50
1-6-76
Special Univ.
Quarterly Distr.
RECEIVED BY TIC JAN 2 1976

MASTER

FE-2028-1
Dist. Category UC-90d

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

First Quarterly Report for Period
June 20, 1975 to September 20, 1975

Prepared by:

James R. Katzer, Bruce C. Gates,
Jon H. Olson, Harold Kwart and Alvin B. Stiles

Departments of Chemical Engineering and Chemistry
University of Delaware
Newark, Delaware 19711

Date Published
September 30, 1975

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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

Under Contract No. E(49-18)-2028

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
fe

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States ERDA, nor any of their employees, nor any of their contractors, subcontractor, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ABSTRACT

The design of the high-pressure liquid-phase micro-reactor has been completed, and assembly of the reactor system is at least half completed. The analytical techniques available for the analysis of sulfur and nitrogen-containing compounds in multicomponent white oil have been thoroughly reviewed, and a satisfactory analysis scheme has been developed. The scheme is centered around high-temperature gas chromatography with a nitrogen-specific detector for analysis of nitrogen-containing organic compounds and a sulfur-specific detector for sulfur-containing compounds. Samples of deactivated catalyst from the Synthoil pilot plant reactor have been analyzed by scanning electron microscopy and electron microprobe. Catalyst near the front of the reactor is 50 to 70% covered with a crust of ferrous sulfide which appears to be responsible for activity reduction. Smaller amounts of Cu, Si, Al, Zn and Ti were also present. Catalyst samples from near the exit of the reactor are essentially free of ferrous sulfide but have an irregular crust of Si-Al ash which covers 20 to 40% of the surface. A 300 cc autoclave has been purchased and set up for the hydrodenitrogenation studies. A catalyst-oil injection system which allows the catalyst and the nitrogen-containing reactant to be injected into the white oil in the autoclave, which is already at reaction conditions has been developed. This avoids the problems associated with the heat-up period.

TABLE OF CONTENTS

	<u>Page</u>
I. Objectives and Scope	2
II. Summary of Progress to Date	3
III. Microreactor for Hydrodesulfurization and Hydrodenitrogenation Studies	4
IV. Analytical Techniques	11
V. Hydrodesulfurization	20
VI Hydrodenitrogenation	27
VII. Reaction Engineering and Catalyst Deactivation	29
VIII. Personnel	40
IX. Literature Cited	42
X. Appendix I	43

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page</u>
1	Phase Behavior of White Oil Mixtures	6

LIST OF FIGURES

<u>Figure No.</u>	<u>Page</u>
1 Schematic of Liquid-Phase High-Pressure Microreactor	8
2 Gas Chromatogram of White Oil obtained with Flame Ionization Detector	12
3 Gas Chromatogram of White Oil with 1.3 wt % Technical Grade Quinoline in it Obtained with Flame Ionization Detector	13
4 Gas Chromatogram of White Oil with 1.3 wt % Technical Grade Quinoline in it Obtained with Nitrogen-Specific Detector	14
5 Gas Chromatogram of Dibenzothiophene in White Oil Obtained by Flame Ionization Detector (Curve a) and Obtained by Sulfur Specific Detector (Curve b)	16
6 Gas Chromatogram of 30 ppm Dibenzothiophene in Hexane-White Oil Mixture Obtained with a Sulfur Specific Detector	17
7 Liquid Chromatogram of 1.3 wt % Technical Grade Quinoline in White Oil:	18
8 Schematic of High Pressure Autoclave for Hydrodenitrogenation Studies Showing Catalyst-Oil Injection System	28
9 Scanning Electron Micrographs of Catalyst Particle from the Upstream End of the Reactor	31a
10 Scanning Electron Micrographs of a Fractured and Plasma Etched Cross Section of a Catalyst Pellet from the Upstream End of the Reactor	32a
11 Electron Microprobe X-Ray Images of the Upstream Catalyst at the Interface with the Inorganic and Organic Crusts	33a
12 Electron Microprobe Concentration Profiles of a Catalyst Particle from the Upstream End of the Reactor	34a
13 Scanning Electron Micrographs of a Catalyst Particle from the Downstream End of the Reactor	35a

<u>Figure No.</u>	<u>Page</u>
14 Scanning Electron Micrographs of a Fractured and Plasma Etched Catalyst Particle from the Downstream End of the Reactor	36a
15 Electron Microprobe X-Ray Images of the Downstream Crust	37a
16 Electron Microprobe Concentration Profiles of a Catalyst Particle from the Downstream End of the Reactor	38a
17 Scanning Electron Micrographs of Two Plasma Etched Catalyst Particles	39a

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

I. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- i) To determine reaction networks and reaction kinetics for catalytic hydrodesulfurization and hydrodenitrogenation of compounds found in coal-derived liquids.
- ii) Develop quantitative data on the chemical and physical properties of deactivated hydroprocessing catalysts used in coal liquifaction processes and to establish the mechanisms of deactivation of these hydroprocessing catalysts
- iii) To provide the reaction engineering information and models required to predict the behavior of catalytic hydroprocessing of coal-derived liquids and to suggest effective methods for improved operation of hydrodesulfurization and hydrodenitrogenation processes.

Toward these objectives a unique high-pressure, liquid-phase microreactor is being developed for pulse (transient) and steady-state modes of operation for kinetic measurements. The relative reactivities of the important types of multi-ring aromatic compounds containing sulfur and nitrogen will be measured under industrially important (300-450°C and 1000-4000 psi) conditions. Following these studies the reaction networks and kinetics of several multi-ring aromatic sulfur- and nitrogen-containing compounds commonly present in coal-derived liquids will be determined. Emphasis will be on the least-reactive compounds. Catalyst deactivation is an important aspect of the commercial scale upgrading of coal-derived liquids. Accordingly, the chemical and physical properties of deactivated coal-processing catalysts will be determined to provide an understanding of the deactivation process; these efforts can lead to improved catalysts or procedures to minimize the problem. In order to utilize the results of this and related research, reaction engineering models of coal-to-oil processing in trickle-bed and slurry-bed catalytic reactors including deactivation will be developed to predict conditions for optimum operation of these processes. Based on the integrated result of all of the above work, recommendations for improved catalytic hydrodesulfurization and hydrodenitrogenation processing will be made.

II. SUMMARY OF PROGRESS TO DATE

During this first quarter the design of the high-pressure liquid-phase microreactor has been completed, all component parts have been ordered and received, and assembly of the reactor system is at least half completed. Assembly and initial testing will be completed in the next quarter.

The analytical techniques available for the analysis of sulfur- and nitrogen-containing compounds in multicomponent white oil have been thoroughly reviewed, and a satisfactory analysis scheme has been developed. The scheme is centered around high-temperature gas chromatography with a nitrogen-specific detector for analysis of nitrogen-containing organic compounds and a sulfur-specific detector for sulfur-containing compounds. Analysis for products not containing sulfur or nitrogen is by flame ionization detector or liquid chromatography depending on which is more appropriate.

A list of the sulfur- and nitrogen-containing compounds which we plan to use in this work has been prepared and will shortly be submitted to ERDA for their approval. Compounds which cannot be obtained commercially will be synthesized.

Samples of deactivated catalyst from the Synthoil pilot plant reactor have been analyzed by scanning electron microscopy and x-ray microprobe. Catalyst near the front of the reactor is 50 to 70% covered with a crust of ferrous sulfide which appears to be responsible for activity reduction. Smaller amounts of Cu, Si, Al, Zn and Ti were also present. Catalyst samples from near the exit of the reactor are essentially free of ferrous sulfide but have an irregular crust of Si-Al ash which covers 20 to 40% of the surface.

A 300 cc autoclave has been purchased and set up for the hydrodenitrogenation studies. A catalyst-oil injection system which allows the catalyst and the nitrogen-containing reactant to be injected into the white oil in the autoclave, which is already at reaction conditions has been developed. This avoids the problems associated with the heat-up period. During the next quarter Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃ and Ni-W/SiO₂-Al₂O₃ will be evaluated with quinoline and carbazole to choose the most active catalyst for the remainder of the hydrodenitrogenation work.

III. MICROREACTOR FOR HYDRODESULFURIZATION AND HYDRODENITRO- GENATION STUDIES

Industrially, hydrodesulfurization and hydrodenitrogenation of petroleum-derived feedstocks is conducted in three-phase (trickle-bed) reactors. Mears (1971) has shown that laboratory trickle-bed reactors must be quite large to give meaningful results; but large laboratory reactors require large quantities of reactant. In this project the reaction networks and kinetics of hydrodesulfurization and hydrodenitrogenation of multi-ring sulfur- and nitrogen- containing aromatic compounds commonly found in coal-derived liquids is to be determined under conditions typical of industrial practice. Since many such compounds are not available commercially and must be synthesized or, if available commercially, are expensive, it is advantageous to operate at the microreactor scale because this mode reduces the quantity of the compounds required. Further it is often far easier to control and operate a small reactor than a larger unit, and exploratory work is conducted much more easily in microequipment. Therefore, the development of a microreactor system for the hydrodesulfurization and hydrodenitrogenation studies has useful potential.

During this quarter, the design of the high-pressure, liquid-phase microreactor (HPL) system was revised and completed. The construction of the reactor is half-completed. In the next quarter, the construction will be finished and the reactor will be tested. The remainder of this section describes some of the important details of this system.

Principle of Operation

Chromatographic microreactors for gas phase catalytic systems have been used for some time; Kokes (1955) at Johns Hopkins likely was the first to develop the basic method for obtaining quantitative information from microreactor data. A similar miniaturization for two- or three-phase fluid flow over a fixed catalyst has not been achieved.

Commercial hydrodesulfurization practice teaches that the petroleum hydrodesulfurization reactions approach zero-order in hydrogen at moderate (2500 psi) hydrogen pressures. These reactors are operated with the gas-phase flow in substantial volumetric excess of the liquid to provide adequate hydrogen supply to catalyst in all parts of the bed. Therefore the key to simple operation of hydrodesulfurization reactors is to maintain a high concentration of hydrogen.

Microreactor systems are made to operate with very small catalyst particles. Not only does the dispersion of the catalyst provide for a close approach to piston flow, but

also the Thiele modulus of the catalyst is reduced, reducing or eliminating intraparticle diffusional limitations. Three-phase fluid systems cannot operate with beds of fine particles because the fluid and gas do not flow across the catalyst bed uniformly. Therefore, the logical choice is to eliminate the gas phase while simultaneously providing for an adequate supply of hydrogen.

The reactants in the hydrodesulfurization/hydrodenitrogenation research are to be dissolved in a paraffin oil (white oil) of moderate molecular weight. This oil has very low activity for hydrogen transfer (Guin *et al.*, 1975), and therefore this oil serves to insure that the observed reactions are catalytic. By operating with dilute reactant in this white oil the total hydrogen demand, even with hydrocracking, can be made quite small. Adjusting the degree of saturation of the white oil carrier provides an easy method for providing excess hydrogen to the catalyst and of setting the hydrogen level if the solubility of hydrogen in the white oil at reaction conditions is sufficient.

It is recognized generally (Prausnitz and Shair (1961)) that the solubility of hydrogen in paraffinic oils increases with increasing temperature. Consequently, the hydrogen content of the oil can be set by saturating the carrier at low temperature. The liquid from the saturator can be placed under additional hydraulic pressure and then heated to higher temperatures without having dissolution of gas and bubble formation. Some aspects of this process are shown in Table 1.

The first section of Table 1 gives the K values for H_2S and H_2 for a liquid containing 1×10^{-5} mole fraction H_2S and 0.005 mole fraction H_2 . The liquid is below the bubble point for the two pressures and the entire temperature range. The K's are almost independent of temperature and are quite low. Consequently, operation entirely in the liquid phase is possible for modest hydrogen levels. The second section of Table 1 gives the liquid-phase mole fractions and the K values for the hydrogen paraffin oil system at the bubble point. These data show that the molar density of hydrogen is larger in the liquid phase than in the vapor phase when the liquid is saturated with hydrogen at reaction conditions. Therefore the reaction rate for dilute pulses of reactants will not be limited by the availability or solubility of hydrogen.

TABLE 1

Phase Behavior of White Oil Mixtures

Mixture Below Bubble Point

Mixture: $x_{H_2S} = 10^{-5}$; $x_{H_2} = 0.005$; $x_{white\ oil} = 0.995$

T, °C	P = 1000 psi		P = 2000 psi	
	K_{H_2S}	K_{H_2}	K_{H_2S}	K_{H_2}
350	2.12	1.55	1.80	1.29
367	2.14	1.53	1.79	1.26
384	2.14	1.52	1.78	1.24
400	2.15	1.50	1.77	1.21
417	2.15	1.49	1.76	1.19
433	2.15	1.47	1.74	1.16

Mixture at Bubble Point

T, °C	P = 1000 psi		P = 2000 psi	
	x_{H_2}	K_{H_2}	x_{H_2}	K_{H_2}
350	0.146	6.59	0.266	3.70
367	0.151	6.31	0.272	3.51
384	0.154	6.05	0.276	3.40
400	0.157	5.79	0.280	3.25
417	0.161	5.33	0.288	3.07
433	0.163	5.27	0.301	2.85

The calculations illustrated in Table I are based upon the N.G.P.A. version of the Chao-Seader vapor-liquid equilibrium of industrial mixtures. These estimates have an uncertainty of about 25%. Because of the indicated excess of dissolved hydrogen the design of the microreactor has a large probability of success. The critical pump in the apparatus will provide pressures in substantial excess of 2000 psi; at high pressure all of the gases are held in solution. During the next quarter the phase equilibrium will be tested critically.

The size of the microreactor must be large enough to supply adequate samples for analysis. The major reaction products are to be analyzed with gas and liquid chromatography; the development of these methods is described in greater detail below. A single pulse containing one milligram of reactant will allow good detection of the reaction products with the current analytical methods even at very low conversions. Thus one gram of a critical reactant is sufficient for a modest research program.

Design of Reaction System

The finalized version of the HPL reactor is shown in Figure 1. The diagram is divided into five sections: the carrier-oil saturator, the pulse-forming network, the reactor, the sample collection system and the flow control system. The reactant dissolved in oil is injected as a pulse into the flow of oil and carried through the reactor in the carrier oil. Ideally, the carrier oil should be nonreactive, but a minor conversion of this oil can be handled by the data reduction methods. Initially, the pulse will be quite large to reduce problems of sample collection, but as experience with the system grows, very small pulses of reactant may be used.

The carrier-oil saturator consists of a 300 cc sparged vessel connected to the high pressure hydrogen cylinder. The carrier-oil saturator typically will be operated at a lower pressure than the reactor. Although the solubility of hydrogen increases with temperature, the solubility of potential product gases (H_2S , NH_3 , H_2O) does not. Therefore, over-pressure is needed to keep all of the product light ends in the liquid phase. The carrier-oil saturator contains enough oil for steady-state operation over several days.

For steady-state operation the reactant is mixed with the carrier oil in the carrier-oil saturator and fed directly to the reactor.

Figure 1. Schematic of Liquid-Phase High-Pressure Microreactor

For the pulse operating mode the pulse samples are mixed with carrier-oil and pressurized with hydrogen in the 25 cc saturator. The mixed charge is supplied to the sample loop with the aid of the window and the dead volume. The dead volume is used to set a back pressure to the sample loop while the sample volume is filled with reactant. The window is used to observe when the sample loop is filled. The run is initiated by valving the carrier oil through the high pressure pulse loop. This network is the high pressure analog of a gas sampling valve. A liquid chromatograph sample valve is to be used when the sample temperature is below 50°C

The reactor is a three-inch length of high pressure nipple with an inside diameter of 1/8 in. Consequently, catalyst up to 0.015 in. (400 μ) in diameter can be used without significant flow bypassing at the walls. To eliminate any major effect of axial dispersion, the bed is 100 particle diameters long, i.e., 1.6 inches. The remainder of the tube is packed with quartz chips which act as a liquid preheater. The Ruska pump, which can operate up to 8000 psi, operates in a flowrate range of 0.1 to 1.2 cm³/hr. This flowrate range corresponds to a LHSV of 0.1 to 1.3 hrs.⁻¹

The reactor oven consists of a stainless steel tube with hexagonal end plates which fit snugly around the high pressure fittings at the ends of the reactor. The heating element is nichrome wire supported in ceramic stand-off beads. The reactor temperature control is provided by an electrical PI controller; the temperature is measured to $\pm 0.1^\circ\text{C}$ with a platinum resistance thermometer.

The sample collection loop is very similar to the pulse loop. The sample loop volume is three times larger than the minimum pulse volume. Although the position of the pulse can be estimated by careful timing, the excess volume of the loop will allow for errors. This method is used because we are not aware of a low-volume, high pressure U.V. or R.I. detector for pulse location. The pulse will be traced with a non-reactive reference compound to establish the conversion ratios of the pulse. The sample loop can also be used without change for continuous operation of the reactor.

The reactor pressure is set by the back pressure loaded into the final dead volume by the back-pressure pump. The pressure drop in the apparatus is extremely low at the required flowrates, and therefore the back pressure reservoir is the system pressure. Plugging will result in an increase in the pump discharge pressure above the backpressure value and eventual failure of the reactor rupture disk.

Safety is an important part of any high pressure system. All of the components have working pressure (at

operating conditions) ratings substantially greater than the maximum pressure planned (for the moment 4000 psi).

The unit is provided with over-capacity rupture disks and is enclosed in a portable barricade. The energy content of the system is small as long as the fluid remains a liquid. A complete parts list for the apparatus is provided in appendix I.

Although it is not very exciting to describe the design and construction of equipment, we believe this reactor system has substantial potential for research on coal-derived synthetic fuels. The assembly of the microreactor system will be completed and debugged during the second quarter, and the system will begin to be used in studies of hydrodesulfurization and hydrodenitrogenation kinetics.

A paper "Microreactors for Catalytic Reaction Studies of Coal-Derived Fuels" by K. F. Eliezer, B. C. Gates and J. H. Olson has been submitted to the AIChE and will be presented in Los Angeles by J. H. Olson in November.

IV. ANALYTICAL TECHNIQUES

The analysis requirements for the hydrodesulfurization and hydrodenitrogenation work are substantial with the analysis being complicated by the broad range of compounds in the white oil and the large possible number of reaction products in the reaction networks. We have therefore carried out a comprehensive evaluation of potential analytical techniques and schemes. This involved substantial discussions with research groups at Oak Ridge National Laboratory, Gulf Oil Company, American Cyanamid Company, E. I. duPont de Nemours and the Pittsburgh Energy Research Center; hands-on operation of several liquid chromatographic and gas chromatographic instruments; and analysis of prepared samples containing a variety of sulfur- and nitrogen-containing compounds in white oil by several equipment suppliers. This demonstrated: (1) that high-temperature gas chromatography utilizing detectors which are specific to sulfur only and to nitrogen only provides a very powerful tool for quantitative analysis for sulfur and nitrogen-containing compounds in a background of white oil species; (2) that the proper column combined with temperature programming would allow the concentration of some of the non-sulfur and non-nitrogen containing products of reaction to be quantitatively determined using flame ionization detection; and (3) that liquid chromatography can also successfully do most of the required analyses as long as the compounds of interest maintain aromatic or olefinic character. Specific examples illustrating these conclusions follow.

Figure 2 shows a gas chromatogram of the white oil obtained using a flame ionization detector (Perkin-Elmer Model 3920 G.C., 6 ft OV-17 on Chromasorb column, temperature programmed 120-280°C at 8°C/min), and Figure 3 shows the white oil with 1.3 wt % technical grade (impure) quinoline in it. The peaks which result from the added quinoline are easily recognized near the front of the white oil peak, but there is no indication which of the new peaks represent nitrogen-containing compounds. However, higher molecular weight nitrogen-containing compounds would easily be masked by the white oil background with the flame ionization detector unless columns which effectively separate them from the white oil could be found.

Figure 4 shows the 1.3 wt % technical grade quinoline in white oil as analyzed by a nitrogen-specific detector (Perkin-Elmer G. C. Model No. 3920 with N-detector, reported detector selectivity nitrogen to hydrocarbon 10⁴:1) under similar chromatographic conditions. Each of the peaks in the technical grade quinoline represents a nitrogen-containing compound; the white oil background causes no interference with the analysis obtained by the nitrogen-specific detector. This detector eliminates all masking problems due to non-nitrogen containing hydrocarbons. The detection limit is below 10⁻⁵

Figure 2 Gas Chromatogram of White Oil Obtained with Flame Ionization Detector: Perkin-Elmer 3290 C.C. with FID detector, 6 ft glass column of OV-17 on Chromasorb Q. Temperature programmed 120-280°C at 8°C/min. 0.5 ul injected, attenuation 100 x 16, later 100 x 64.

Figure 3 Gas Chromatogram of White Oil with 1.3 wt % Technical Grade Quinoline in it Obtained with Flame Ionization Detector: operating conditions as for Figure 2.

Figure 4 Gas Chromatogram of White Oil with 1.3 wt % Technical Grade Quinoline in it Obtained with Nitrogen-Specific Detector: Perkin-Elmer G. C. with Nitrogen-Specific Detector, operating conditions similar.

weight fraction of quinoline or other nitrogen-containing hydrocarbons, and thus the nitrogen-specific detector has more than adequate sensitivity for nitrogen-containing products which appear at very low concentrations in the hydrodenitrogenation reaction network.

Figure 5 is a chromatogram of dibenzothiophene in white oil obtained by the flame ionization detector (Curve a) and obtained by a sulfur-specific detector (Perkin-Elmer 3920 FID/FPD*, Dexsil SCOT column 0.02 in. by 50 ft, temperature programmed 150-300°C at 4°C/min, FPD attenuation 64×10 , FID attenuation 32×10) (curve b). The open tubular column gives greater resolution of the white oil (compare with Figure 2), but sulfur analysis by flame ionization detector would be very difficult because of the hydrocarbon background; the sulfur-specific detector eliminates all such problems. Figure 6 shows the chromatographic trace obtained for 30 ppm dibenzothiophene in a hexane-white oil mixture (Tracor Model 550 GC, Flame Photometric Detector reported selectivity sulfur to hydrocarbon $10^4:1$) at an attenuation of 8×10^4 . Sulfur-specific detection is sensitive for concentrations below our requirements ($<10^{-6}$ weight fraction), even for very minor sulfur-containing reaction products. On the other hand, the limit of detectability of biphenyl (a reaction product of dibenzothiophene desulfurization) is about 10^{-5} weight fraction, and this sensitivity would have been even less if we had not been able to find a G. C. Column (OV-1 on chromasorb) which achieved satisfactory separation of the biphenyl from the white oil background.

Figure 7 shows the 1.3 wt % technical grade quinoline in white oil run on a liquid chromatograph (Perkin-Elmer Model 601, ultraviolet detector, column 2.54 mm by 0.5 m packed with OD SIL-X-IRP, 55°C isothermal, solvent 40% MeOH in H_2O). The component separation (peak resolution) is not as good as by gas chromatography using the nitrogen-specific detector. There are fewer distinct peaks; this is due either to incomplete separation, to loss of some of the components on the column or to a lack of detection because some of the components were neither aromatic or olefinic in character. The ultraviolet detector is highly sensitive to hydrocarbon unsaturation but will not detect saturated species. Thus if saturation of the nitrogen- or sulfur-containing species occurs before hetero-atom removal, liquid chromatography would not provide analysis for these species. Refractive index detection appears to be insufficiently sensitive for these analyses as indicated by our work. Similarly as soon as nitrogen or sulfur atom removal occurs, the N- and S-specific detectors with gas chromatography will provide no further analytical information. Because of the high sensitivity of the ultraviolet to hydrocarbon unsaturation the limit of detectability is below 10^{-5} weight fraction.

Thus either gas chromatography or liquid chromatography could satisfy most of our analytical needs. However, there are certain reaction products for which either one analytical technique or the other will not provide adequate analysis.

*FID = Flame ionization detector

FPD = Flame photometric detector-sulfur specific detector

Figure 5 Gas Chromatogram of Dibenzothiophene in White Oil Obtained by Flame Ionization Detector (Curve a) and obtained by Sulfur Specific Detector (Curve b): Perkin-Elmer 3920 GC with Dexsil SCOT column 0.02 in. by 50 ft., temperature programmed 150 to 300°C at 4°C/min, FPD attenuation 64 x 10, FID attenuation 32 x 10.

Figure 6 Gas Chromatogram of 30 ppm Dibenzothiophene in Hexane-White Oil Mixture Obtained with a Sulfur Specific Detector: Tracor Model 550 GC, Flame Photometric Detector, attenuation 8×10^4 , temperature programmed 160-250°C at 8°C per minute

Figure 7 Liquid Chromatogram of 1.3 wt % Technical Grade Quinoline in White Oil: Perkin-Elmer Model 601 liquid chromatograph, ultra-violet detector, column 2.54 mm by 0.5 m packed with OD SIL-X-IRP, 55°C isothermal, solvent 40% MeOH in H₂O.

In most of these cases the opposite technique will give the required analysis, and thus a combination of the two analytical techniques should provide the most complete analytical information. We can use, on a part-time basis, a liquid chromatograph in the Chemistry Department but do not have available to us nitrogen- and sulfur-specific detectors.

Based on the above information we have decided that our analytical scheme should be centered around high-temperature gas chromatography with a nitrogen-specific detector for analysis for nitrogen-containing compounds and a sulfur-specific detector for sulfur-containing compounds. Analysis for products not containing sulfur or nitrogen will be by flame ionization detector or liquid chromatography depending on which is the most appropriate. Identification of compounds in complex product mixtures will be by combined gas chromatography-mass spectrometry. Column types, solvent systems and operating conditions for the gas chromatographic and liquid chromatographic analyses have been determined for the sulfur- and nitrogen-containing compound systems with which we are starting. Analysis of the gas phase from the reactor will be by gas chromatography utilizing a thermal conductivity detector. The high temperature gas chromatograph with the nitrogen-specific and sulfur-specific detectors is being purchased for this work. Gas chromatographs with a standard flame ionization detector and with a thermal conductivity detector and the combined gas chromatography-mass spectrometry system are already available in the Chemical Engineering Department, and the liquid chromatograph is available in the Chemistry Department but we can use it only a small fraction of the time.

Further improvement and modification of these analytical procedures will be made as required for the work.

V. HYDRODESULFURIZATION

A. Compounds to be Studies

According to the contract, ERDA shall review the sulfur-containing compounds nominated by this group for research upon reaction networks of hydrodesulfurization. The following subsection outlines the selection and preparation routes for two- and three-ring thiophene and thianthrene compounds. This subsection is presented in a self-contained mode as an aid to the review process.

The benzothiophene and dibenzothiophene structures are expected to desulfurize slowly and to show substantial rate inhibition from substituent groups. Therefore, we recommend that the relative reactivity of the following methyl substituted benzothiophenes be determined.

Similarly we recommend that the relative reactivity of the following methyl substituted dibenzothiophenes be determined.

No information is available on the relative reactivity of sulfur-containing compounds containing sulfur in the six-membered ring. These compounds are expected to be among the least reactive of the organic sulfur compounds found to a significant extent in synthetic fuels. Therefore, we recommend that the relative reactivity of the following sulfur-containing compounds be determined along with that of several methyl substituted thioxanthenes.

B. Benzothiophenes to be Synthesized and Methods of Preparation

- 1) 3-methylbenzo[b]thiophene is to be prepared by the methods of Werner (1949) and Banfield (1956) from 1-phenylmercaptopropanone-2.

- 2) 2,3-dimethylbenzo[b]thiophene is to be prepared by the analogous method starting from 3-phenylmercaptobutanone-2.

- 3) 2-methylbenzo[b]thiophene is scheduled for preparation from a (o-carboxyphenylmercapto) propionic acid by the methods of Hansch and Lindwall (1945).

- 4) 7-methylbenzo[b]thiophene is to be prepared by the method of Sunthakar and Tilak (1950).

- 5) All the above compounds have been examined in the gas phase over cobalt-moly catalysts. Their kinetic behavior in high pressure hydrodesulfurization over such catalysts in the liquid-phase microreactor, simulating conditions which prevail in the Synthoil process, must be studied from the following viewpoints: (a) how does alkyl substitution influence the rate in the liquid phase under high pressure? (b) under these conditions does the presence of such nitrogenous impurities as pyridines and indoles influence the rate and course of hydrodesulfurization?

C. Dibenzothiophenes to be Synthesized and Methods of Preparation

Recent studies by the ERDA group (Akhtar et al., 1974) indicate that dibenzothiophenes and related structures (see below) are among the most abundant sulfur containing residues in coal hydrogenation products. Since a quantitative understanding is lacking as to just how much more resistant dibenzothiophene is compared to benzothiophene under the circumstances of the Synthoil process, studies directed along these lines using the high-pressure liquid-phase microreactor represent an important objective of the current program.

- 1) Dibenzothiophene; this compound has been purchased from Aldrich (D3,220-2). This commercial material (95%) was first recrystallized from ethanol then sublimed.

- 2) Benzo[def]dibenzothiophene; this compound which was a principal component among the sulfur-containing residues of the Synthoil process (as established by the ERDA group (Akhtar *et al.*, 1974)) will be prepared by a method analogous to that used by Suter *et al.* (1943) and illustrated by

- 3) The 4-methyldibenzothiophene constitutes a decisive test of the inhibiting effect of peri-alkylation. This factor which is tested in the benzothiophene system (see above) is bound to be of even greater consequence in the dibenzothiophene system. The possibility of steric hindrance factors involved in hydrodesulfurization of the most refractory (Akhtar *et al.*, 1974) of the classes of sulfur-containing substrates to be tested is a matter of particular concern in the HPL microreactor studies.

The preparation of this compound by the method of Campaigne *et al.* (1964) (Eq. 2) is planned.

- 4) Di-substituted di-benzothiophenes represent another important class of thiophene structures. Because of the large number of methyl groups in coal, these compounds are expected to be abundant. The inhibition anticipated for the

reaction of 4-methyl dibenzothiophene, for example, should only be more pronounced in the case of the 4, 6-dimethyl dibenzothiophene. On the other hand, the retardation of reaction rate should diminish somewhat with the 3,7-dimethylated dibenzothiophene and further with the 2,8 dimethylated compound as the likelihood of steric hindrance is lessened.

This series of compounds will be prepared according to the procedure of Gerdil and Lucken (1965).

D. Thianthrene-like Compounds to be Synthesized and Method of Preparation

P. H. Given (1975) speaking on sulfur compounds present in coal-derived liquids (and as reported in the monthly bulletin of the British Coal Research Association 1958) has claimed that this class of compounds is among the most abundant prior to the application of hydrodesulfurization procedures.

Compounds in this category are to be studied in the HPL reactor. Preparation procedures are indicated where required.

- 1) Thianthrene itself (X=S) can be obtained commercially from Aldrich (12,244-0) and procedures for its purification are well known.

- 2) Thioxanthene (X=CH) can also be purchased Aldrich (T3,380-4) and readily purified.

- 3) Thioxanthone (X=C=O) is similarly available (T3,400-2).

- 4) Phenoxathin (X=O) is to be made according to the procedure of Suter (1943) from diphenylether and sulfur in the presence of AlCl₃.

- 5) Phenothiazine (X=NH) can be purchased from Aldrich (P1,483-1) and can be readily purified.

- 6) The analogue benzo-1,4-oxathiin is to be prepared by the method of Verheijen and Kloosterziel (1975) through the reaction of β -phenoxyethyl bromide with the appropriate thiosulfonate, followed by ring closure with AlCl₃ and aromatization with SO₂Cl₂ and quinoline.

- 7) The analogue benzo-1,4-dithiin is to be made analogously by the same procedure starting from β -mercaptophenylethyl bromide.

- 8) The analogue benzo-1, 4-triazin is also to be made by this procedure starting from β -aminophenylethyl bromide.

- 9) The studies projected on the members of this series are also expected to provide some further insight into the relative rates and synergistic effects of heteroatoms (compare X=CH, NH, O, S) on the ease and course of hydrodesulfurization in the HPL reactor.

VI. HYDRODENITROGENATION

In addition to the development of the required analytical schemes discussed in Section IV, the hydrodenitrogenation research during the first quarter of this project has involved procuring the required equipment and materials and developing reaction study conditions and procedures. One 300-ml autoclave has been purchased, received and set up; and it is currently being tested. A one-liter autoclave, which was available in the Department has been refurbished and is also operational for this work. Figure 8 shows a schematic of the set-up of these autoclaves. A catalyst-oil injection system has been developed which allows the white oil in the autoclave to be brought to reaction conditions (temperature and pressure), and then the catalyst and nitrogen-containing species are injected into it. This prevents the problems of reaction and/or catalyst deactivation during the heat-up period and should allow more quantitative kinetics to be determined.

Large batches (~50 lbs) of the three prescribed catalysts Co-Mo/Al₂O₃ (American Cyanamid HDS-2A), Ni-Mo/Al₂O₃ (American Cyanamid HDS-9A) and Ni-W/SiO₂-Al₂O₃ (Harshaw) have been obtained and evaluation of these catalysts for relative activity will be started shortly. The catalyst which shows the highest activity for quinoline and carbazole hydrodenitrogenation will be used for the remainder of the hydrodenitrogenation work. Although comparison will be made between unsulfided and sulfided catalysts, the work will be carried out essentially exclusively with presulfided catalysts. Sulfiding is being done at 325°C in 10% H₂S in H₂ for two hours prior to loading the catalyst into the reactor.

During the next quarter the evaluation of the relative activity of the three catalyst types for nitrogen removal from quinoline and carbazole will be completed, and product distribution as a function of conversion will be determined using the batch autoclave systems. From this work the most active catalyst will be chosen for future work. When the high-pressure pulse and flow microreactor is completed, hydrodenitrogenation studies will be started using this reactor with carbazole. The results will be compared with those obtained from the batch, autoclave reactor. Since the microreactor which is being constructed will be dedicated to the hydrodesulfurization studies, a second system similar to it will be constructed as soon as we have demonstrated its applicability to the hydrodenitrogenation studies. Studies to determine the reaction network and kinetics of hydrodenitrogenation of carbazole and acridine will be started during the second quarter. Synthesis of substituted carbazole and acridines and of other nitrogen-containing compounds to be used in the studies of relative reactivity will also be begun upon approval by ERDA.

Figure 8 Schematic of High Pressure Autoclave for Hydrodenitrogenation Studies Showing Catalyst-Oil Injection System.

VII. REACTION ENGINEERING AND CATALYST DEACTIVATION

During this quarter two catalyst samples from the 5/16" Synthoill reactor were analyzed with electron microprobe, scanning electron microscope and light microscope techniques. The results of this investigation are being prepared for submission to the A.I.Ch.E. Journal. The major results will be discussed in summary below; the completed paper will be included in the next progress report. The work reported here has been done with funds from both NSF RANN (Grant to H. Kwart and B. C. Gates) and this ERDA Contract.

The samples of deactivated catalyst were from the 5/16" Synthoill pilot plant reactor at the Pittsburgh Energy Research Center at Bruceton and were supplied as a cemented mass contained in one foot sections sawed from the reactor. One section was taken from the upstream or entrance zone and the other was taken from the downstream zone. The catalyst was removed from the reactor sections by milling the wall lengthwise. The catalyst was covered with solidified Synthoill liquid mass but was otherwise free from gross damage.

The catalyst was Harshaw 0402T, a commercial hydrodesulfurization catalyst, initially containing 3% CoO, 15% MoO₃ on a 5% SiO₂-77% Al₂O₃ support. The reactor had been operated for 15 days at nominally 2000 psi and 420°C, before it was shut down and the catalyst was removed.

The catalysts were prepared for scanning electron microscope (SEM) and x-ray microprobe analysis by mounting them in epoxy resin followed by lapping three grits down to a final polish with a 0.25 μ m diamond paste. To provide a better definition of the inorganic constituents, the organic material was removed by plasma etching. Some of the particles were simply fractured, plasma etched and mounted on a post prior to analysis, whereas others were plasma etched after being embedded and polished. The work was performed at Micron, Inc., Wilmington, Del.

The catalysts were initially analyzed qualitatively by dispersive x-ray analysis (EDAX) for elements above argon. The EDAX analysis of the polished samples yielded semi-quantitative estimates of the major constituents. These qualitative determinations were used to select the elements for analysis with the electron microprobe and to confirm the chemical composition. Crystals were tentatively identified by crystal habit.

The electron microprobe was used in a scanning mode to map element positions with a resolution of about 1 μ m and then used in a line-sweep mode to make a concentration profile of selected elements near the surface of the catalyst. For the profile experiments the composition was averaged over a 100 μ m line oriented parallel to the surface.

The pore size distribution of the catalysts also is being determined, but these data are not yet internally consistent. These data show a substantial reduction in the micropore volume of the catalyst.

Representative results are shown in Figures 9 through 12 for catalyst samples taken from the upstream section and in Figures 13 through 16 for the downstream end. These figures are accompanied by extensive captions reporting the details of the analysis. The figure captions are intended to provide a separate, detailed statement of the results.

In summary the upstream catalyst samples are 50 to 70% covered with an inorganic crust of ferrous sulfide containing minor amounts of Ca, Si, Al, Zn, and Ti. The ferrous sulfide forms irregular crystals which are oriented with the long axis normal to the surface. The ferrous sulfide penetrates extensively into the macropores of the catalyst. The activity of the catalyst appears to be reduced by the ferrous sulfide crust.

The downstream samples are essentially free of ferrous sulfide; an irregular crust of Al-Si ash on these samples covers 20 to 40% of the surface. Minor quantities of Ca, Zn, Ti, Fe and S are distributed in the crust. The activity of the catalyst for decomposition of organotitanium is much greater downstream than upstream. Although Kovacks and Bennett (1975) did not find a strong correlation between titanium deposition and their test for hydrogen transfer activity, the absence of an ferrous sulfide crust certainly implies less transport resistance for the downstream catalyst than the upstream sample. The titanium profiles are consistent with this viewpoint.

In the next quarter the blocking of the catalyst will be identified more completely by pore size distribution measurements. The hydrodesulfurization activity of spend and fresh catalyst will be tested in a gas-phase, pulse microreactor.

Figure 9 Scanning electron micrographs of a catalyst particle from the upstream end of the reactor. The catalyst was sectioned along a radial plane. In the upper picture, a crust of inorganic deposit about 60 μm thick is evident on the exterior of the catalyst. Organic material forming an irregular additional deposit about 1000 μm thick is seen in the lower right hand corner of the micrograph. The lower micrograph details the interface between the catalyst, inorganic and organic deposits. An energy dispersive x-ray analysis (EDAX) showed that the crust at the location indicated was primarily FeS with minor amounts of calcium, titanium and zinc.

100 μm

10 μm

Figure 9

31a

Figure 10 Scanning electron micrographs of a fractured and plasma etched cross section of a catalyst particle from the upstream end of the reactor. Each picture shows the different structures observed in the inorganic crust. The catalyst is at the bottom of each picture. Those areas marked (X) are shown by EDAX to be made up of primarily Fe and S. The trace elements, Al, Si, Ca, Ti, Cr, and Zn, vary randomly from region to region. Those areas marked (O) are primarily Al and Si as determined by EDAX. Likewise, the trace elements in this structure are Fe, S, Ca, Ti and Zn and vary from site to site.

10 μm

10 μm

Figure 10

Figure 11 Electron microprobe x-ray images of the upstream catalyst at the interface with the inorganic and organic crusts. These pictures show the qualitative distribution of selected elements. The catalyst can be found in the upper left. The light area in the upper right is part of the mounting and was included as a reference point. The inorganic crust, which in this example measures $\sim 40 \mu\text{m}$ wide is shown to be primarily FeS_x by the similarity of the two x-ray images. This material also penetrated into the macropores ($2 \mu\text{m}$) of the catalyst and is distributed as 5-10 μm diameter particles in the organic crust. AlO_x , identified from the good correlation between the Al and O images, is found in the catalyst and dispersed through the organic layer as 10-15 μm particles. Si is found in high concentration in the organic phase, correlating to some degree with the Al and O images, and at a lower level in the catalyst. Small quantities of Ca and Ti are found probably as TiS_x and CaS_x because of similarities with S image. Zn is found in small quantities in the inorganic layer near the catalyst surface. Ti is found in small clumps in the inorganic crust as a trace component of the Ca ash. In addition, Ti is dispersed more finely near the catalyst surface.

Electron

Fe

S

Al

O

Si

Ca

Zn

Ti

50µm

Figure 11

Figure 12 Electron microprobe concentration profiles of a catalyst particle from the upstream end of the reactor. The microprobe profiles represent a 100 μm segment about 0.5 μm wide oriented parallel to the catalyst surface. The profiles have a lateral resolution of about 2 μm . The aluminum profile serves to identify the exterior catalyst surface and shows variations in the interior, in part because the signals have not been corrected for varying local absorption of x-rays.

The Fe and S signals are approximately proportional in the exterior crust and the S/Fe ratio is much higher in the interior of the catalyst, which is a sulfide in operation. The irregularities indicate variations in the macropore structure.

Ti was deposited primarily in the interior of the catalyst and the concentration profile shows the presence of finely dispersed Ti. The irregular Si profile suggests the incorporation of mineral constituents of the coal within the macropores.

The Co and Mo profiles show large variations inside the catalyst which may be attributed to low dispersion of these components. These two elements clearly penetrate into the inorganic crust.

Figure 13 Scanning electron micrographs of a catalyst particle from the downstream end of the reactor. These pictures parallel those in Figure 9 for the upstream catalyst samples. The upper picture shows a polished section of the catalyst. The catalyst is the upper portion; the inorganic crust below is a thin band attached to the surface. The organic deposit further below is irregular with a maximum thickness of 1200 μm . The lower micrograph shows a small region of the inorganic crust at higher magnification. An EDAX indicates that this zone contains primarily Si and Al with some Ti, Fe and S.

Figure 13

Figure 14 Scanning electron micrographs of a fractured and plasma etched catalyst particle from the downstream end of the reactor. These pictures are similar to those of Figure 10, but the sample has been tilted to reveal much more of the catalyst surface (upper portion). The catalyst surface is much less encrusted than that of the upstream sample. The lower picture shows a region of high Si-Al concentration similar to the deposits marked (0) in Figure 2.

100 μm

20 μm

Figure 14

Figure 15 Electron microprobe x-ray images of the downstream crust. These pictures parallel those of Figure 11 for the upstream crust. The electron image shows about a 200 μm thickness of the organic crust. The crust contains a large number of particles less than 10 μm in size.

The iron and sulfur images show a direct correspondence to one another with a higher background level of sulfur in the interior of the catalyst. In contrast to the catalyst from the upstream section, the downstream catalyst has macropores which do not appear to be blocked with FeS_x . The ~ 10 μm pit in the interior, however, are partially filled with FeS_x . There are a few particles in the organic crust containing iron but not sulfur. These may be tramp iron.

There are a large number of relatively small particles of silica and alumina in the organic deposit. These are probably mineral components from the coal. Silica penetrates into the interior of the catalyst. A high titanium concentration is found in the catalyst and in clusters in the organic crust.

Figure 15

37a

Figure 16 Electron microprobe concentration profiles of a catalyst particle from the downstream end of the reactor. These profiles parallel those shown in Figure 12 for the upstream sample. The aluminum profile shows a 25 μm wide notch at the interior surface. The silicon profile indicates a large inclusion of mineral matter. The aluminum in the exterior is also attributed to mineral matter.

The iron and sulfur profiles indicate formation of FeS_x in small quantities. The interior sulfur concentration is substantially in excess of the background level.

The titanium concentration is much greater for the downstream catalyst than for the upstream catalyst. The notch at the surface mirrors the aluminum profile.

The silicon profile is irregular since the mineral components are incorporated as 1-10 μm particles. The cobalt and molybdenum profiles show some transport of catalytically active material toward the exterior of the crust.

Figure 16

Figure 17 Scanning electron micrographs of two plasma etched catalyst particles. The upper picture is of a pellet from the upstream section of the reactor at high magnification. The catalyst surface is at the bottom of the picture. Above is the fluted structure, previously identified as iron sulfide, partially broken away from the catalyst. The lower picture was taken at low magnification and shows the round surface of the catalyst taken from the downstream portion of the reactor. The pocked surface behind the pellet is the potting compound. The small piece of crust (Al and Si) at the outer surface of the catalyst is partially broken away from the surface. Both photographs depict events consistent with some periodic removal of the inorganic crust.

10 μm

400 μm

Figure 17

VIII. PERSONNEL

The project started June 20, 1975. At that time, Kenneth Eliezer and Edward Reiff joined the project. Ken Eliezer is responsible for the design and assembly of the high-pressure liquid-phase microreactor. Design, assembly and demonstration of the operation of the microreactor system will make up his M.Ch.E. thesis. Ed Reiff is starting on the hydrodenitrogenation work initially as his M.Ch.E. thesis and plans to extend it to a Ph.D. thesis. He has been responsible for the procurement, assembly and testing of the autoclaves and has been involved in our comprehensive evaluation of gas and liquid chromatographic analysis schemes. He will continue with the autoclave evaluation of the three catalysts for hydrodenitrogenation and with the continuing development of our analytical schemes.

Dr. Stuart Shih joined the project as a post-doctoral fellow from Purdue (Chemical Engineering) on August 1st and is also involved in the hydrodenitrogenation work. He has been involved in our evaluation of analytical methods and is responsible for setting up our analysis scheme using equipment which is available in the Department or which has been or will soon be ordered. He will be responsible for substantial portions of our autoclave and flow microreactor studies of carbazole and acridine (and methyl substituted species) hydrodenitrogenation.

Manoj Bhinde, Dennis Broderic, and Minshon Chiou joined the project on September 19. Manoj Bhinde will be responsible for applying the flow microreactor which is being built to hydrodenitrogenation as soon as it is completed and tested. He will be responsible for evaluating its applicability and constructing a second unit if the first is applicable to the determination of hydrodenitrogenation kinetics and reaction networks, as we expect it will be. His Ph.D. thesis will involve studies of relative reactivity, reaction kinetics and reaction networks for hydrodenitrogenation. Dennis Broderic will be responsible for applying the high pressure microreactor which is being assembled to studies of the relative reactivity of sulfur-containing compounds and determination of reaction kinetics and reaction networks in hydrodesulfurization. Minshon Chiou will be involved in the reaction engineering and catalyst deactivation studies which are being done under this contract.

Dr. John Stanulonis, who has an NSF energy post-doctoral fellowship, is working on the catalyst deactivation studies which were discussed in this report. He will continue to do so during the next quarter although he is not being supported on this contract.

We have an offer of a post-doctoral position to Dr. V. H. J. de Beer, who is at Eindhoven, The Netherlands. He has just completed a Ph.D. thesis on hydrodesulfurization with Dr. G. C. A. Schuit and will work on hydrodesulfurization if he comes. He has indicated that he probably will come, but we will not know for certain for several weeks yet. Meanwhile we have a file of other candidates which we will take action on as soon as Dr. de Beer informs us of what he will do.

IX. LITERATURE CITED

1. Akhtar, S., Sharkey, A. G., Schultz, J. L., Yavorsky, P. M.,
Abs 167th Meeting, Amer. Chem. Soc., Los Angeles, Calif.,
March 31-April 5, 1974.
2. Banfield, J. E., Davies, W., Gamble, N. W., and Middleton,
S. J., J. Chem. Soc., 4791 (1956).
3. Campaigne, E., Hewitt, L., and Ashby, J., J. Heterocyclic
Chem. 6, 553 (1969).
4. Drausnitz, J. M., and Shair, F. H., A.I.Ch.E. J. 7, 682-687
(1961).
5. Gerdel, R., and Lucken, E. A. C., J. Amer. Chem. Soc.
87, 213 (1965).
6. Given, P. H., private communication, July, 1975.
7. Hansch, C., and Lindwall, H. G., J. Org. Chem. 10, 383
(1945).
8. Kokes, R., J. Am. Chem. Soc. 71, 5860 (1955).
9. Kovach, S. M., and Bennett, J. "Coal Liquefaction I:
Catalyst Poisons Present in Coal presented at
the 169th ACS meeting 6-11 April, 1975.
10. Mears, D. E., Chem. Eng. Sci. 26, 1361 (1971).
11. Sunthankar, A. V., and Tilak, B. D., Proc. Ind. Acad.
Sci. 324, 396 (1950).
12. Suter, C. M., and Maxwell, C. E., Org. Syn. Coll. Vol. 2,
485 (1943).
13. Verheijen, J. H., and Kloosterziel, H., Synthesis 451
(1975).
14. Werner, E. G. G., Rec. Trav. Chim. 68, 509 (1949).

X. APPENDIX I

Parts List

1. Fittings

A. Swagelok

3 1/16" NPT x 1/16" Sw	male connector
1 1/16" NPT x 1/8" Sw	male connector
4 1/8" NPT x 1/8" Sw	male connector
2 1/4" NPT x 1/4" stud	male adapter
4 1/8" NPT x 1/8" Sw	female connector
1 1/8" NPT x 1/4" Sw	female connector
1 1/4" NPT x 1/4" Sw	female connector
2 1/8" Sw x 1/8" Sw	union
2 1/16" Sw x 1/8" Sw	reducing union
6 1/8" Sw x 1/4" Sw	reducing union
4 1/4" Sw x 1/2" Sw	reducing union
3 1/16" Sw	union tee
7 1/8" Sw	union tee
4 1/16" Sw x 1/8" stud	reducer

B. High Pressure Equipment Company

3 1/8" tube x 1/4"	high pressure adapter
2 1/16" tube 3/8"	high pressure adapter

C. Cajon

2 1/8"	male tee
1 1/16"	female tee
1 1/4" O-ring x 1/8" NPT	female connector
1 1/4" O-ring x 1/8" Sw	reducing union
2 1/8" plugs	

2. Pressure Gauge

A. Matheson

1 gas regulator 0-4000 psi cylinder, 0-2000 psi delivery
2 0-1000 psi pressure gauges

B. High Pressure Equipment Company

1 0-5000 psi pressure gauge

3. Valves

A. High Pressure Equipment Company

10 1/8" two way straight valves

5 1/16" two way straight valves
1 1/8" metering valve

B. Whitney

2 1/8" severe service union bonnet valves

4. Reactor

1 1/8" ID x 3/8" OD x 3" long H.P. ends nipple

1 oven - cylinder with hexagonal plates to cover high pressure fittings and hole to admit sensor
(Chemical Engineering Shop)

5. Tubing

1/8" OD x .069" ID, 1/4" OD x .180" ID, 1/16" OD x .006" ID
stainless steel

6-7 mm OD x 3/4" - 1 1/4" ID type one glass tubing

6. Temperature Control

Electron Marketing Associates (RFL Distribution)

1 Model 71/115 proportional temperature controller
1 Direct reading dial assembly 0-500°C
1 RTD platinum sensor

7. Scientific Glass Company

1 12 ft. length beaded ceramic heating wire

8. Spargers

1 25 cc (Chemical Engineering Shop) with 1 Magne-Matic
magnetic stirrer (Scientific Glass Company)

1 300 cc - SPV-1 autoclave without heater (High
Pressure Equipment Company)

9. Pumps

1 Ruska Model 2252 positive displacement pump 0.1-1.2cc/hr
1 Aminco Model 46-4025 diaphragm pump

10. Cart (barricade)

1/8" plate steel, 1" x 1/4" angle iron, 4" wheels for
construction of 4 1/2" wide x 1/32" high x 2" deep
barricade.

11. Miscellaneous

2 inline removable filters (Nupro) with 2 μ size filters
1 rupture disc assembly with 4500 psi discs (High
Pressure Equipment Company)