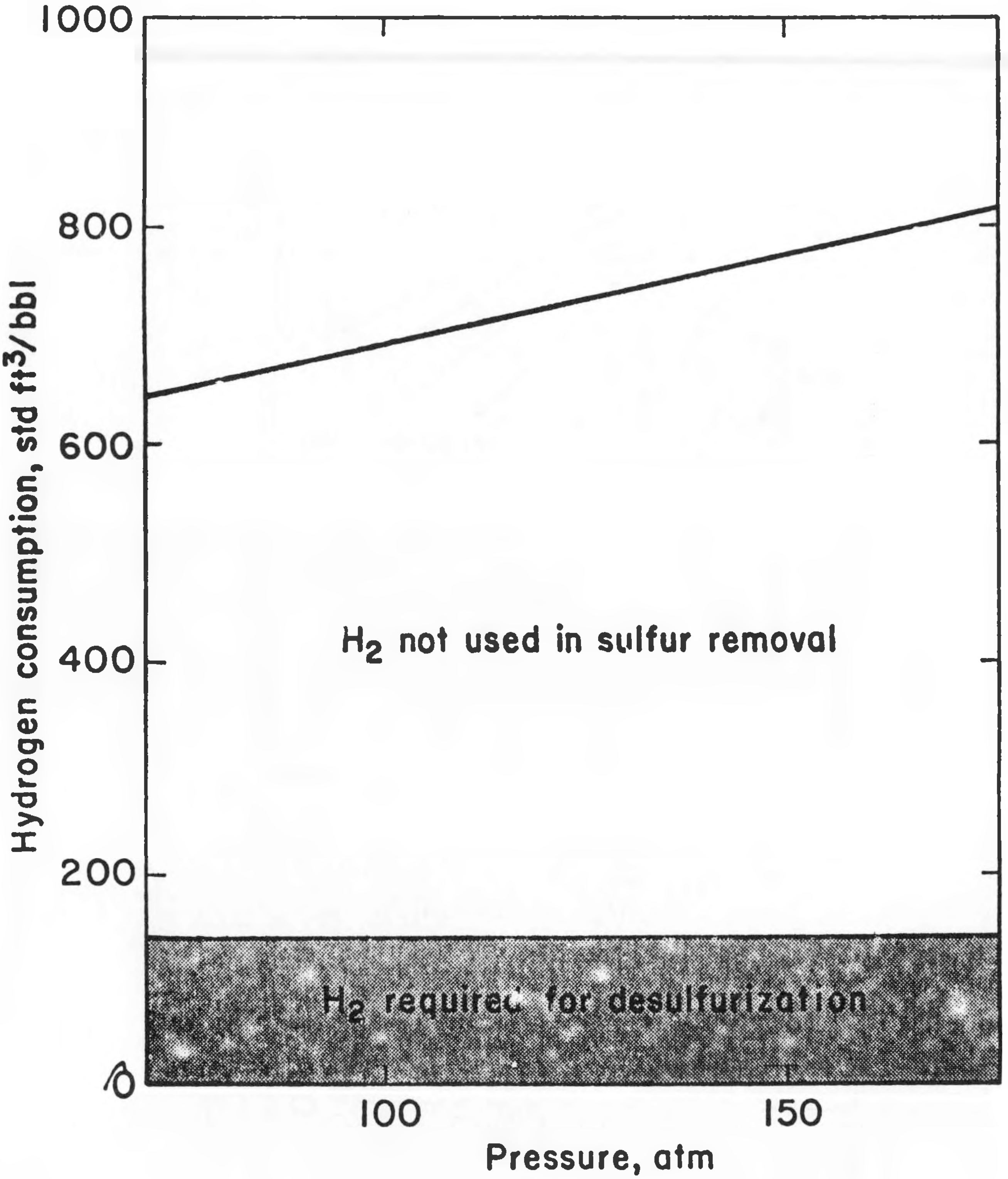

1000
800
600
400
200
0
100
150
Pressure, atm
Hydrogen consumption, std ft^3/bbl
H$_2$ not used in sulfur removal
H$_2$ required for desulfurization

Figure 9

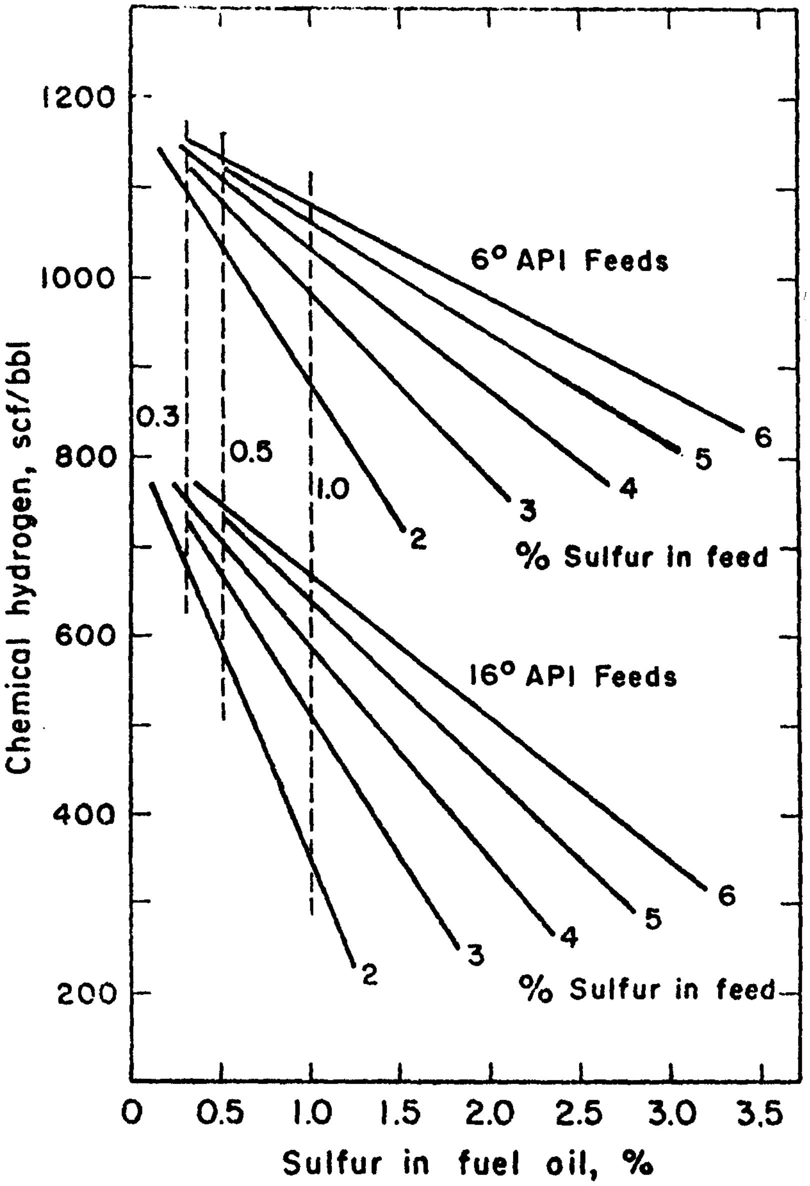

Chemical hydrogen, scf/bbl
1200
1000
800
600
400
200
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Sulfur in fuel oil, %
0.3
0.5
1.0
6° API Feeds
2
3
4
5
6
% Sulfur in feed
16° API Feeds
2
3
4
5
6
% Sulfur in feed

Figure 10

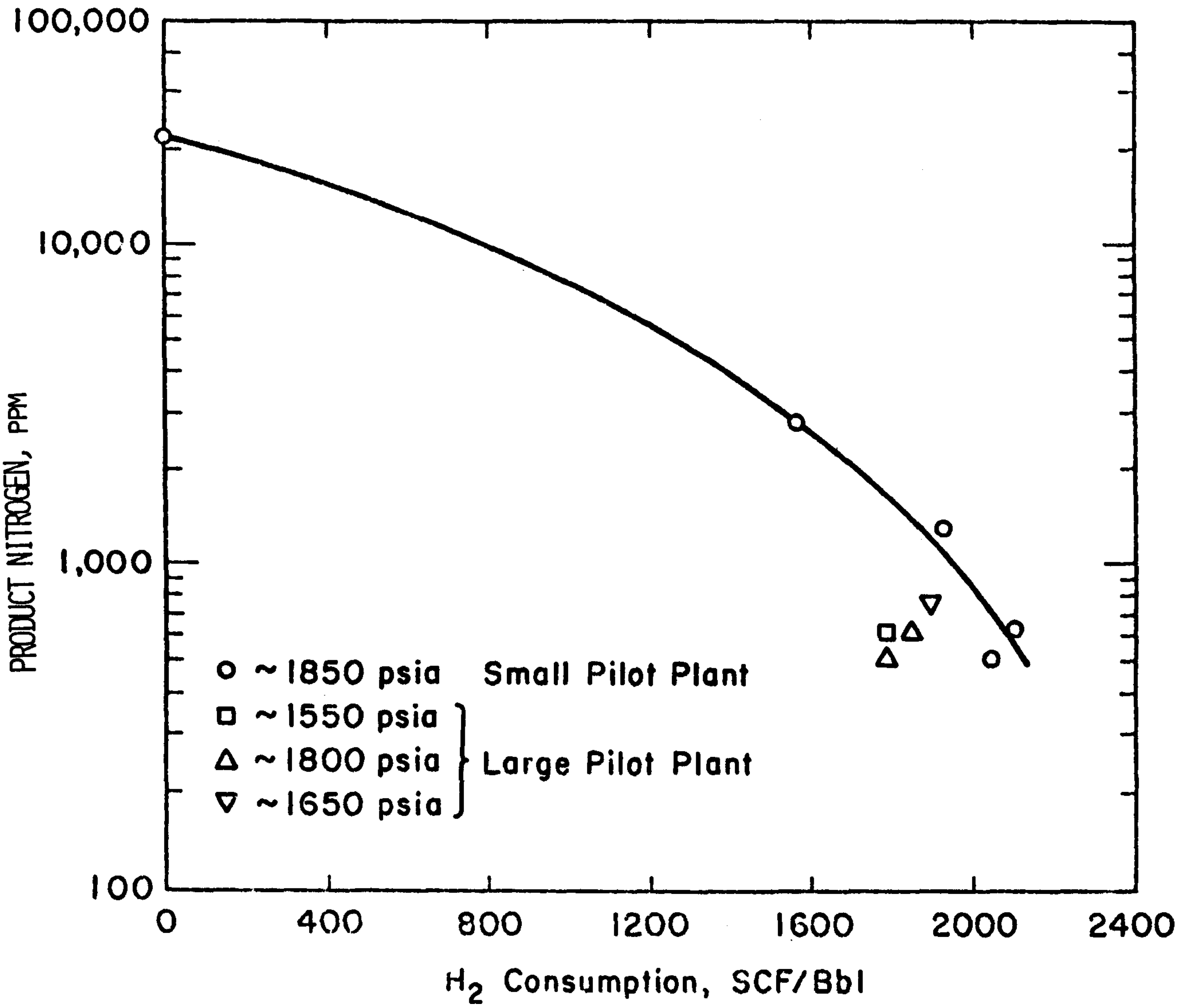

100,000
10,000
1,000
100
PRODUCT NITROGEN, PPM
0
400
800
1200
1600
2000
2400
H_2 Consumption, SCF/Bbl
○ ~1850 psia Small Pilot Plant
□ ~1550 psia
△ ~1800 psia
▽ ~1650 psia
Large Pilot Plant

Figure 11

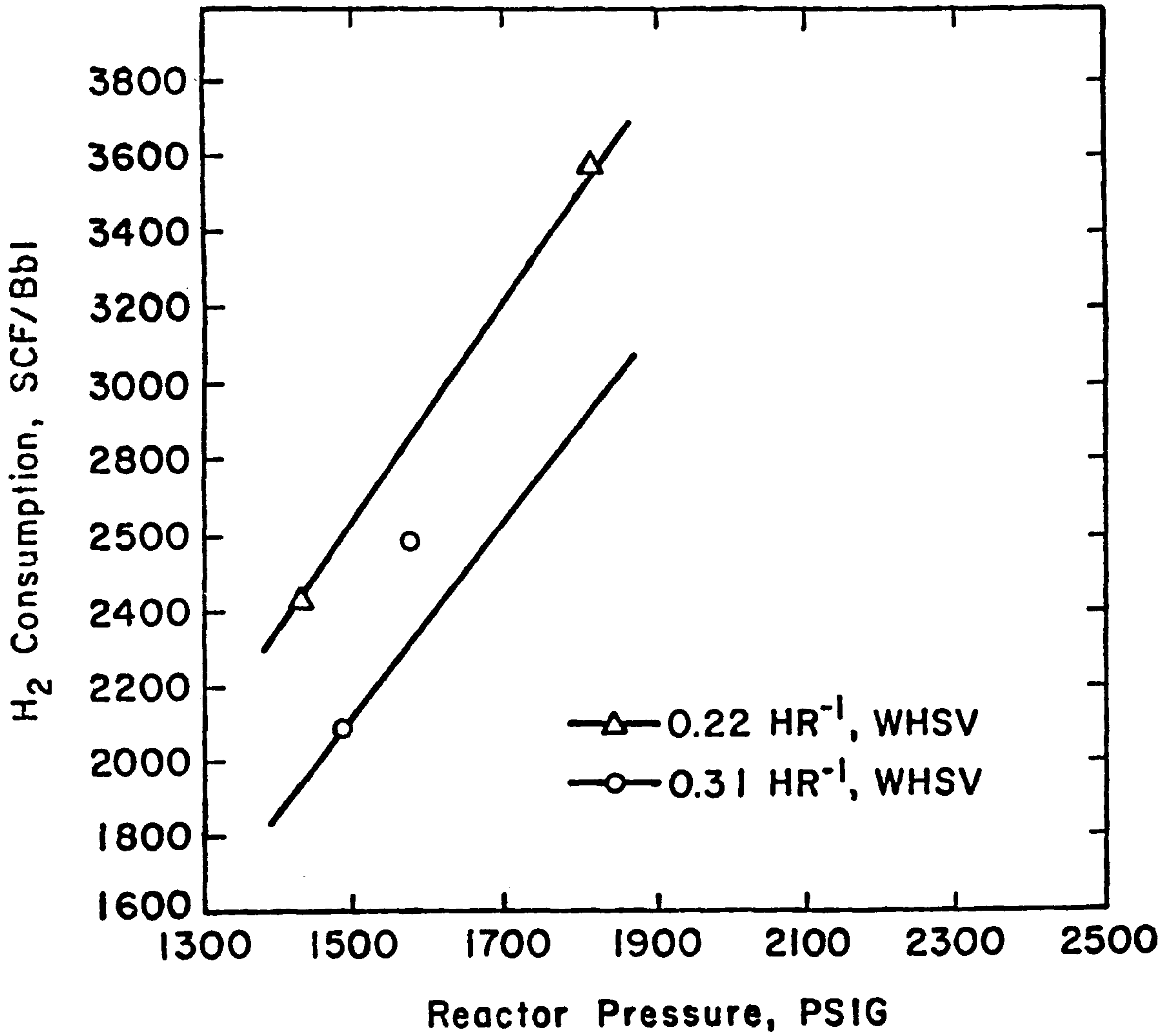

3800
3600
3400
3200
3000
2800
2500
2400
2200
2000
1800
1600
H_2 Consumption, SCF/Bbl
1300
1500
1700
1900
2100
2300
2500
Reactor Pressure, PSIG
0.22 HR^{-1}, WHSV
0.31 HR^{-1}, WHSV

Figure 12

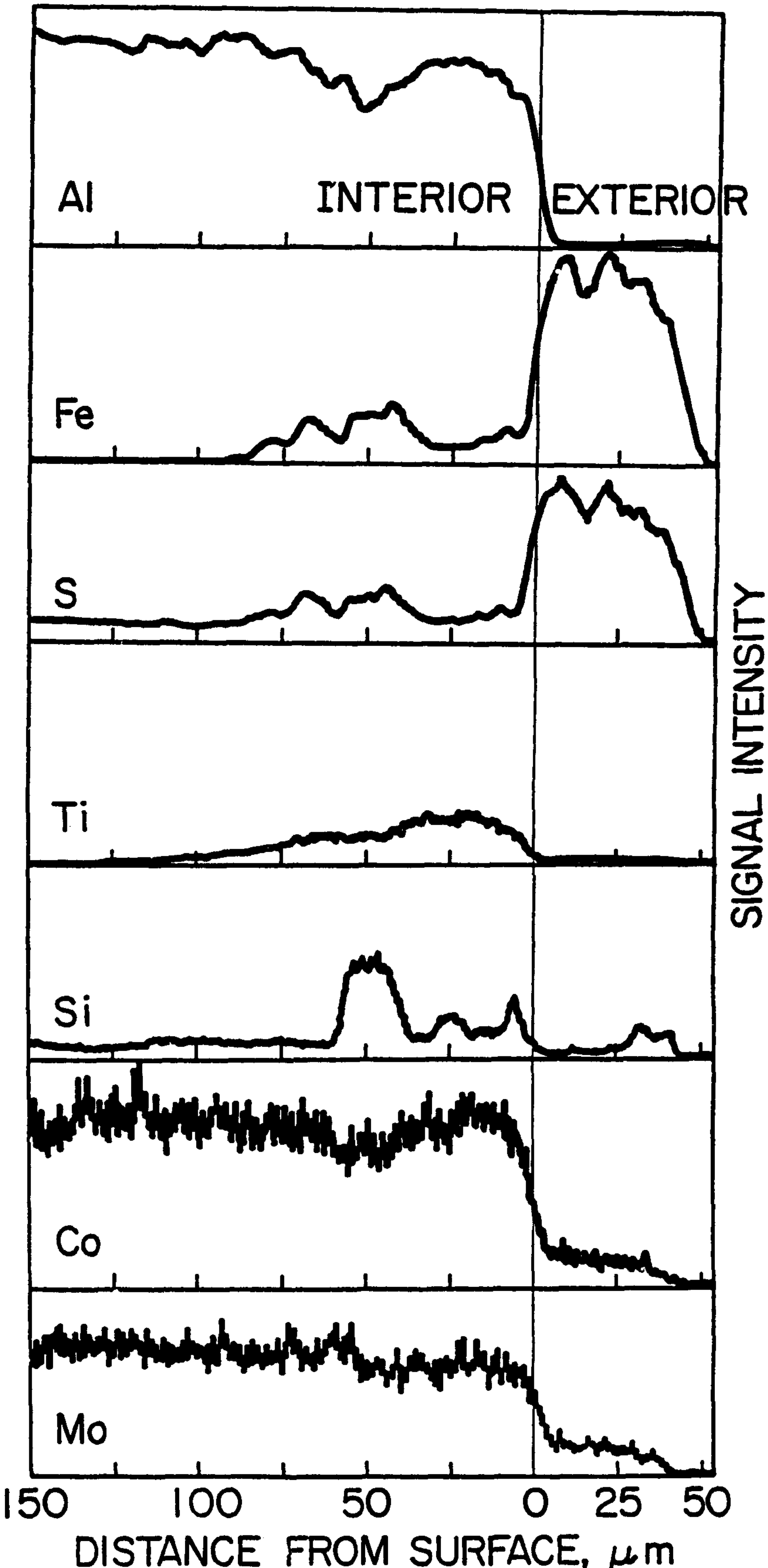

Al
INTERIOR
EXTERIOR
Fe
S
Ti
Si
Co
Mo
SIGNAL INTENSITY
150
100
50
0
25
50
DISTANCE FROM SURFACE, μm

Figure 13

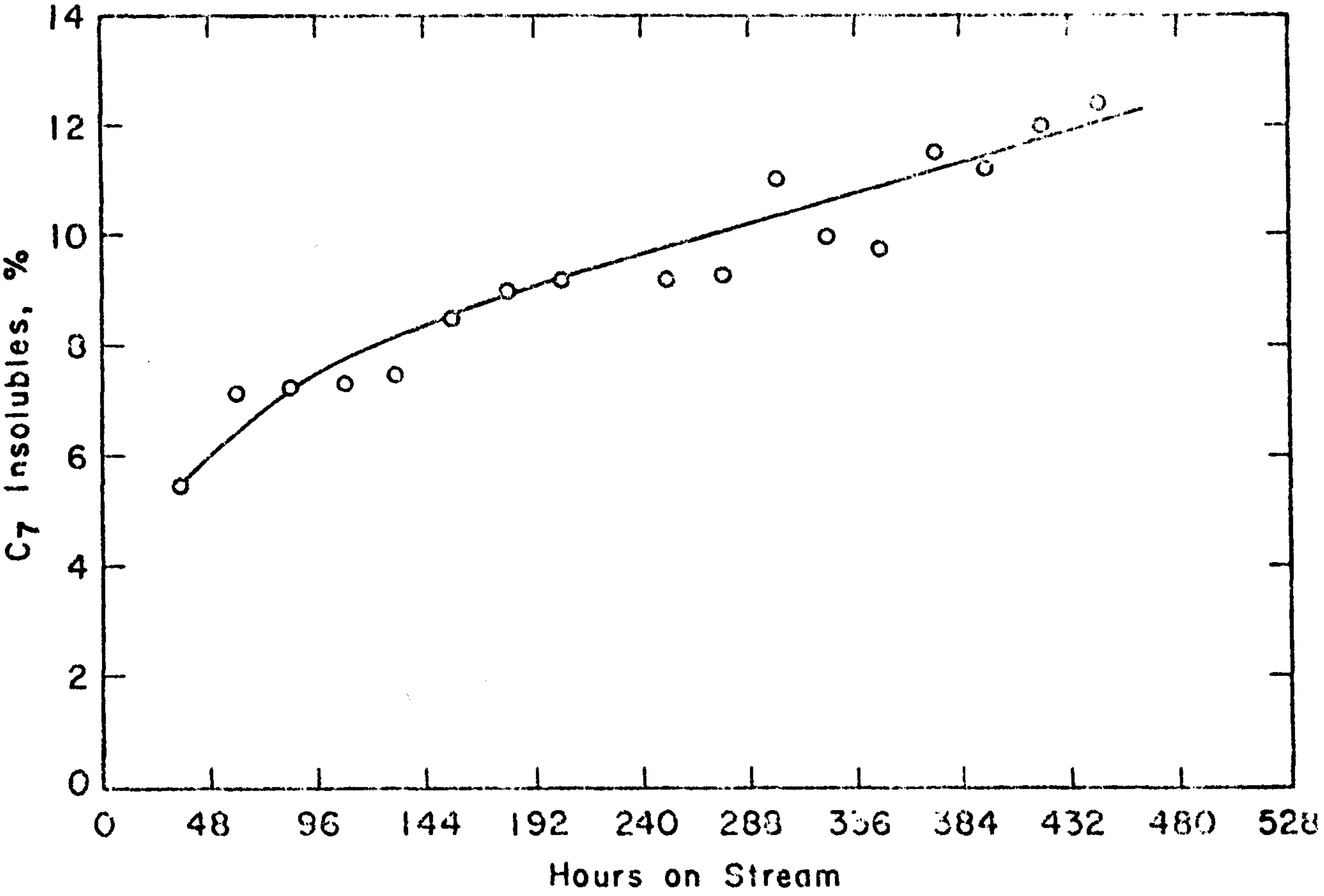

C_7 Insolubles, %
0
2
4
6
8
10
12
14
0
48
96
144
192
240
288
336
384
432
480
528
Hours on Stream

Figure 14

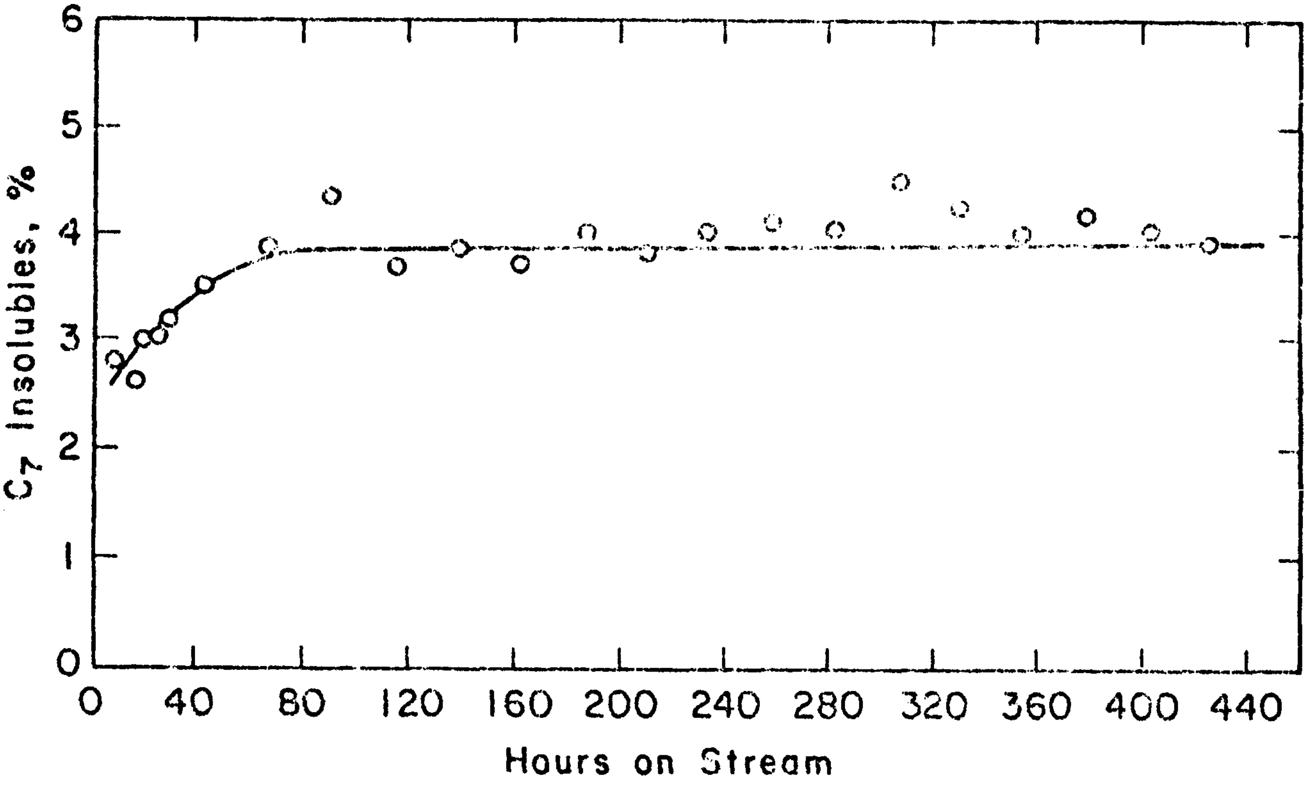


Figure 15

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