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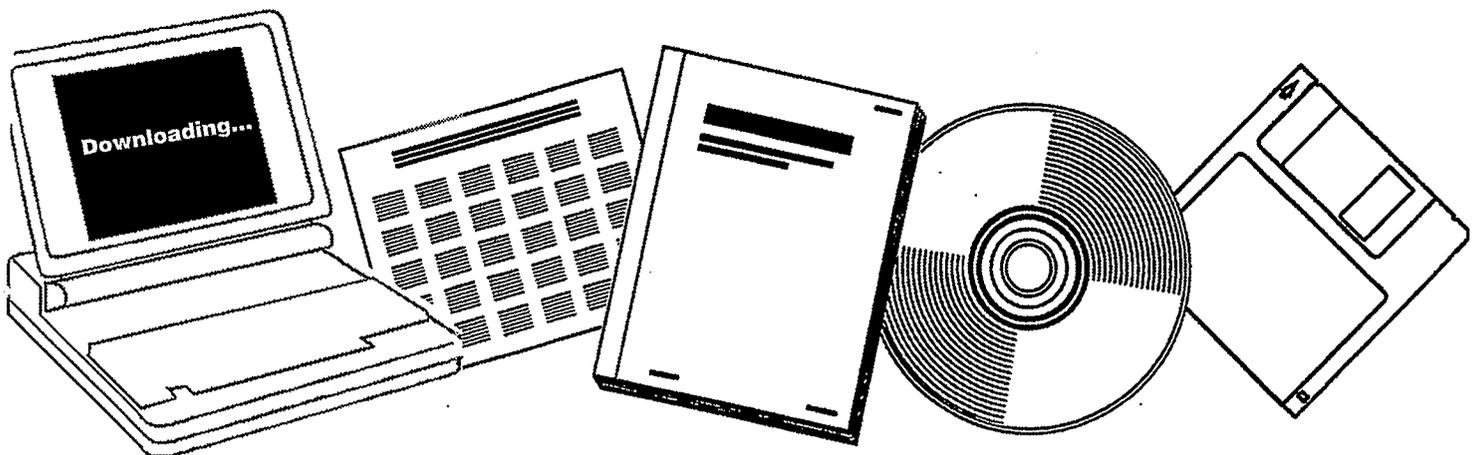
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**CHEMISTRY AND CATALYSIS OF COAL
LIQUEFACTION: CATALYTIC AND THERMAL
UPGRADING OF COAL LIQUID AND HYDROGENATION
OF CO TO PRODUCE FUELS. QUARTERLY PROGRESS
REPORT, JANUARY-MARCH 1980**

UTAH UNIV., SALT LAKE CITY. DEPT. OF
MINING AND FUELS ENGINEERING

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Chemistry and Catalysis of Coal Liquefaction:
Catalytic and Thermal Upgrading of Coal Liquid
and Hydrogenation of CO to Produce Fuels

Quarterly Progress Report
for the Period Jan - Mar 1980

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OBJECTIVE AND SCOPE OF WORK

I. The chemistry and Catalysis of Coal Liquefaction.

Task 1 Chemical-Catalytic Studies

Coal will be reacted at subsoftening temperatures with selective reagents to break bridging linkages between clusters with minimal effect on residual organic clusters. The coal will be pretreated to increase surface area and then reacted at 25 to 350°C. Reagents and catalysts will be used which are selective so that the coal clusters are solubilized with as little further reaction as possible.

Task 2 Carbon-13 NMR Investigation of CDL and Coal

Carbon-13 NMR spectroscopy will be used to examine coal, coal derived liquids (CDL) and residues which have undergone subsoftening reactions in Task 1 and extraction. Improvements in NMR techniques, such as crosspolarization and magic angle spinning, will be applied. Model compounds will be included which are representative of structural units thought to be present in coal. Comparisons of spectra from native coals, CDL and residues will provide evidence for bondings which are broken by mild conditions.

Task 3 Catalysis and Mechanism of Coal Liquefaction

This fundamental study will gain an understanding of metal salt chemistry and catalysis in coal liquefaction through study of reactions known in organic chemistry. Zinc chloride and other catalytic materials will be tested as Friedel-Crafts catalysts and as redox catalysts using coals and selected model compounds. Zinc chloride, a weak Friedel-Crafts catalyst, will be used at conditions common to coal liquefaction to participate in well defined hydrogen transfer reactions. These experiments will be augmented by mechanistic studies of coal hydrogenation using high pressure thermogravimetric analysis and structural analysis. The results of these studies will be used to develop concepts of catalysis involved in coal liquefaction.

Task 4 Momentum Heat and Mass Transfer in CoCurrent Flow of Particle-Gas Systems for Coal Hydrogenation

A continuation of ongoing studies of heat and transport phenomena in cocurrent, co-gravity flow is planned for a one-year period. As time and development of existing work permits, the extension of this study to include a coiled reactor model will be undertaken. Mathematical models of coal hydrogenation systems will utilize correlations from these straight and coiled reactor configurations.

Task 5 The Fundamental Chemistry and Mechanism of Pyrolysis of Bituminous Coal

Previous work at the University of Utah indicates that coal pyrolysis, dissolution (in H-donor) and catalytic hydrogenation all have similar rates and activation energies. A few model compounds will be pyrolyzed in the range of 375 to 475°C. Activation energies, entropies and pro-

duct distributions will be determined. The reactions will assist in formulating the thermal reaction routes which also can occur during hydro-liquefaction.

II. Catalytic and Thermal Upgrading of Coal Liquids

Task 6 Catalytic Hydrogenation of CD Liquids and Related Polycyclic Aromatic Hydrocarbons

A variety of coal derived (CD) liquids will be hydrogenated with sulfided catalysts prepared in Task 10 from large pore, commercially available supports. The hydrogenation of these liquids will be systematically investigated as a function of catalyst structure and operating conditions. The effect of extent of hydrogenation will be the subject of study in subsequent tasks in which crackability and hydrolysis of the hydrogenated product will be determined. To provide an understanding of the chemistry involved, model polycyclic arenes will be utilized in hydrogenation studies. These studies and related model studies in Task 7 will be utilized to elucidate relationships between organic reactants and the structural-topographic characteristics of hydrogenation catalysts used in this work.

Task 7 Denitrogenation and Deoxygenation of CD Liquids and Related Nitrogen- and Oxygen-Containing Compounds

Removal of nitrogen and oxygen heteroatoms from CD liquids is an important upgrading step which must be accomplished to obtain fuels corresponding to those from petroleum sources. Using CD liquids as described in Task 6, exhaustive HDN and HDO will be sought through study of catalyst systems and operating conditions. As in Task 6, catalysts will be prepared in Task 10 and specificity for N- and O-removal will be optimized for the catalyst systems investigated. Model compounds will also be systematically hydrogenated using effective HDN/HDO catalysts. Kinetics and reaction pathways will be determined. A nonreductive denitrogenation system will be investigated using materials which undergo reversible nitridation. Conditions will be sought to cause minimal hydrogen consumption and little reaction of other reducible groups.

Task 8 Catalytic Cracking of Hydrogenated CD Liquids and Related Polycyclic Naphthenes and Naphthoaromatics

Catalytic cracking of hydrogenated CD liquid feedstocks will be studied to evaluate this scheme as a means of upgrading CD liquids. Cracking kinetics and product distribution as a function of preceding hydrogenation will be evaluated to define upgrading combinations which require the minimal level of CD liquid aromatic saturation to achieve substantial heteroatom removal and high yields of cracked liquid products. Cracking catalysts to be considered for use in this task shall include conventional zeolite-containing catalysts and large-pore molecular sieve, CLS (cross-linked smectites) types under study at the University of Utah. Model compounds will be subjected to tests to develop a mechanistic understanding of the reactions of hydro CD liquids under catalytic cracking conditions.

Task 9 Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

Heavy petroleum fractions can be thermally hydrocracked over a specific range of conditions to produce light liquid products without excessive hydrogenation occurring. This noncatalytic method will be applied to a variety of CD liquids and model compounds, as mentioned in Task 6, to determine the conditions necessary and the reactivity of these CD feedstocks with and without prior hydrogenation and to derive mechanism and reaction pathway information needed to gain an understanding of the hydropyrolysis reactions. Kinetics, coking tendencies and product compositions will be studied as a function of operating conditions.

Task 10 Systematic Structural-Activity Study of Supported Sulfide Catalysts for Coal Liquids Upgrading

This task will undertake catalyst preparation, characterization and measurement of activity and selectivity. The work proposed is a fundamental study of the relationship between the surface-structural properties of supported sulfide catalysts and their catalytic activities for various reactions desired. Catalysts will be prepared from commercially available supports composed of alumina, silica-alumina, silica-magnesia and silica-titania, modification of these supports to change acidity and to promote interaction with active catalytic components is planned. The active constituents will be selected from those which are effective in a sulfided state, including but not restricted to Mo, W, Ni and Co. The catalysts will be pre-sulfided before testing. Catalyst characterization will consist of physico-chemical property measurements and surface property measurements. Activity and selectivity tests will also be conducted using model compounds singly and in combination.

Task 11 Basic Study of the Effects of Coke and Poisons on the Activity of Upgrading Catalysts

This task will begin in the second year of the contract after suitable catalysts have been identified from Tasks 6, 7 and/or 10. Two commercial catalysts or one commercial catalyst and one catalyst prepared in Task 10 will be selected for a two-part study, (1) simulated laboratory poisoning/coking and (2) testing of realistically aged catalysts. Kinetics of hydrogenation, hydrodesulfurization, hydrodenitrogenation and hydrocracking will be determined before and after one or more stages of simulated coking. Selected model compounds will be used to measure detailed kinetics of the above reactions and to determine quantitatively how kinetic parameters change with the extent and type of poisoning/coking simulated. Realistically aged catalysts will be obtained from coal liquids upgrading experiments from other tasks in this program or from other laboratories conducting long-term upgrading studies. Deactivation will be assessed based on specific kinetics determined and selective poisoning studies will be made to determine characteristics of active sites remaining.

Task 12 Diffusion of Polyaromatic Compounds in Amorphous Catalyst Supports

If diffusion of a reactant species to the active sites of the catalyst is slow in comparison to the intrinsic rate of the surface reaction, then only sites near the exterior of the catalyst particles will be utilized effectively. A systematic study of the effect of molecular size on the sorptive diffusion kinetics relative to pore geometry will

be made using specific, large diameter aromatic molecules. Diffusion studies with narrow boiling range fractions of representative coal liquid will also be included. Experimental parameters for diffusion kinetic runs shall include aromatic diffusion model compounds, solvent effects, catalyst sorption properties, temperature and pressure.

III. Hydrogenation of CO to Produce Fuels

Task 13 Catalyst Research and Development

Studies with iron catalysts will concentrate on promoters, the use of supports and the effects of carbiding and nitriding. Promising promoters fall into two classes: (1) nonreducible metal oxides, such as CaO, K₂O, Al₂O₃ and MgO, and (2) partially reducible metal oxides which can be classified as co-catalysts, such as oxides of Mn, Mo, Ce, La, V, Re and rare earths. Possible catalyst supports include zeolites, alumina, silica, magnesia and high area carbons. Methods of producing active supported iron catalysts for CO hydrogenation will be investigated, such as development of shape selective catalysts which can provide control of product distribution. In view of the importance of temperature, alternative reactor systems (to fixed bed) will be investigated to attain better temperature control. Conditions will be used which give predominately lower molecular weight liquids and gaseous products.

Task 14 Characterization of Catalysts and Mechanistic Studies

Catalysts which show large differences in selectivity in Task 13 will be characterized as to surface and bulk properties. Differences in properties may provide the key to understanding why one catalyst is superior to another and identify critical properties, essential in selective catalysts. Factors relating to the surface mechanism of CO hydrogenation will also be investigated. Experiments are proposed to determine which catalysts form "surface" (reactive) carbon and the ability of these catalysts to exchange C and O of isotopically labelled CO. Reactions of CO and H₂ at temperatures below that required for CO dissociation are of particular interest.

Task 15 Completion of Previously Funded Studies and Exploratory Investigations

This task is included to provide for the orderly completion of coal liquefaction research underway in the expiring University of Utah contract, EX-76-C-01-2006.

III Summary of Progress to Date

Analysis of a group of coal liquids produced by catalytic hydrogenation of Utah coals with $ZnCl_2$ catalyst was begun. Carbon-13 nuclear magnetic resonance and liquid chromatography techniques will be used to correlate chemical properties with hydrogenation reactivity. Equipment previously used for downflow measurements of heat and momentum transfer in a gas-coal suspension was modified for upflow measurements.

The catalytic hydrodeoxygenation of methyl benzoate has been studied to elucidate the reactions of ester during upgrading of coal-derived liquids. The kinetics of hydrogenation of phenanthrene have also been determined. The catalytic cracking mechanism of octahydroanthracene is reported in detail. Studies of the hydrodesulfurization of thiophene indicate that some thiophene is strongly adsorbed as a hydrogen-deficient polymer on cobalt-molybdate catalyst. Part of the polymer can be desorbed as thiophene by hydrogenation. Poisoning of the catalyst inhibits the hydrodesulfurization activity to a greater degree than the hydrogenation activity.

Iron-manganese catalysts for carbon monoxide hydrogenation is studied to determine the role of iron carbide formation on selectivity. Pure iron catalyst forms a Hagg iron carbide phase under reaction conditions.

Papers and Presentations

"The Initial Stage of Coal Conversion," D.M. Bodily, R. Yoshida, Rocky Mountain Fuel Society, Salt Lake City, Utah, February 1980.

Task 2

Carbon-13 NMR Investigation of CDL and Coal

Faculty Advisor: R.J. Pugmire
Post Doctoral: D.K. Dalling

Introduction

Carbon-13 NMR (CMR) spectroscopy can provide significant insights into the structure of solid coal by means of direct examination. In addition, comparison of solid coal spectra with that obtained from the corresponding residue and coal derived liquids provides a valuable new means for exploring the details of the chemistry of the coal liquefaction process. The effect of strong dipolar fields in the solid together with the large chemical shift anisotropy of aromatic carbons in the solid state combine to limit the availability of the extensive detail common in liquid spectra. The C-H dipolar interaction can produce ^{13}C linewidths of up to 40 KHz while the chemical shift anisotropy can be as large as several KHz even at moderate fields strengths. The detection of a nucleus of low natural abundance (e.g., ^{13}C at 1.1%) presents sensitivity problems in crystalline solids that are also challenging. Recently, developed experimental techniques now provide powerful methods for investigating the intricate structural details in solid coal. The use of high power proton polarization techniques can be used to reduce the dipolar broadening arising from C-H interactions while rapid magic angle spinning reduces not only the dipolar broadening but also the chemical shift anisotropy of the resonance lines. The combination of these two experimental techniques produces lines of 3-50 Hz width at a half height depending upon the spectral and operating parameters. Work under this task will attempt to improve on these experimental techniques and apply them to the measurement of solid coal, coal liquids and model compounds.

Project Status

Work on spinner development is continuing as there is a major need for improvement in the cross polarization/magic angle spinning experiments.

Work has begun on the ^{13}C NMR analysis of coal derived liquids at 75 MHz. On the previous DOE contract, 24 coals from producing Utah mines were converted into coal liquids using the short contact ZnCl_2 catalyzed hydrogenation process developed at the University of Utah. The coal liquids produced provide a valuable set of samples for comparison as the conversion percentages vary by a factor of 3 on this group of coal samples of similar rank. The preliminary NMR data on the three liquid samples studied to date exhibit surprisingly similar spectral patterns. While minor variations in the spectral patterns are noted, the liquid structural moieties can not yet be correlated with differences in conversion efficiency.

Future Work

Following the completion of this probe design for solids work, the process coal and coal char will be examined to compare structural features that may be of use in interpreting the data on liquids. This work will begin during the next quarter.

Task 3

Catalysis and Mechanism of Coal Liquefaction

Faculty Advisor: D.M. Bodily
Graduate Student: Jason Miller

Introduction

The hydroliquefaction of coal may be characterized by a mechanism which involves the initial rupture of covalent bonds to form reactive intermediates. These intermediates may be stabilized by hydrogen transfer to form lower molecular weight products or they may polymerize to form insoluble char or coke. Metal halides such as zinc chloride have been shown to be active in the bond scission stage of the reaction where as many catalysts are active only in stabilizing the intermediates, often by regenerating a hydrogen donor. The combination of thermal and catalytic reactions occurring simultaneously results in a complicated reaction mechanism. The chemistry of $ZnCl_2$ will be studied with model compounds and coal by such reactions as hydrogen transfers, cleavage of specific bonds and interaction with π electron systems.

A high performance liquid chromatograph, HPLC, will be used to analyze liquid products of the reactions under study. Further characterization of the products will be by nuclear magnetic resonance, NMR, structural analysis and vapor pressure osmometry.

Project Status

The components for the HPLC were received and assembled. The system includes two pumps with pressure limits of 6000 and 4500 psi, a solvent programmer, automatic injection system, differential refractometer detector, UV detector at 254 nm and data module. Individual components have been checked and the overall system tested with model compounds.

A series of five coal hydrogenation liquids have been selected to develop separation schemes. The liquids were prepared from well-characterized coals. In addition, the liquids are being characterized by carbon-13 NMR and pyrolysis mass spectroscopy. The HPLC will provide supplementary information on the samples while developing separation procedures. The samples have been separated by extraction procedures into asphaltenes and hexane soluble oils.

Future Work

Separation procedures for coal liquids will be developed by HPLC.

Task 4

Momentum, Heat and Mass Transfer in Cocurrent Flow

Faculty Advisor: J.D. Seader
Graduate Student: R. Sorensen

Introduction

The project is concerned with the investigation of both the momentum and heat transfer phenomena for a gas-solid suspension flowing vertically through a heated tube. This research is motivated since consistent data and/or correlations are not found in the literature for upward and downward configurations. The system being studied presently is a coal particle-air system.

Project Status

This work is a modification of the previous research of B.S. Brewster. His downflow system was modified, as shown in Figure 1, to accommodate coal transport in upflow. This required the reversal of all units of the previous system including supporting equipment, feeder and receiver hoppers, and the column tubing. The closely spaced pressure taps were positioned at the lower end of the tower to observe acceleration effects of the transported material.

To insure a uniform entrance-flow environment, a ten-foot section of the stainless steel tubing of the same type as the tower was bent over a 2 1/2 foot radius. This forms the 180 degree bend at the lower end of the tower, which was required since the feeder and vibratory hoppers are gravity fed.

Once the basic system was in place the manometer switching bank was replaced. All pressure taps, coal traps and pressure lines were cleared of any residual coal dust. Higher pressure drops are required in the upflow case than were used in the previous experiments. Therefore, all joints were securely tightened and sealant used on hose connections, gaskets, etc. to minimize leakage.

The previous electrical system was modified so that all control is exercised from the control board located on the second floor. Previous data from the downflow experiments used a -72/+28 mesh size coal sample. The upflow experiments will use approximately the same size distribution for comparison purposes. Therefore, it was necessary to screen about 90 pounds of coal particles. These coal particles were the same samples used in the previous experiments. Attrition due to mechanical breakage had increased the relative amount of smaller diameter particles. The smaller particles were then removed and discarded such that the -42/+28 mesh was more nearly approximated.

Future Work

Experiments will be run at various solid mass flow rates to obtain pressure drop profiles along the column. These results will be compared with other data in the literature.

The upper pressure drop test section will be replaced by a heat transfer test section, and the heat transfer to the particles will be observed.

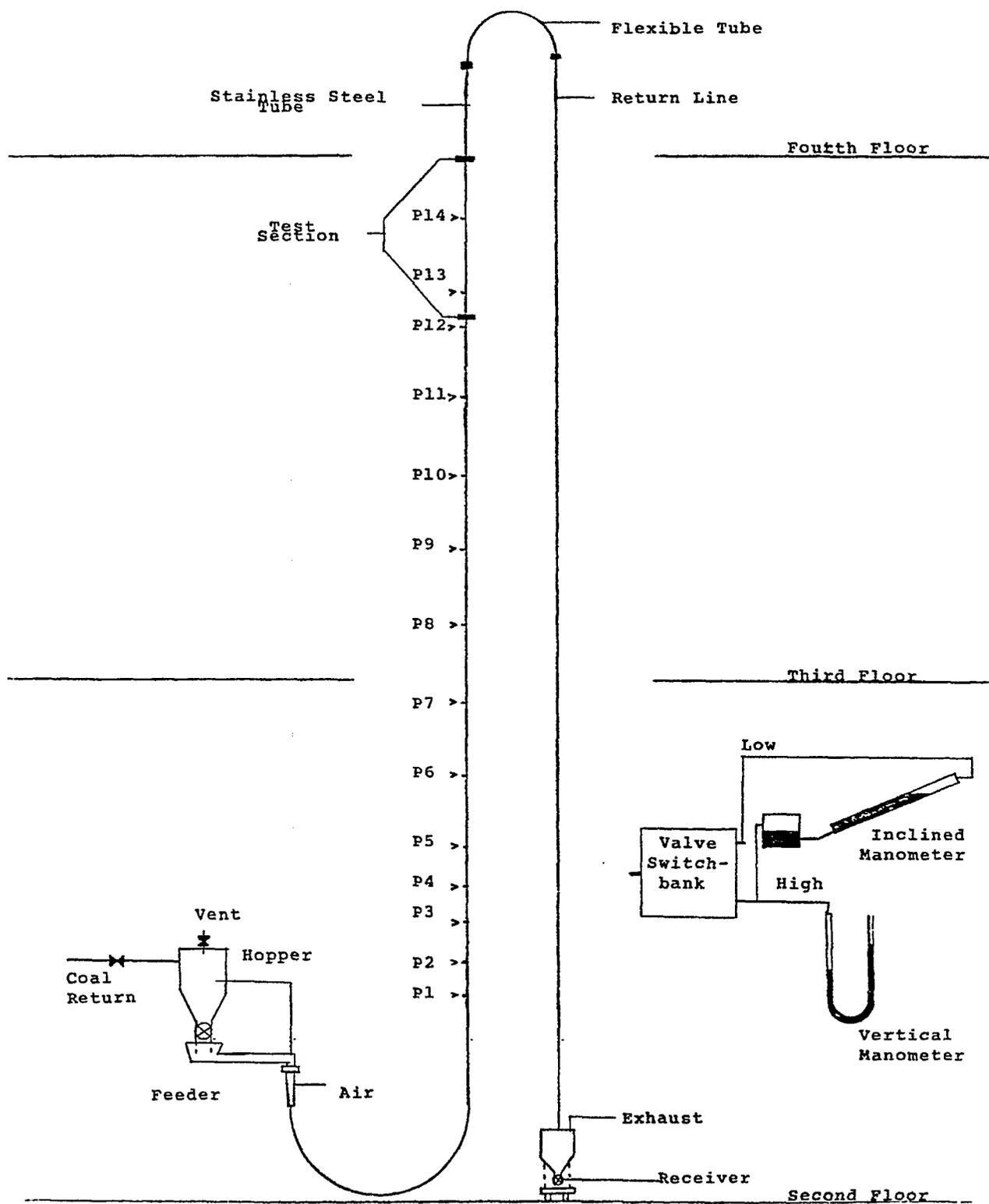


Figure 1. Modified Flow System for Upflow Tests

Task 5

The Mechanism of Pyrolysis of Bituminous Coal

Faculty Advisor: W.H. Wiser
Graduate Student: J.K. Shigley

Introduction

In the present state of knowledge concerning the fundamental chemistry of coal liquefaction, the liquefaction reactions are initiated by thermal rupture of bonds in the "bridges" joining configurations in the coal, yielding free radicals. The different approaches to liquefaction, except for Fischer-Tropsch variations, represent ways of stabilizing the free radicals to produce molecules. The stabilization involving abstraction by the free radicals of hydrogen from the hydroaromatic structures of the coal is believed to be the predominant means of yielding liquid size molecules in the early stages of all coal liquefaction processes, except Fischer-Tropsch variations. The objective of this research is to understand the chemistry of this pyrolytic operation using coal model compounds.

Project Status

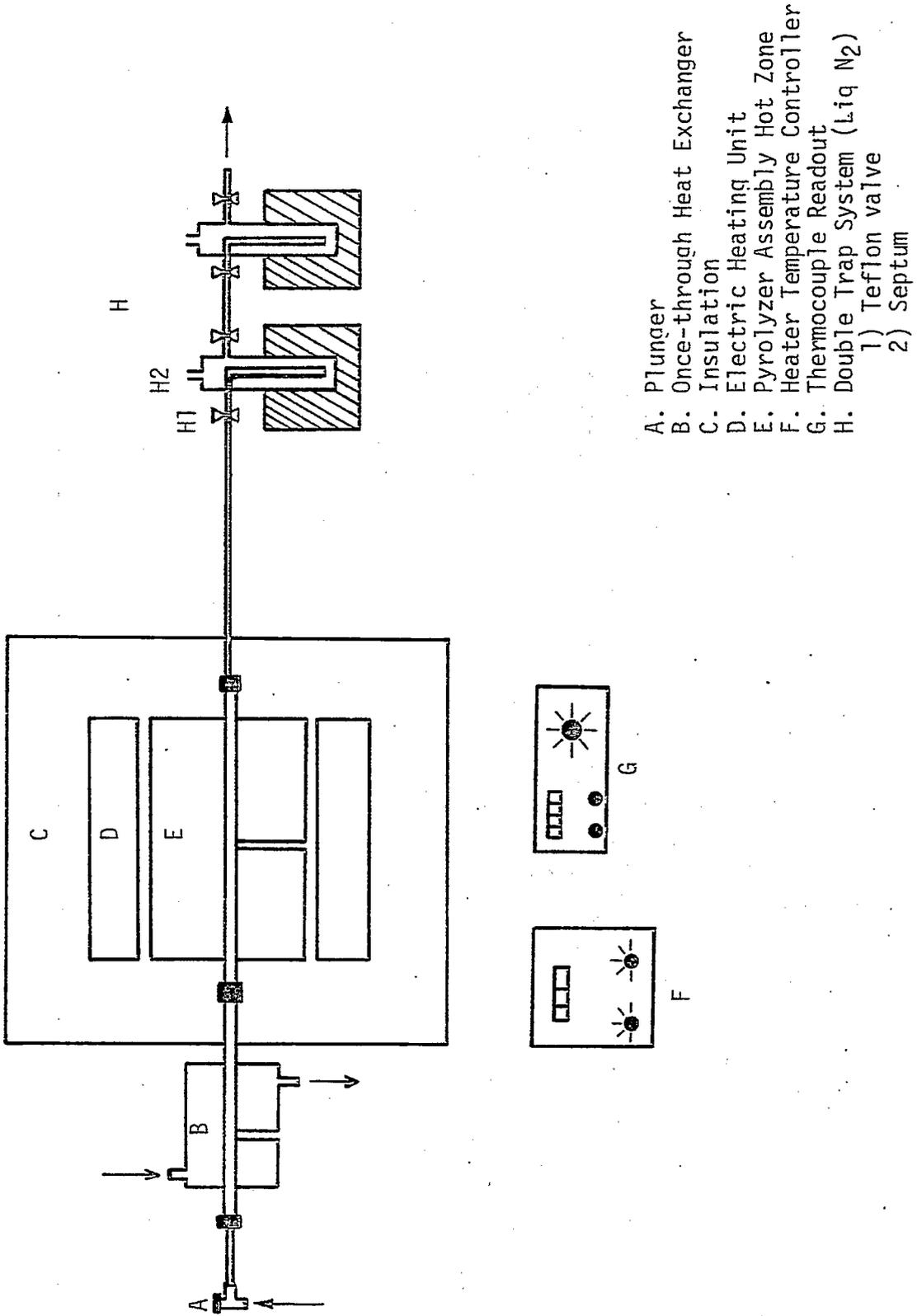
The pyrolysis assembly has been designed and will be built by the University of Utah machine shop. The assembly consists of two zones, a cool and a hot zone (Fig 1). The cool zone is a 0.375 in. stainless steel tube with a once-through heat exchanger built around it. The hot zone is a 6 in. long copper cylinder lined inside with a 0.375 in. stainless steel tube and outside with a 3.5 in. stainless steel pipe. The hot zone will be heated by Lindberg electric resistant heating units and surrounded by adequate insulation to maintain a safe exterior temperature.

A sample of the model compound will be sealed in a glass tube and placed in the 3/8 in. center tube in the cool zone. After the hot zone has reached a constant temperature and other preparations are made, the glass tube containing the sample will be pushed in the 0.375 in. stainless steel tube into the "hot" zone by the plunger. The plunger consists of a thick-walled 0.25 in. stainless steel tube with a Swagelock union tee on the exterior end. One side of the union tee will be plugged. Upon completion of the experiment at a predetermined time, the tube is crushed with the plunger and the reaction products are swept out of the "hot" zone by argon gas flowing through the plunger. The reaction product vapors are swept into a pair of traps in liquid nitrogen baths and condensed. The traps are designed to permit sampling of the gas and the liquid collected in the trap. The collected products will be analyzed by gas chromatography, mass spectrometry and any other analytical method considered necessary.

Future Work

The pyrolysis assembly will be built and support materials (Swagelock fittings, controllers, etc.) will be ordered. A method will be decided

to enable analysis of any gases which would not be condensed in the liquid nitrogen traps, i.e., H_2 , CH_4 . The literature search for related work will continue.



- A. Plunger
- B. Once-through Heat Exchanger
- C. Insulation
- D. Electric Heating Unit
- E. Pyrolyzer Assembly Hot Zone
- F. Heater Temperature Controller
- G. Thermocouple Readout
 - 1) Teflon valve
 - 2) Septum
- H. Double Trap System (Liq N₂)

Figure 1. Pyrolysis Assembly.

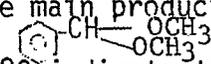
Catalytic Hydrodeoxygenation of Coal-Derived Liquids and Related Oxygen-Containing Compounds

Faculty Advisor: J. Shabtai
A.G. Oblad
Graduate Student: G. Haider

Introduction

Coal-derived liquids (CDL) are characterized by a high proportion of oxygen-containing compounds. Therefore, a systematic catalytic hydrodeoxygenation (HDO) study of CDL and related model compounds is being carried out. The study provides information not only on the mechanism of HDO as related to catalytic upgrading of coal-derived liquids, but also on the role of oxygen-containing coal components in the primary coal liquefaction processes.

Project Status

In continuation of previous studies (see preceding reports), the catalytic hydrodeoxygenation of an ester, i.e., methyl benzoate (1) was examined, and the results obtained are presented in this report. Figure 1 summarizes the change in product composition from 1 as a function of reaction temperature in the range of 200-320°C (hydrogen pressure, 1550 psi) using a sulfided Ni-W/Al₂O₃ catalyst, i.e., Sphercat 550 (1/16") which was supplied by Nalco Chemical Co. As seen from Figure 1, the main products derived from compound 1 at 230°C are benzaldehyde acetal (, 2) and toluene (3). Extrapolation to temperatures below 230°C indicate that the main product under such conditions is the acetal 2. With a gradual increase in temperature above 230°C, there is a gradual decrease in the concentrations of acetal (2) and toluene (3). Parallel to this there is a gradual increase in the yield of benzene (5) as well as some formation of methyl benzyl ether (4). After reaching a maximum around 260°C, compound 4 decreases at higher temperatures. The product from 1 contains also small amounts (< 5%) of benzyl alcohol (6) and xylenes (9).

The results in Figure 1 can be rationalized by considering the mechanism outlined in Figure 2. In the first reaction step, methyl benzoate (1) probably undergoes reduction to form a highly reactive intermediate, i.e., the hemi-acetal (7) which can undergo hydrogenolysis either at the (a) or (b) positions to form benzyl alcohol (6) or methyl benzyl ether (4), respectively. In subsequent steps compound 6 can either undergo hydrogenolysis to toluene (3) or etherification to 4 by interaction with methanol (8). The latter is formed as a by-product in various steps shown in Figure 2. Likewise, acetal 2 is probably derived by acid-catalyzed interaction of the hemi-acetal (7) with methanol. In the final hydrodeoxygenation steps, compounds 2 and 4 undergo hydrogenolysis to yield toluene. As indicated above, the latter undergoes gradual dealkylation to benzene at temperatures > 230°C.

The present study has elucidated the nature of oxygen-containing intermediates in the HDO of 1, i.e., acetal (7) and ether (4). Such compounds apparently have not been detected in previous investigations of HDO of methyl benzoate or other esters.

Identification of products from HDO of methyl benzoate was carried out by gas chromatography/mass spectrometry and by comparison with reference samples. A typical gas chromatogram of products from HDO of 1 is shown in Figure 3.

Future Work

Systematic HDO studies are being presently carried out with coal-derived liquids.

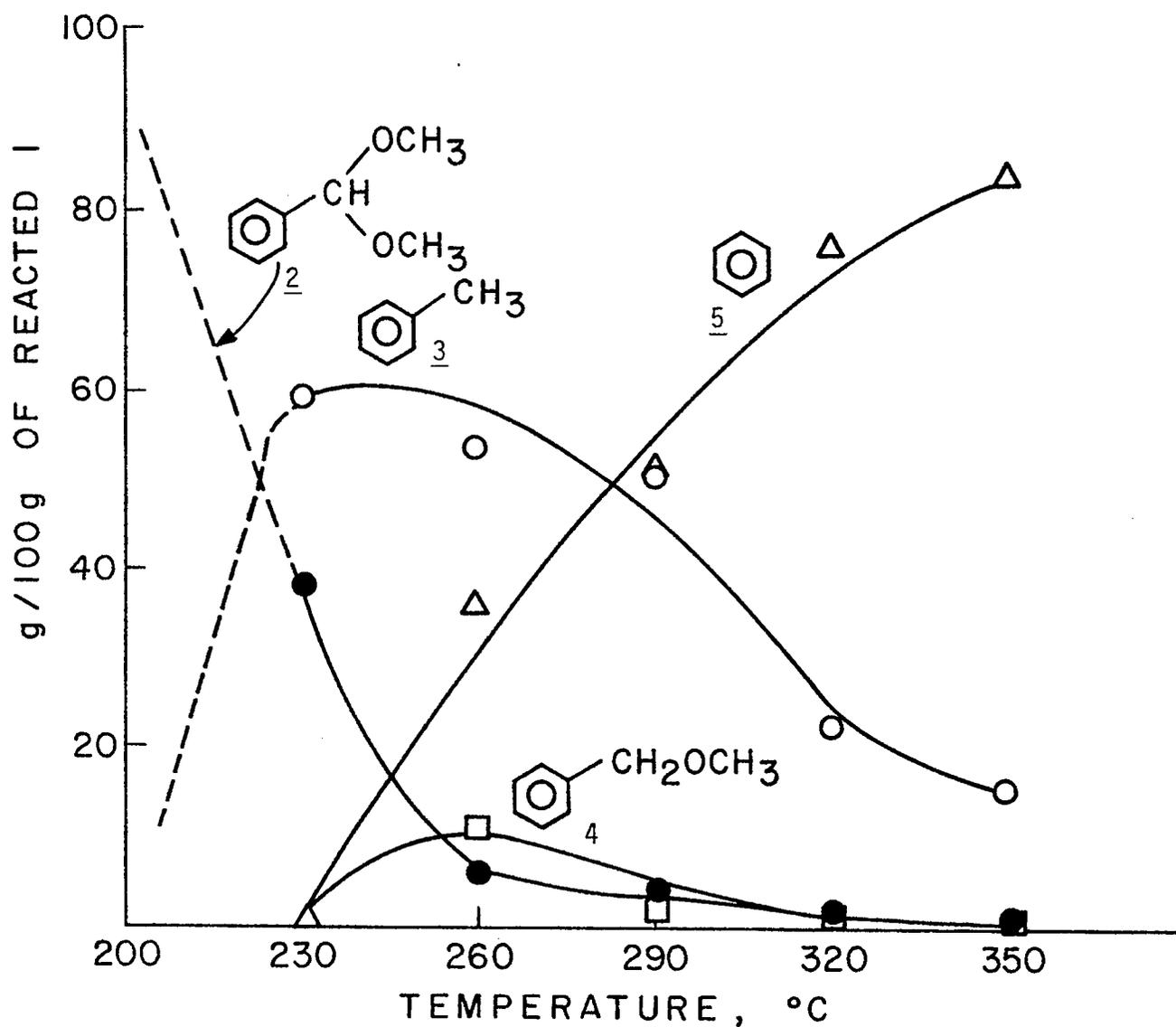


Figure 1. Change in Composition of Product from Hydrodeoxygenation of Methyl Benzoate (1) as a function of Temperature (Pressure: 1550 psig; Reaction Time: 30 min; Catalyst: Sulfided Ni-W/Al₂O₃).

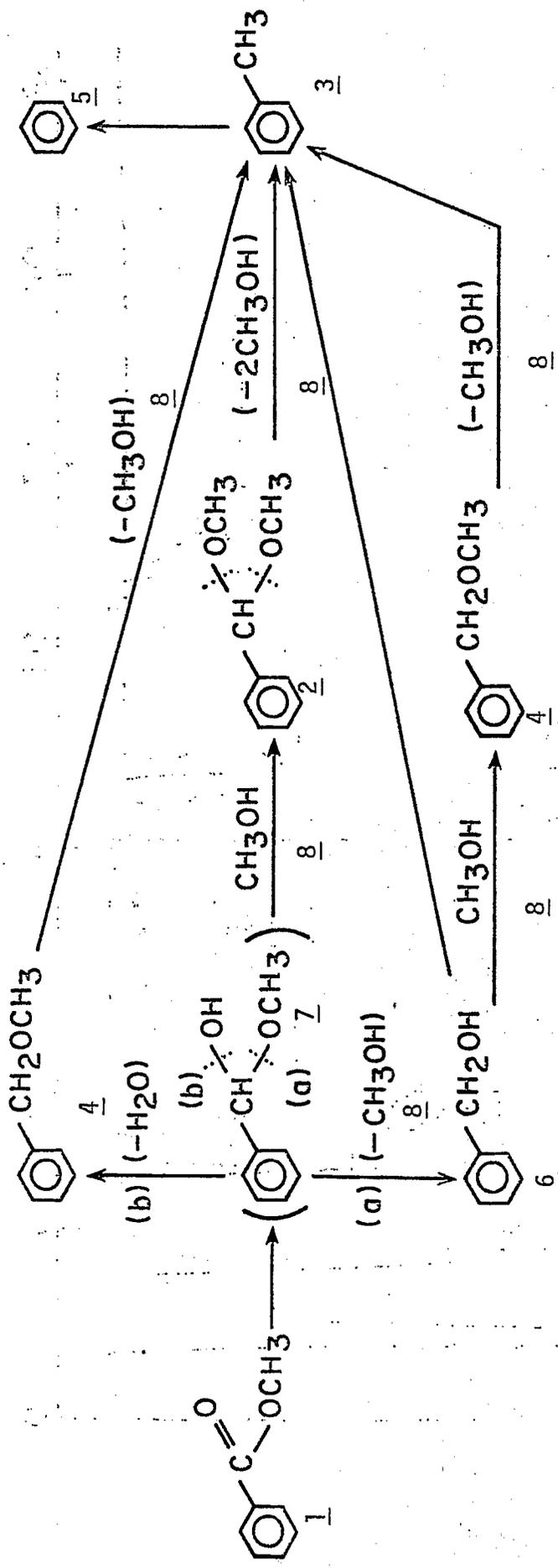


FIGURE 2. SUGGESTED MECHANISM FOR HDO OF METHYL BENZOATE

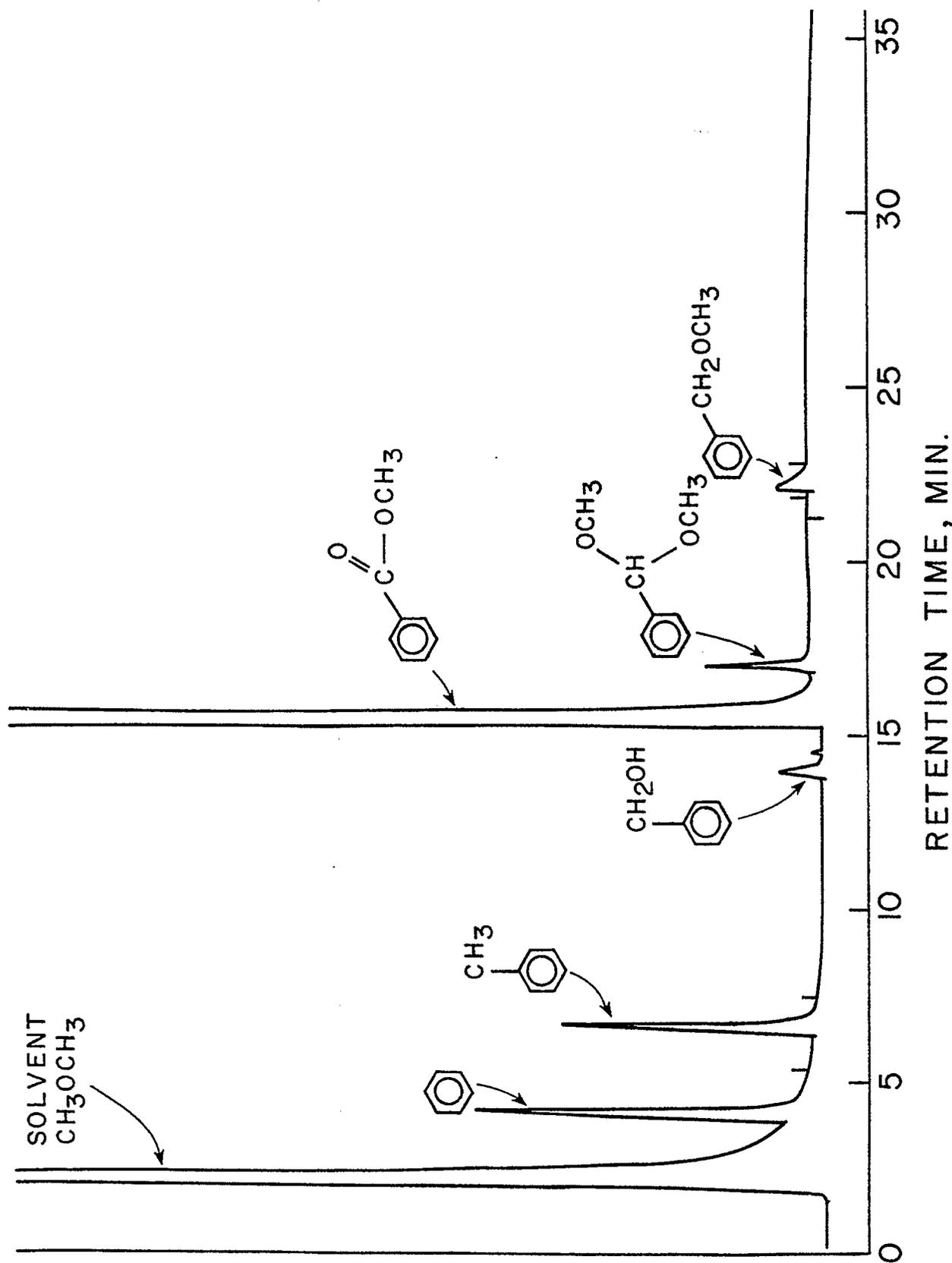


Figure 3. Typical Gas Chromatogram of Liquid Products from Hydrodeoxygenation of Methyl Benzoate.

Task 7

Denitrogenation and Deoxygenation of CD Liquids and Related N- and O- Compounds

Faculty Advisor: J. Shabtai
C. Russell
Graduate Student: J. Peterson

Introduction

The main objective of this research project is to develop a versatile process for controllable hydrotreating of highly aromatic coal liquids, viz., a process permitting production of naphthenic-aromatic feedstocks containing variable relative concentrations of hydroaromatic vs. aromatic ring structures. Such feedstocks, including the extreme case of a fully hydrogenated coal liquid, are highly suitable starting materials for catalytic cracking, as applied for preferential production of light liquid fuels.¹ The overall objective of this project and of a parallel catalytic cracking study is, therefore, to develop and optimize a hydrotreating-catalytic cracking process sequence for conversion of coal liquids into conventional fuels.¹

The present project includes also a study of metal sulfide-catalyzed hydrogenation of model polycyclic arenes present in coal liquids, e.g., phenanthrene, pyrene, anthracene and triphenylene, as a function of catalyst type and experimental variables. This part of the study provides basic information on the rate, mechanism and stereochemistry of hydrogenation of structurally distinct aromatic systems in the presence of sulfided catalysts.

Project Status

The present report provides data on the kinetics of hydrogenation of phenanthrene (1) in the presence of a sulfided Ni-W/Al₂O₃ catalyst. Determinations were made using an autoclave system, specially designed for kinetic studies.² An example of the product composition change as a function of time is given in Figure 1. Data obtained in a wide range of conditions were analyzed by a modification of the Himmelblau method³ to obtain the rate constants for the reaction network indicated in Fig 2. Activation energies for the various reaction steps were calculated.

Figure 3 summarizes the kinetic rate constants for phenanthrene hydrogenation as a function of temperature in the range of 230-380°C (pressure, 2500 psig). Fig 3 indicates that (2) is the most rapidly formed initial product above 270°C, while (3) is the most rapidly formed initial product below 270°C. However, for complete hydrogenation to saturated products, the path via (3) remains more important than the path via (2) over the whole temperature range. At 230°C, 75% of the reaction proceeds via (3) while at 375°C, 60% of the reaction proceeds via (3) as calculated from the rate constants in Fig 3.

Future Work

The kinetics of hydrogenation of anthracene and triphenylene are presently under investigation.

References

1. S. Sunder, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1980.
2. J. Shabtai, C. Russell, L. Veluswamy and A.G. Oblad, to be published.
3. P.M. Himmelblau, C.R. Jones and K.B. Bischoff, I&EC Fundamentals, 6 (4), 539 (1967).

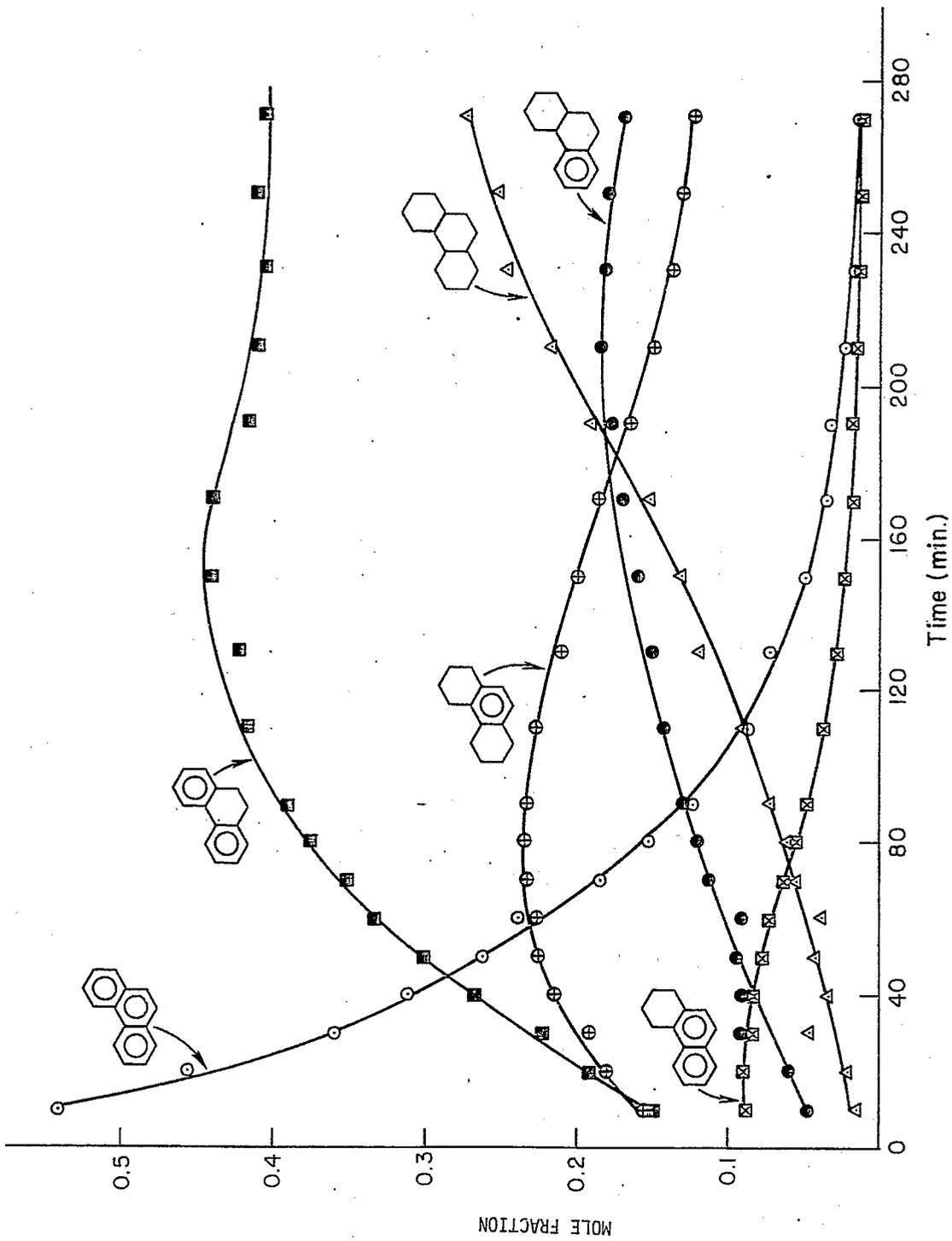


FIGURE 1.

PHENANTHRENE HYDROGENATION PRODUCT COMPOSITION AS A FUNCTION OF TIME ,AT 306° C, 2500 PSIG H₂

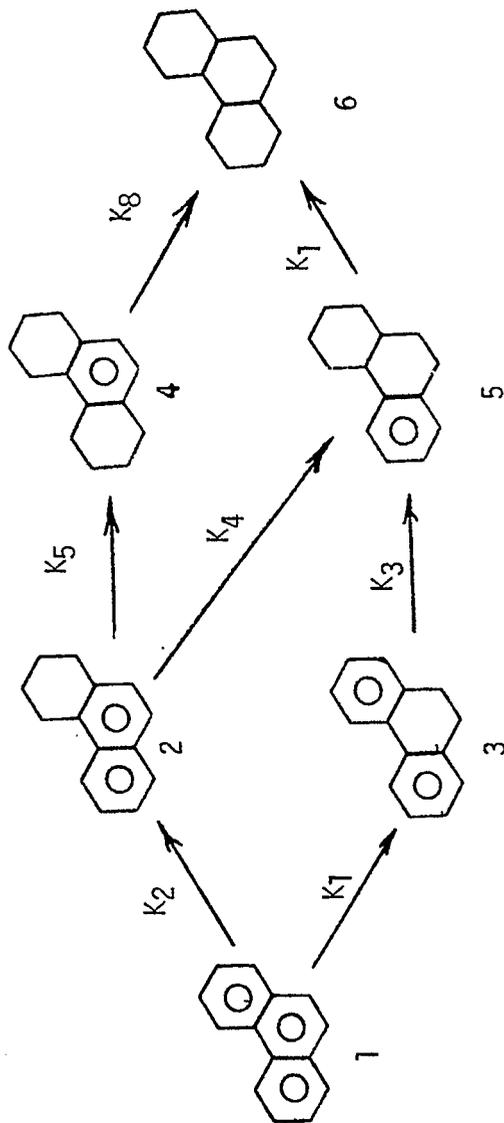


Figure 2. Indicated reaction network of phenanthrene hydrogenation over Ni-W-S/Al₂O₃ catalyst.

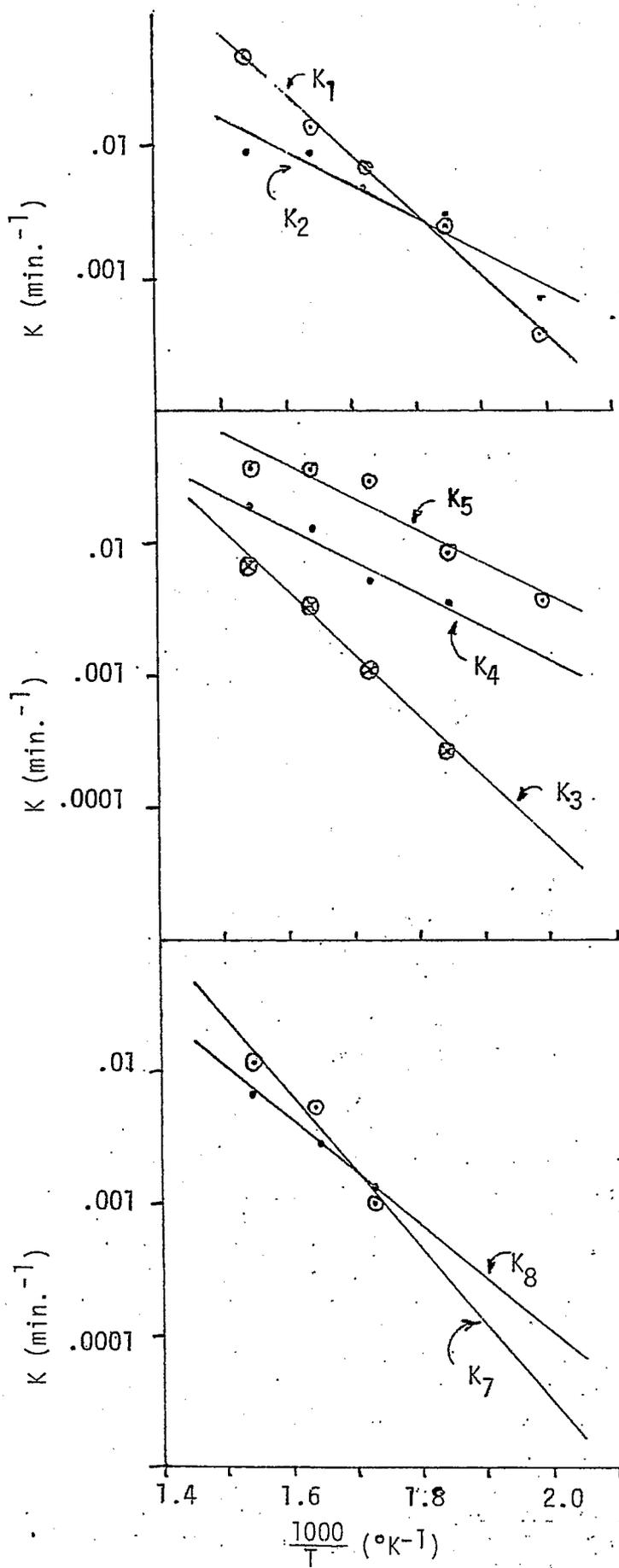


Figure 3. Kinetic rate constants for phenanthrene hydrogenation as a function of temperature between 230-280°C (Pressure, 2500 psig). 25

Task 8

Catalytic Cracking of Hydrogenated Coal-Derived Liquids and Related Compounds

Faculty Advisor: J. Shabtai
A.G. Oblad
Graduate Student: S. Sunder

Introduction

Hydrogenation followed by catalytic cracking provides a feasible process sequence for conversion of coal liquids into conventional fuels. Such a sequence has certain advantages in comparison with a hydrocracking-catalytic reforming scheme.¹

The present project is concerned with the following interrelated subjects: (1) systematic catalytic cracking studies of model polycyclic naphthenes and naphthenoaromatics found in hydrogenated coal liquids, e.g., decalin, perhydrophenanthrene, tetralin, 1,2,3,4,5,6,7,8-octahydroanthracene, and 9,10-dihydrophenanthrene, as a function of catalyst type and operating conditions, and (2) systematic catalytic cracking studies of hydro-treated middle-heavy distillate from SRC II as a function of the same variables.

Project Status

Results from catalytic cracking studies of model polycyclic naphthenes, e.g., decalin and perhydrophenanthrene, were reported earlier. Systematic catalytic cracking studies of model polycyclic naphthenoaromatics, which are typical components of partially hydrogenated coal liquids, were also carried out. The preceding report provided results obtained with tetralin as starting feed, whereas the present report summarizes the results obtained with 1,2,3,4,5,6,7,8-octahydroanthracene as feed.

The catalytic cracking reactions of 1,2,3,4,5,6,7,8-octahydroanthracene (26) were investigated as a function of reaction temperature, using the same apparatus and catalyst (Durabead-8) as in the study of decalin (1). Table 1 and Figures 1-3 summarize the change in product composition from catalytic cracking of a solution of 1,2,3,4,5,6,7,8-octahydroanthracene (26) in benzene (26/solvent ratio 1:2 by wt),* as a function of reaction temperature in the range of 300-450°C, keeping a constant LHSV=1.7 hr⁻¹. The total process time in each experiment was kept constant at 30 minutes.

As seen from Table 1 and Figure 1, the conversion of 26 increases gradually with increase in temperature (from 51 to 86% by wt) with preservation of high selectivity for liquid products (86-91%). Coke formation

* Benzene was used as an inert solvent. It was shown in separate runs that benzene does not produce any gaseous or liquid products under the same conditions (and up to 500°C). Appropriate corrections were made for some coke formation from the solvent (<1%).

is more pronounced at 300-325°C (10-14%), but decreases steadily at higher temperatures (e.g., 4.7% at 450°C). The formation of gases steadily increases from 0.23% at 300°C to 8.1% at 450°C, while the liquid yield passes through a maximum between 325-425°C and then slightly decreases at 450°C. As indicated in Figure 42, the gaseous products consist mainly of saturated C₃ and C₄ hydrocarbons.

Table 1 and Figures 3A, 3B, and 3C summarize the change in liquid product composition as a function of reaction temperature. For the purpose of clarity in presentation the compositional data are subdivided into three sets, viz., tricyclic products formed by skeletal rearrangement and/or hydrogen transfer reactions (Fig 3A); bicyclic products formed in the early cracking stages (Fig 3B); and monocyclic and open-chain products formed in the later stages of the cracking process (Fig 3C). As seen, 1,2,3,4,5,6,7,8-octahydrophenanthrene (30) is the predominant product at low temperatures (51% at 300°C) and, therefore, indicated as a primary product derived by skeletal rearrangement of 26. As seen from Fig 3A, the concentration of 30 gradually decreases with increase in temperature, while two other partially hydrogenated phenanthrene derivatives, i.e., 1,2,3,4,9,10,11,12-octahydrophenanthrene (29) and 1,2,3,4-tetrahydrophenanthrene (31), are formed in increasing yields. Compounds 29 and 31 pass through maxima between 350-400°C and then decrease at higher temperatures. Perhydrophenanthrene (22) is also formed but in negligible amounts, while the concentration of phenanthrene (32), which is apparently derived from the partially hydrogenated compounds 29, 30, and 31, slowly increases between 350-450°C.

As seen from Fig 3B, a variety of bicyclic products, anticipated from cracking of a saturated ring in the starting compound 26 or in the hydrophenanthrene derivatives 22, 29, 30, 31, are gradually formed with increase in the depth of the reaction (mainly above 350°C). Tetralin (18), C₁₄-alkylnaphthalenes (27a) and C₁₄-alkyltetralins (27b) pass through a maximum at ca. 400°C before undergoing further cracking. Also observed as product components are 1-ethyl-2-phenylcyclohexane (28a) and 1-cyclohexyl-2-phenylethane (28b), which are anticipated products from cracking of a middle saturated ring, passing through a maximum at 350-375°C. Methylnaphthalenes (20a), methyltetralins (20b), naphthalene (19), and methylindans (17) are formed in increasing yields with increase in temperature. C₁₂-alkylnaphthalenes (21a) and C₁₂-alkyltetralins (21b) are also formed in small amounts.

As seen from Fig. 3C, monocyclic and open-chain products, derived from the bicyclic products by additional cracking, increase steadily with increasing temperature, and become the main liquid products at 450°C. These include C₅-C₆ paraffins and olefins (2,3,4,5), methylcyclopentane (7), dimethylcyclopentane (8a), methylcyclohexane (8b), methylethylcyclopentanes (9a), dimethylcyclohexanes (9b), toluene (13), C₈-alkylbenzenes (14a, 14b), C₉-alkylbenzenes (14c), and C₁₀-benzenes (15,16,24,25). Any benzene formed in the reaction could not be measured, since benzene was used as a solvent.

The observed change in product composition from 26, as a function of reaction temperature (Table 1, Fig 1-3), can be rationalized in terms of the mechanistic scheme proposed in Figure 4. The compound 1,2,3,4,5,6,7,8-octahydroanthracene (26) readily undergoes skeletal rearrangement on acidic catalysts to give 1,2,3,4,5,6,7,8-octahydrophenanthrene (30). The Schroeter mechanism, proposed for this reaction² is indicated at the top of Fig 4.

The rearranged product 30 could then undergo hydrogen transfer and hydrogen rearrangement reactions to yield perhydrophenanthrene (22), 1,2,3,4,9,10,11,12-octahydrophenanthrene (29), 1,2,3,4-tetrahydrophenanthrene (31) and phenanthrene (32). Compound 31 undergoes subsequent cracking of the saturated ring to yield C₁₄-alkylnaphthalenes (27a), which by further complete or partial dealkylation could yield naphthalene (19), methylnaphthalenes (20a), and C₁₂-alkylnaphthalenes (21a). On the other hand, compounds 30 and 29 (and to some extent the feed (26)) could undergo cracking of an end saturated ring to yield C₁₄-alkyltetralins (27b), which by further complete or partial dealkylation yield tetralin (18), methyltetralins (20b), and C₁₂-alkyltetralins (21b). In a competing reaction 1,2,3,4,9,10,11,12-octahydrophenanthrene (29) could undergo cleavage of the middle ring to yield 1-ethyl-2-phenylcyclohexane (28a) and 1-cyclohexyl-2-phenylethane (28b). Compounds 28a and 28b could easily undergo secondary cleavage reactions to yield monocyclic compounds. Secondary cleavage reactions of the tetralin derivatives (18, 20b, and 21b) could proceed by pathways indicated for tetralin, (18).³ Alkylation of phenanthrene (32) to yield some C₁₅, C₁₆-alkylphenanthrenes apparently also occurs to a small extent.

Future Work

Studies of other model naphthenoaromatic compounds and of hydrotreated coal liquids are continuing.

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Table 1

Change in Product Composition from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene (26)
as a Function of Reaction Temperature^{a-d}.

Experiment Number	OA-107	OA-102	OA-109	OA-108	OA-106	OA-105	OA-101
Reaction Temperature, °C	300	325	350	375	400	425	450
Conversion, % by wt. of feed <u>26</u>	51.0	51.3	60.4	70.0	71.0	80.6	86.0
Yield, % by wt. of reacted <u>26</u>							
Gases	0.23	0.29	0.77	1.73	3.80	5.02	8.12
Liquids	85.70	89.71	91.23	88.87	89.70	90.18	87.18
Coke	14.07	10.00	7.98	9.40	6.50	4.80	4.70
Product Distribution, mol./100 mol. of reacted <u>26</u>							
CH ₄	-	-	-	0.02	0.05	0.11	0.30
C ₂ H ₆	-	-	-	0.01	0.05	0.11	0.30
C ₂ H ₄	-	-	-	-	-	0.26	0.75
C ₃ H ₈	0.15	0.23	0.58	1.38	3.05	4.40	7.62

Table 1 - Continued

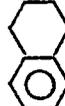
	Reaction Temperature, °C	300	325	350	375	400	425	450
C_3H_6		-	-	-	-	-	-	0.84
$i-C_4H_{10}$		0.10	0.13	0.57	1.46	3.33	4.64	7.30
$n-C_4H_{10}$		0.11	0.15	0.44	1.04	2.17	2.89	4.72
C_4H_8		-	-	-	-	-	-	-
$C_5 - C_6$ Paraffins & Olefins(2,3,4,5)		0.14	0.16	0.37	0.88	4.00	6.90	9.12
$C_6 - C_8$ Cycloanes(7,8,9)		0.14	0.16	2.79	5.67	8.43	11.10	14.06
Toluene(13)		-	-	0.55	1.79	3.14	5.21	7.71
Ethylbenzene(14a) + xylenes(14b)		-	-	0.21	0.71	1.66	3.26	5.43
C_9 -Alkylbenzenes(14c)		-	-	-	0.55	0.98	1.79	2.89
C_{10} -Benzenes(15,16,24,25)		-	0.16	0.48	2.76	5.57	8.39	10.52
Methylindans(17),		-	-	0.10	0.70	1.14	2.23	3.25
Tetraalin(18),		7.56	9.81	10.95	12.67	13.14	12.59	8.52

Table 1 - Continued

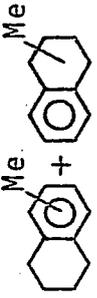
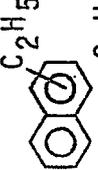
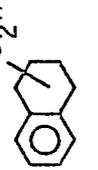
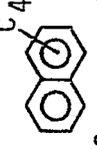
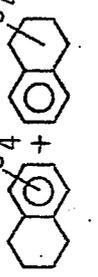
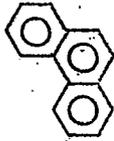
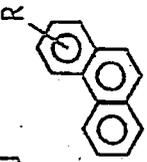
Reaction Temperature, °C	300	325	350	375	400	425	450
Naphthalene (<u>19</u>), 	-	0.29	0.66	1.54	2.98	5.05	9.05
Methylnaphthalenes (<u>20a</u>), 	-	-	-	0.54	1.38	2.74	5.26
Methyltetralins (<u>20b</u>), 	0.52	0.87	1.59	2.80	2.66	3.70	3.33
C ₁₂ -alkylnaphthalenes (<u>21a</u>), 	0.15	0.39	0.91	1.07	1.05	0.98	1.04
C ₁₂ -alkyltetralins (<u>21b</u>), 	-	0.14	0.29	0.45	0.52	0.42	0.23
C ₁₄ -alkenylnaphthalenes ^e (<u>27a</u>), 	-	-	0.12	0.52	1.02	1.60	1.72
C ₁₄ -alkyltetralins ^e (<u>27b</u>), 	1.88	2.98	4.04	4.90	4.88	3.51	1.52

Table 1 - Continued

Reaction Temperature, °C	300	325	350	375	400	425	450
1-ethyl-2-phenyl... cyclohexane (<u>28a</u>), 1-cyclohexyl-2-phenylethane (<u>28b</u>),	1.96	3.34	4.14	3.94	3.42	2.48	0.89
Perhydrophenanthrene (<u>22</u>), 1,2,3,4,9,10,11,12-octa... hydrophenanthrene (<u>29</u>), 1,2,3,4,5,6,7,8-octa... hydrophenanthrene (<u>30</u>), 1,2,3,4-tetrahydro... phenanthrene (<u>31</u>),	1.52	2.32	2.27	1.56	1.99	1.29	1.03
	13.94	18.19	19.41	16.85	13.45	8.77	5.72
	50.93	41.27	31.45	18.40	12.50	7.43	3.79
	8.44	11.72	14.62	16.02	15.51	12.22	6.74

Table 1 - Continued

Reaction Temperature, °C	300	325	350	375	400	425	450
Phenanthrene (<u>32</u>), 							
C ₁₁ , C ₁₂ -alkylphenanthrenes (<u>33</u>), 	0.36	1.08	2.21	5.04	7.48	10.31	11.63
	0.59	0.28	0.17	0.30	2.26	1.51	2.61

^aIn each run 1.5 g of 26 was used, dissolved in 3.0 g of benzene;

^bCatalyst, Durabead-8, 5 g;

^cRun time, 30 min.;

^dLHSV, 1.7 hr⁻¹;

^eIncludes mono- and dialkylsubstituted products.

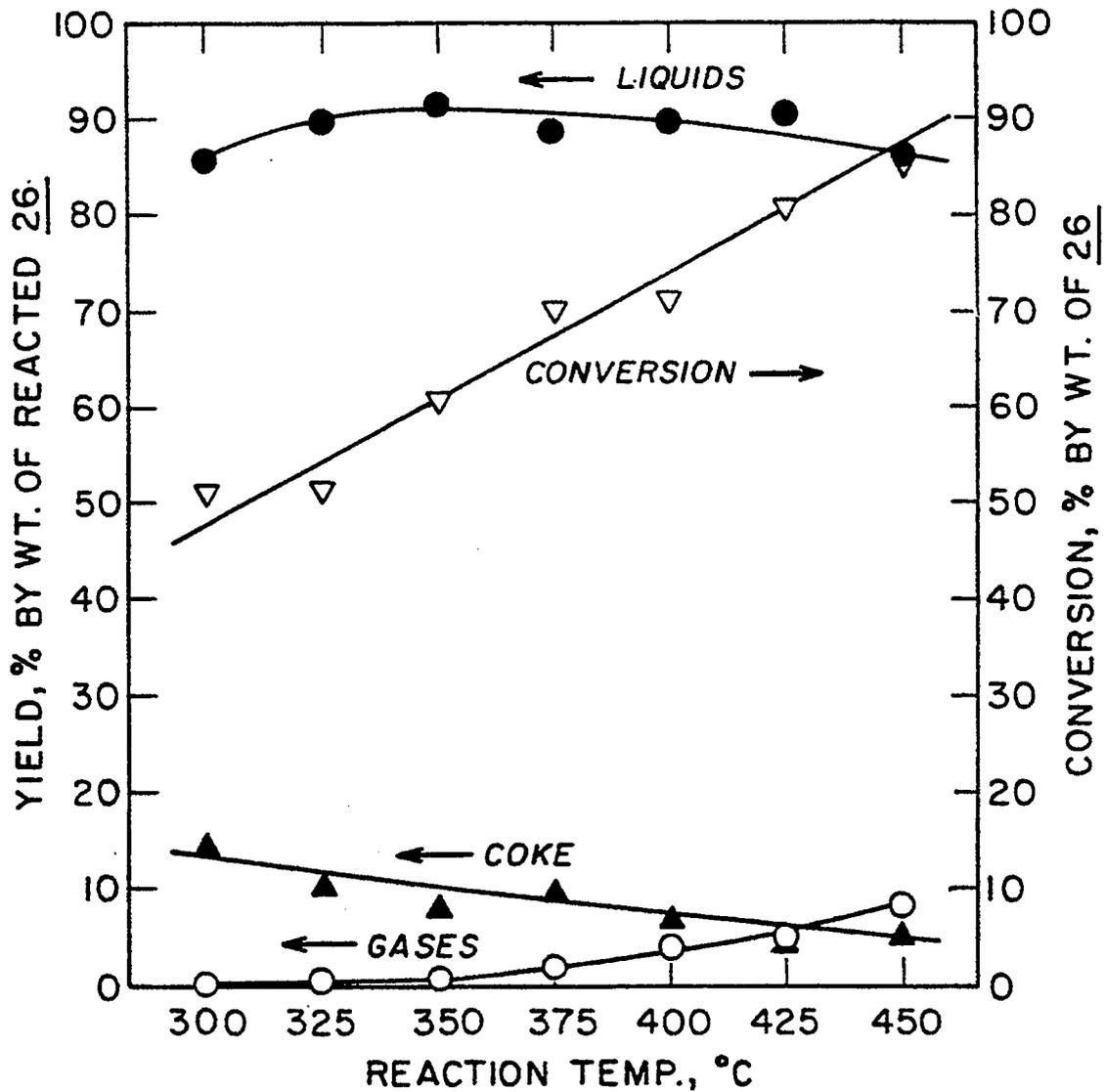


Figure 1. Distribution of Coke, Liquid and Gaseous Products from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene(26), as a Function of Reaction Temperature (catalyst, Durabead-8; LHSV, 1.7 hr^{-1}).

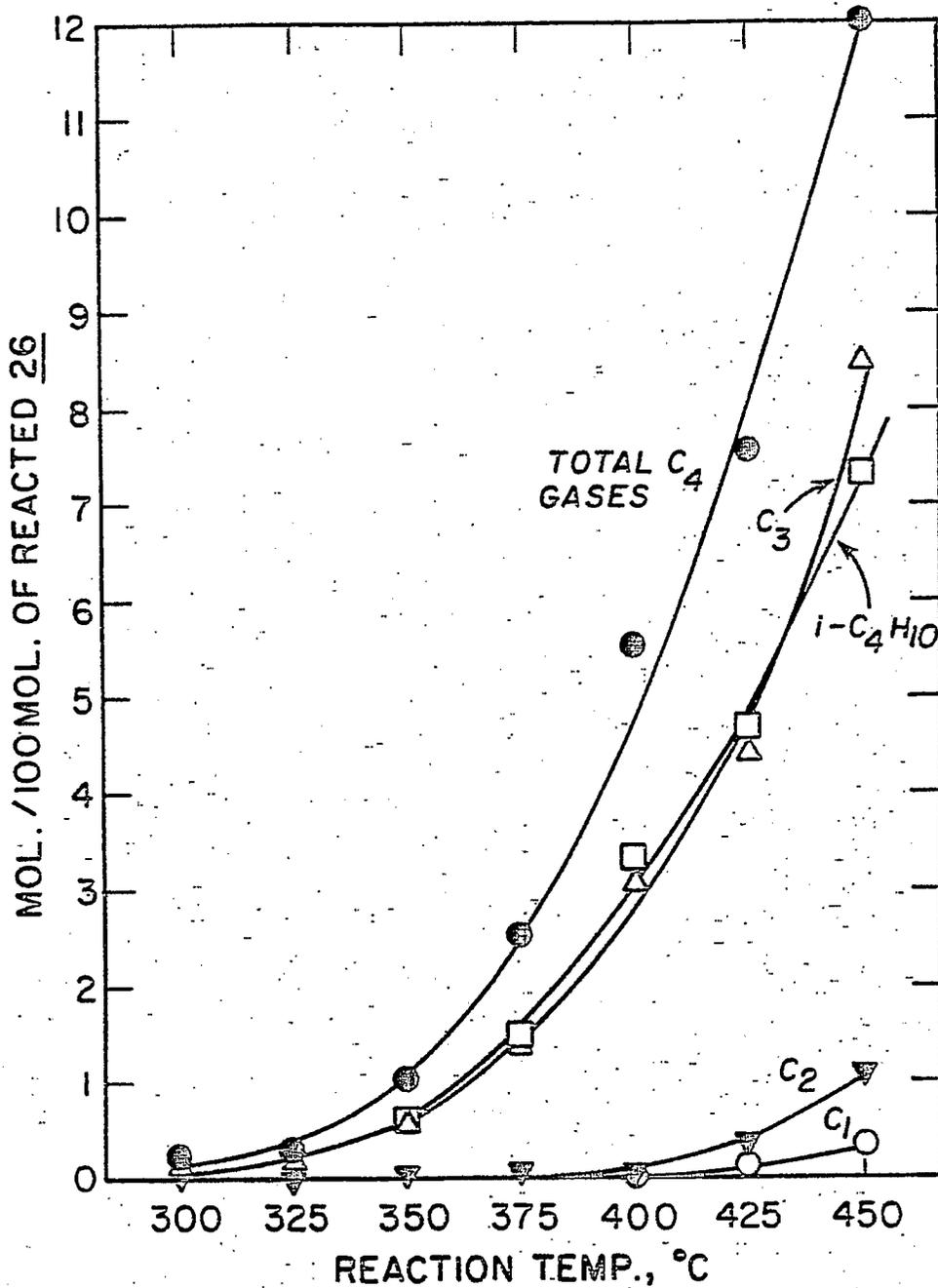


Figure 2. Change in Gaseous Product Composition from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene(26) as a Function of Reaction Temperature (catalyst, Durabead-8; LHSV, 1.7 hr^{-1}).

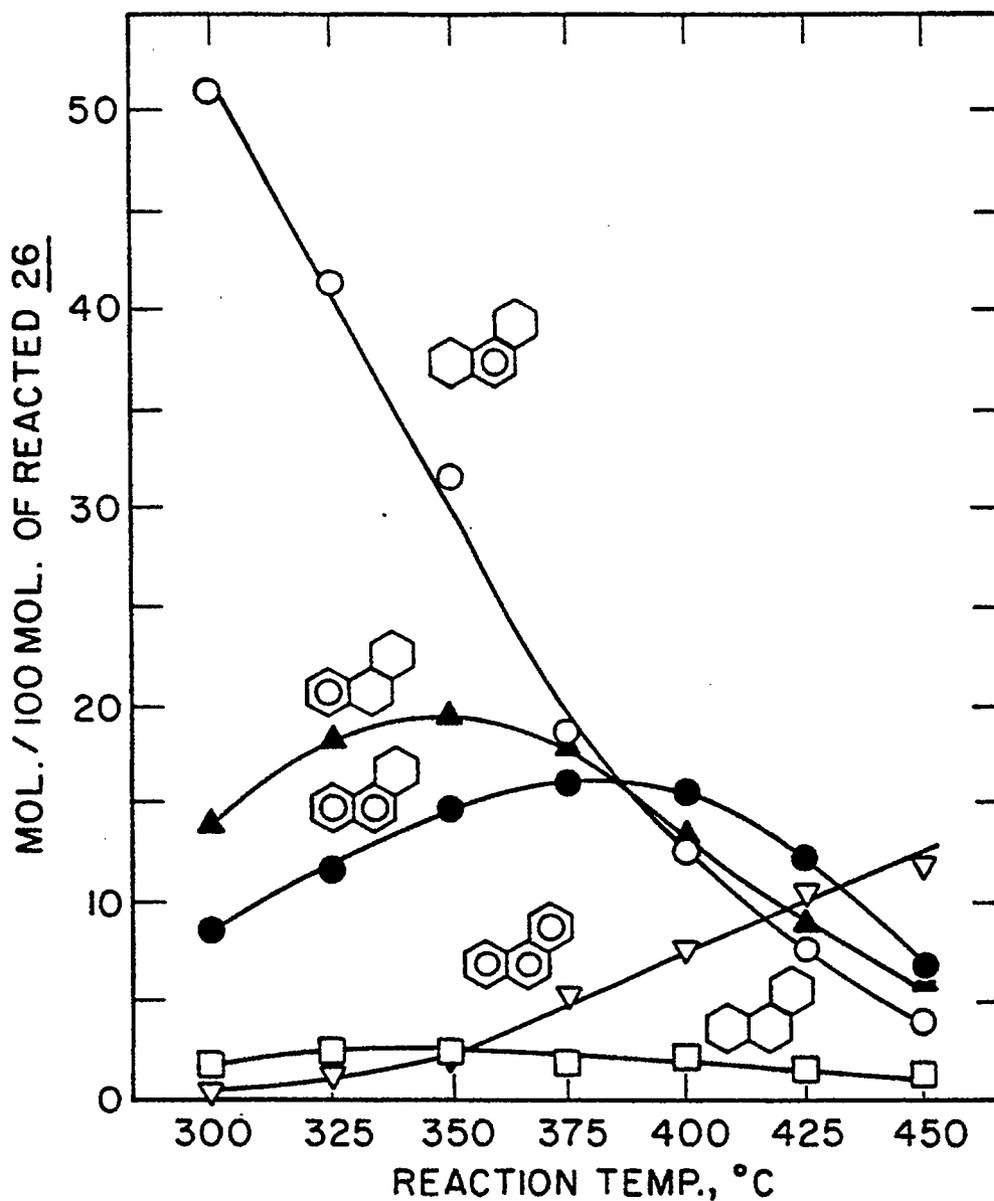


Figure 3A. Distribution of Liquid Products (Tricyclics) from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene(26), as a Function of Reaction Temperature (catalyst, Durabead-8; LHSV, 1.7 hr^{-1}).

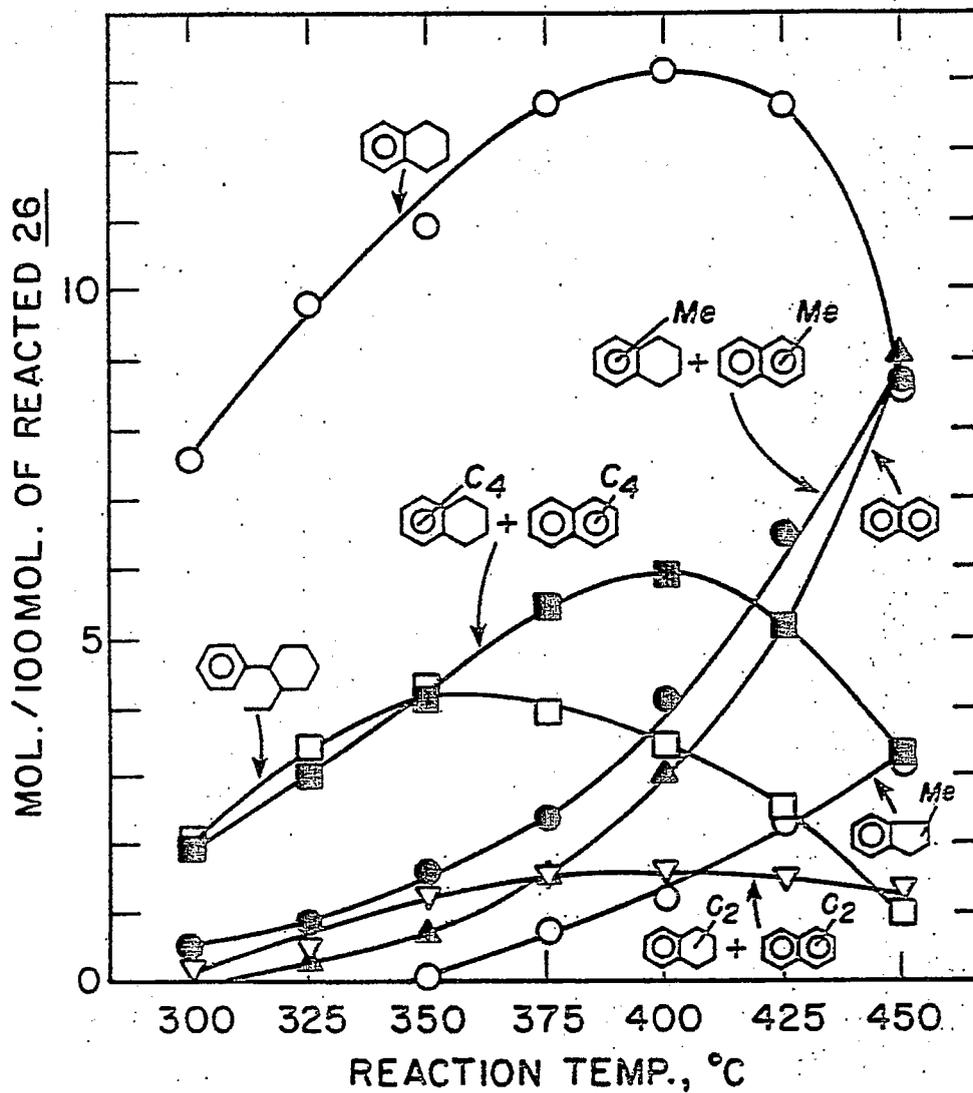


Figure 3B. Distribution of Liquid Products (Bicyclics) from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene(26), as a Function of Reaction Temperature (catalyst; Durabead-8, LHSV, 1.7 hr^{-1}).

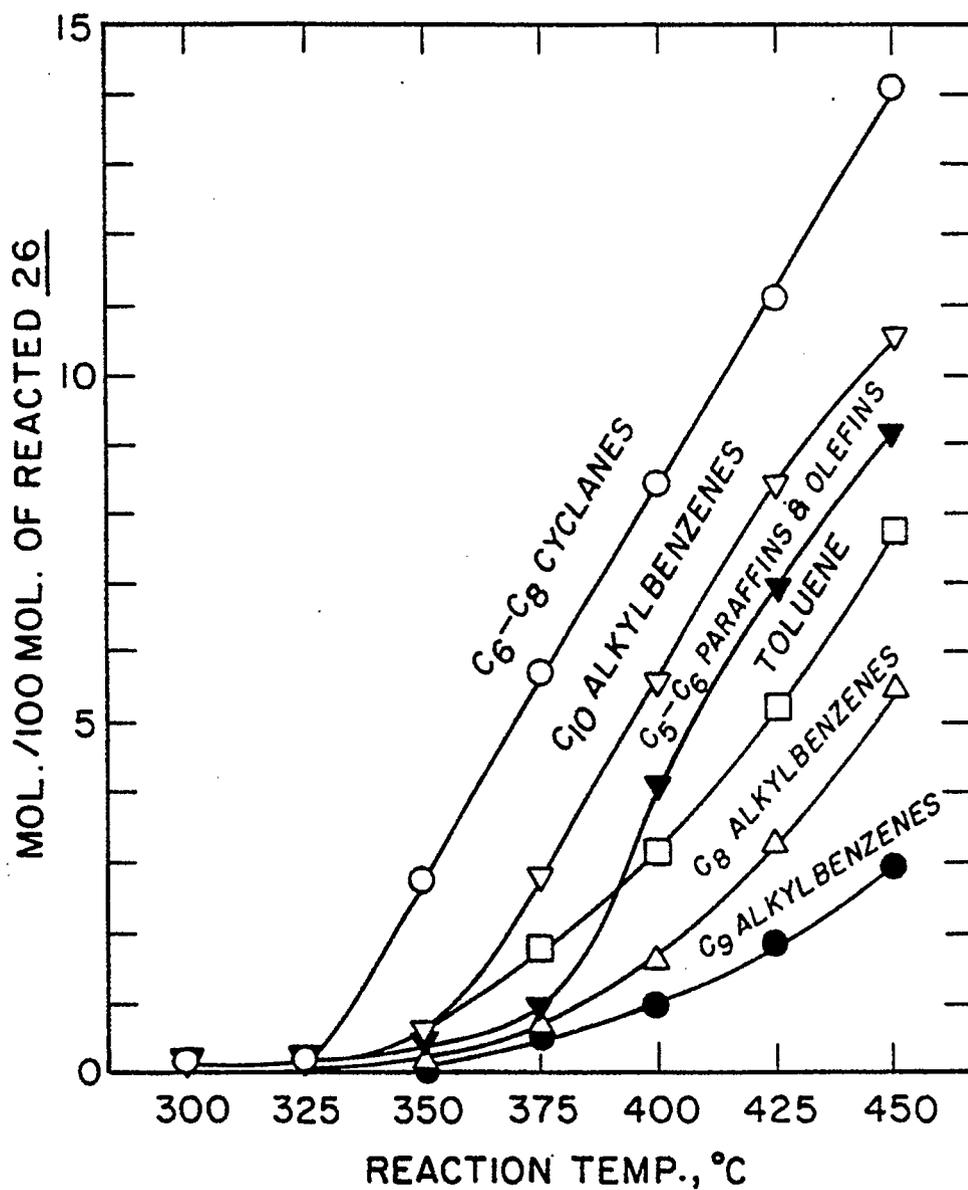
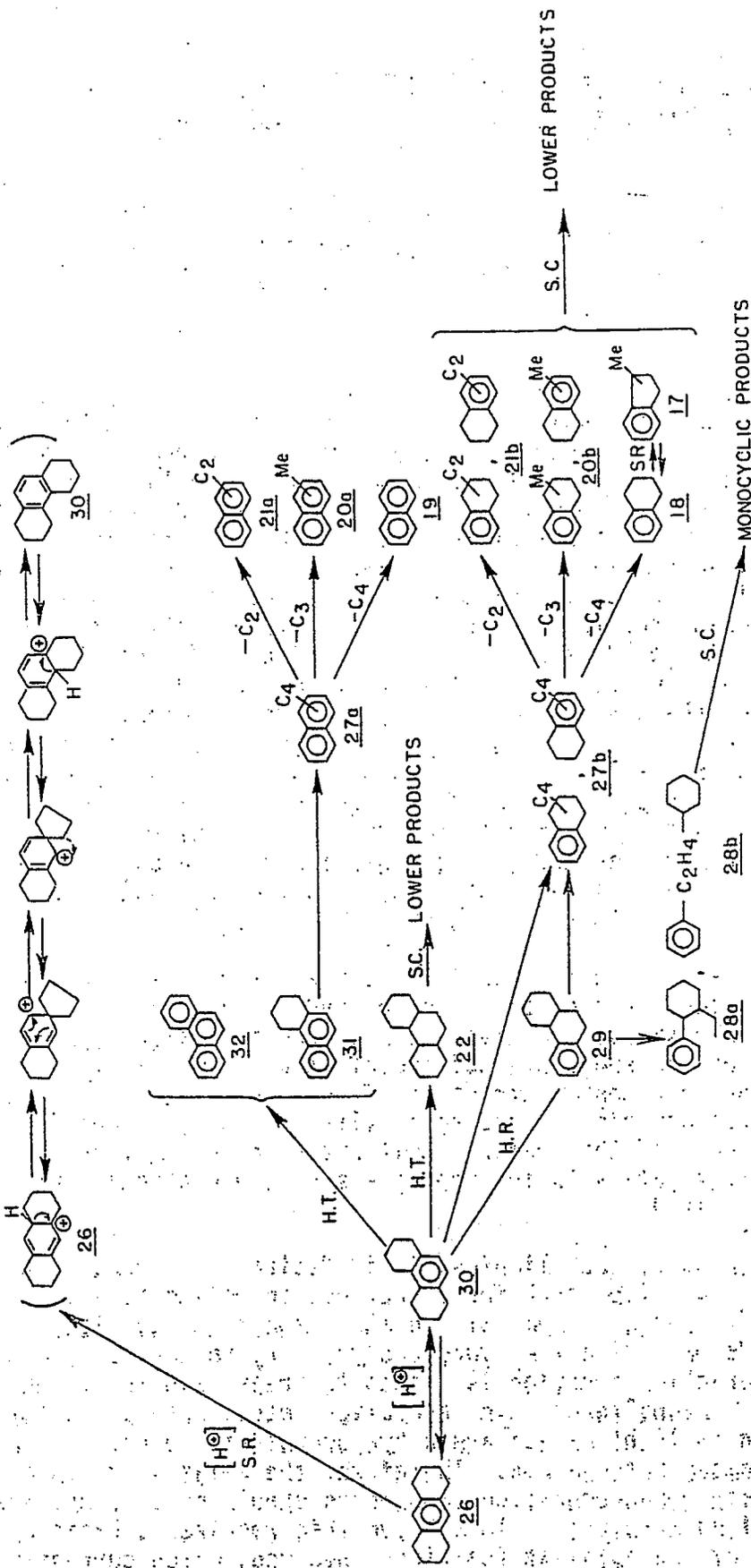


Figure 3C. Distribution of Liquid Products (Monocyclics & Open-Chain) from Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene(26), as a Function of Reaction Temperature (catalyst, Durabead-8; LHSV, 1.7 hr^{-1}).



H.T. — HYDROGEN TRANSFER H.R. — HYDROGEN REARRANGEMENT
 S.R. — SKELETAL REARRANGEMENT S.C. — SECONDARY CLEAVAGE

Figure 4. Proposed Mechanistic Scheme for Cracking of 1,2,3,4,5,6,7,8-Octahydroanthracene (26).

Systematic Structural Activity Study of Supported
Sulfide Catalysts for Coal Liquids Upgrading

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Introduction

The objective of this research is to develop an insight into basic properties of supported sulfide catalysts and to determine how these relate to coal liquids upgrading. The proposed program involves a fundamental study of the relationship between the surface-structural properties of various supported sulfide catalysts and their catalytic activities for various types of reactions. Thus, there are two clearly defined and closely related areas of investigation, viz., (1) catalyst characterization, especially of the sulfided and reaction states and (2) elucidation of the mode of interaction between catalyst surfaces and organic substrates of different types. The study of subject (1) will provide basic data on sulfided catalyst structure and functionality, and would allow the development of catalyst surface models. Subject (2), on the other hand, involves systematic studies of model reactions on sulfide catalysts, and the utilization of data obtained for development of molecular level surface reaction models correlating the geometry (and topography) of catalyst surfaces with the steric-conformational structure of adsorbed organic reactants. The overall objective of the project is to provide fundamental data needed for design of specific and more effective catalysts for upgrading of coal liquids.

Supported sulfide catalysts are extensively used in the oil and related industries for hydrocracking and hydrotreating of fuel oil, distillates and residuals. They have also received attention for liquefied coal processing and even coal liquefaction. Despite this, little is known of the fundamental structure of the operating catalyst and the active sites responsible for its reactivity. This is especially true with regard to the role of the support. Without such information, development of new and better catalysts for the more severe operations currently demanded is seriously limited.

For upgrading of coal liquids, it is desirable to reduce the molecular weight to produce a feedstock for direct use in refineries with a minimum consumption of hydrogen. Some of the most important reactions involved in coal liquids upgrading are hydrogenolysis, hydrogenation and hydrocracking. Thus, a hydrocracking function is needed to break down larger molecular entities, e.g., asphaltenes, hydroaromatics, etc., but not so strong as to cause cracking to light gases; and a hydrogenolysis function is needed to selectively remove heteroatoms. Therefore, the relative ratio of acidic to hydrogenation-dehydrogenation components should be critical for development of optimized catalysts. To achieve this requires a basic and detailed understanding of the catalyst functions involved, which currently does not

exist. Furthermore, the design and optimization of specific catalysts for CDL upgrading requires that studies of sulfided catalyst activity and selectivity in model reactions be pursued with due consideration of the critically important relationship between catalyst structure (including surface geometry and topography) and the steric-conformational characteristics of organic reactants. This has been so far a largely neglected subject as evidenced by the virtual absence of any stereochemical studies of hydrogenation processes in the presence of sulfided catalysts.

The catalyst support can affect the character of the sulfide phase obtained as well as the catalytic activity of these catalysts.¹ In the preparation, the metal oxide can interact with the carrier forming rather complex interaction phases. The degree of this interaction, which depends on the particular metal and support involved, can greatly affect the subsequent phases and their disposition on the support during sulfiding of the catalyst. These interactions can be greatly affected by the manner of preparation and the chemical nature of the support. In the preparation of the catalyst, the mode of addition of the active components, the calcination temperature and the gaseous environment, all have a bearing on the final state of the catalyst.^{2,3} The chemical nature of the carrier greatly determines the degree of interaction with the active components. For example, with molybdenum or cobalt, silica shows little interaction, γ -alumina strong interaction, and silica-alumina intermediate interaction. Alteration of a given support by different modifiers can influence this interaction, e.g., gallium-doped γ - Al_2O_3 gave stronger interaction with nickel⁴ or cobalt⁵ than the original Al_2O_3 .

It is well known that the addition of various promoters can greatly increase catalytic activity.⁶ These usually encompass transition metals in conjunction with group VIB metals, for example, Ni added to WS_2 catalysts, or Co added to MoS_2 catalysts. The former combination is more active for hydrogenation while the latter is better for hydrogenolysis reactions. For example, combinations of these components have been studied for hydrodesulfurization of gas oil,⁷ simulated middle distillates,⁸ and residuals;⁹ hydrodenitritification of shale oil;¹⁰ and hydrotreating of heterocyclics and polynuclear aromatics,¹¹ solvent refined coal, COED pyrolysis oil, and synthoil.¹²

The acidity of the surface is another important property of sulfided catalysts. The acidity can greatly influence the selectivity of the catalyst. Even activated alumina itself, e.g., γ - or η - Al_2O_3 , cannot be considered as a neutral carrier, since aside from its intrinsic Lewis acidity, it can exhibit increased acidity¹³ and, especially, to develop Bronsted acidity when molybdenum is added to it.¹⁴ Preparation conditions can greatly affect the residual acidity of sulfided alumina catalysts.¹⁵

Many of the sulfide catalysts currently used for hydrotreating or hydrocracking of coal liquids are supported on amorphous silica-aluminas. These catalyst supports exhibit Bronsted (as well as Lewis) acidity, which is responsible for cracking activity. However, a problem here is that these catalysts also tend to coke more rapidly and become deactivated. The addition of alkali to these catalysts should suppress undesirable cracking side reactions.

Techniques for characterizing supported sulfided catalysts are many and varied, which can be a good gauge of the complexity of these catalysts. Standardized techniques have been well developed for metallic catalysts and acidic-type catalyts, which in many instances can be related to catalytic activity. No such standard techniques have yet emerged for characterizing sulfide catalysts, and there is no single technique adequate to define these catalysts. Major techniques which have been applied to these catalysts are:¹⁶ (1) X-ray diffraction--to identify the bulk phases present, e.g., WS_2 , Co_9S_8 , etc.; (2) gravimetric/volumetric measurements--to measure adsorption of various gases and reduction/sulfidation reactions; (3) magnetic susceptibility--to assess the coordination of transition metals; (4) electron microscopy--to establish the degree of homogeneity of components throughout the catalyst; (5) diffuse reflectance spectroscopy--to determine the coordination of active components; (6) infra-red spectroscopy--to assess surface structures of active components and type of acidity present; and (7) photo-electron spectroscopy--to establish surface phases present.

One of the more useful concepts developed for molybdena catalysts is the surface stoichiometry of the sulfided catalyst.¹⁷ This can be characterized in terms of surface concentrations of oxide, sulfide and anion vacancies. These vacancies are postulated to be the active sites for hydrogenolysis.¹⁸ Different sites may be responsible for hydrogenolysis and for hydrogenation;¹⁹ the latter may consist of Al sites adjacent to Mo vacancies. The importance of such correlations may be illustrated by the following example. Recent studies indicate that hydrogenation of a partially blocked benzene ring in condensed multiring compounds, e.g., the middle ring in phenanthrene, is sterically hindered and requires vertical adsorption of the ring through its unobstructed side.²⁰ Examination of surface models of a Co-Mo/ Al_2O_3 catalyst indicates the critical adsorption of such rings is possible at certain "valley" (slit) sites. It is tentatively deduced that an increase in the concentration of such sites by an appropriate change in catalyst composition could increase the hydrogenation rate for such hydrogenation-resistant substrates.

In summary, much of a qualitative nature is known of certain factors influencing catalysis over supported sulfide catalysts. However, there is a dearth of quantitative, fundamental information relating catalyst structural properties to catalyst activity.

The scope of the work involved on this project encompasses catalyst preparation, characterization and activity testing. A flow chart showing catalysts to be prepared is given in Figure 1. Commercial catalyst supports will be used as available. Only those having moderate to large pore sizes will be chosen to avoid diffusional effects in the catalytic tests to be employed. Different types of supports will include: alumina, silica, magnesia and titania and combinations of these. Those not available will be prepared by appropriate techniques. Altered supports will involve modification of the carriers to change acidity and/or possible interaction effects with the active components. Various additives will also be incorporated to change the acidity or basicity of the support.

The most common active components for these types of catalysts are those of Mo, W, Ni and Co, and study will concentrate on combinations of these.

Standard impregnation and precipitation techniques will be used to incorporate these onto the preformed supports. Some combinations will be prepared by coprecipitation, in which the support is precipitated concurrently with the active components. A number of catalysts will be prepared directly in the sulfided form by precipitation in a sulfiding medium. Selective additives will also be incorporated in some of the preparations. Use of various supports, preparation methods and additives should generate catalysts having appreciable differences in catalytic activity, the object being to relate the different catalyst functions to the active phases present.

Figure 2 gives the flow chart for evaluation of catalysts. This involves characterization of catalyst properties and catalytic activity tests on selected model compounds. Characterization will be done on the oxide, sulfided and reacted states. Measurements will include: surface area, pore volume, X-ray analysis, electron microscope, reflectance spectra, acidity, adsorption, ESCA and temperature-programmed desorption. Not all of these will be employed on all catalysts, but rather on selective examples of catalysts showing important differences in catalytic activity and selectivity.

Two types of activity tests are envisioned, viz., low pressure screening tests and high pressure activity tests. The low pressure tests are designed to allow rapid screening of many catalysts to obtain relative activity data. Simple model compounds are used to evaluate catalyst activity for hydrodesulfurization, hydrogenation and hydrocracking reactions. These will be useful for evaluating different catalysts with respect to their activity and selectivity for these particular functions. The high pressure tests are carried out on selective catalysts showing wide differences in activity and selectivity from the screening tests. The high pressure tests are designed to determine activity for aromatic hydrogenation, hydrodenitrogenation, hydrodesulfurization and hydrodeoxygenation using mixtures of model compounds. Also, selected model compounds will be employed having special stereochemical requirements to obtain insight into geometric-topographical characteristics of the catalyst surface for the various types of reactions important in functioning of these catalysts in coal liquids upgrading.

Project Status

Since this project has just recently been activated, sufficient results are not yet at hand to warrant presentation at this time. A number of Co-Mo catalysts on several different supports has been prepared and characterization and activity testing is in progress.

Future Work

Prepared catalysts will be tested for catalytic activity. Additional catalysts will be prepared and tested.

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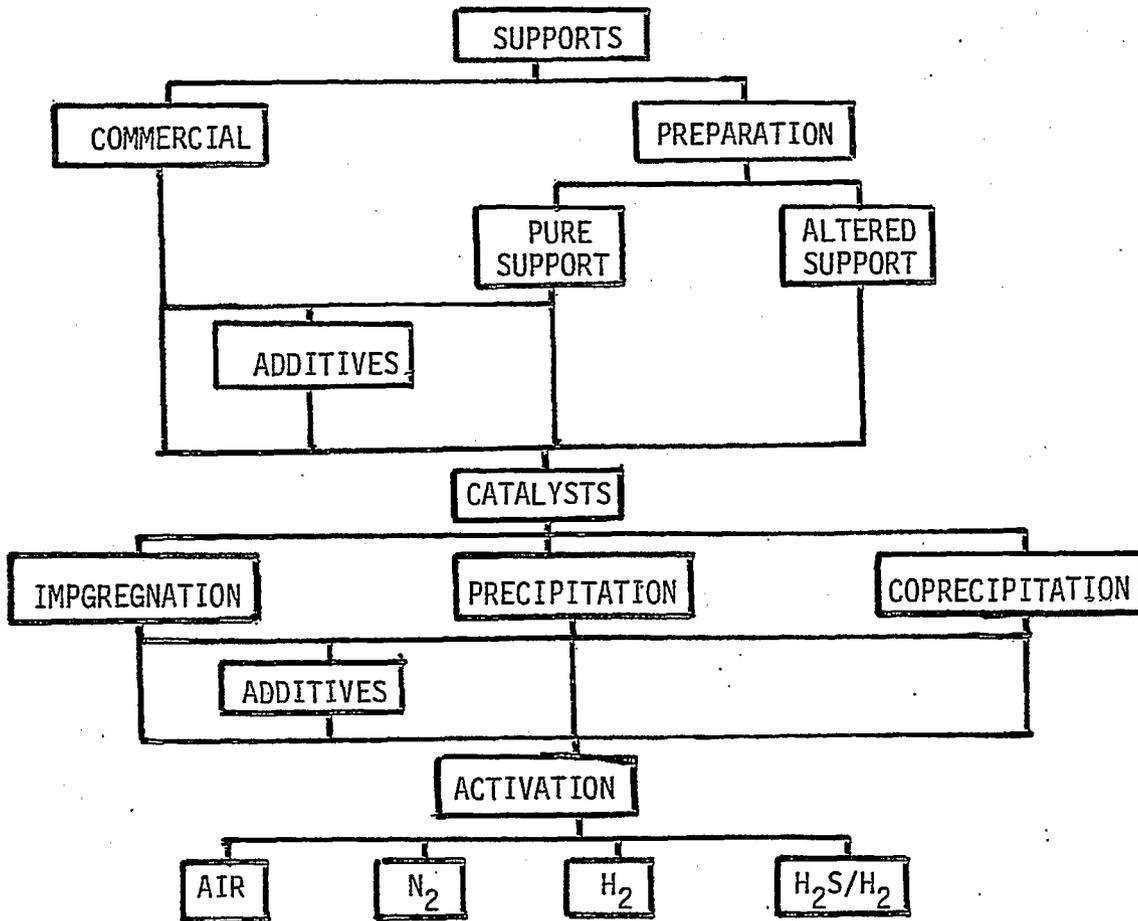


Figure 1. Flow chart for catalyst preparations.

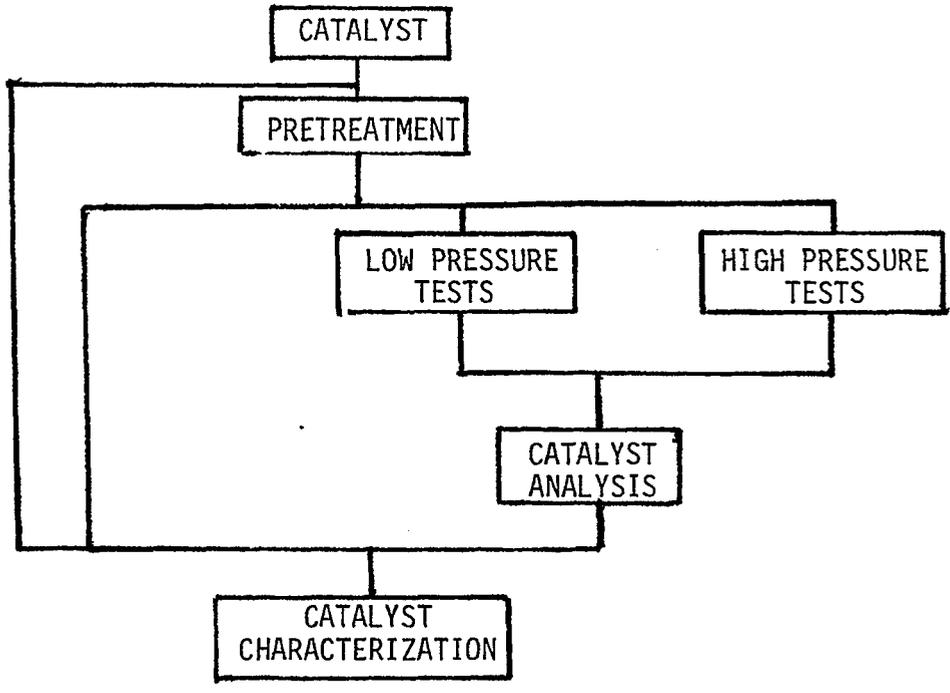


Figure 2. Flow chart for catalyst evaluations.

The Effects of Poisoning on the Desulfurization Activity of Cobalt-Molybdate Catalysts

Faculty Advisor: F.E. Massoth.
Graduate Student: R. Ramachandran

Introduction

The importance of cobalt-molybdena catalysts for hydrotreating and hydrodesulfurization of petroleum feed stocks is well-known. These catalysts are also being studied for hydrodesulfurization and liquefaction of coal slurries and coal-derived liquids. However, these complex feed stocks result in rapid deactivation of the catalysts. To gain an insight into the deactivation mechanism, detailed kinetics of the hydrodesulfurization of the model compound benzothiophene are compared before and after addition of various poisons and coke precursors. The studies are planned using a constant stirred microbalance reactor, which enables simultaneous measurement of catalyst weight change and activity. Additional temperature programmed desorption studies provide information on changes in strength of adsorption sites with poison/coke.

The rate of benzothiophene (BT) hydrodesulfurization over a commercial CoMo/Al₂O₃ catalyst was first order in BT, first order in H₂ and inhibited by BT, H₂S and H₂. Data analysis showed a good correlation with a dual site mechanism, with BT and H₂S competing for one type of site and H₂ for another. Adsorption of BT was much stronger than H₂S. The data did not permit distinguishing between associative and dissociative adsorption of H₂. Pyridine and quinoline were partial poisons for the reaction, but their effect was reversible to a large extent.

Separate gravimetric adsorption measurements of H₂S over the sulfided and the BT reacted catalyst, showed reversible adsorption and good data conformance to a Langmuir isotherm. The presence of pyridine lowered H₂S adsorption, indicating competition for adsorption sites.

Temperature programmed desorption studies of thiophene on the CoMo/Al₂O₃ catalyst showed a complex desorption pattern — appreciable amounts of butene were found, as well as desorbed thiophene, signifying partial decomposition of the thiophene during temperature programmed desorption. Studies with H₂S as adsorbate, indicated some dissociative adsorption of H₂S occurred during temperature programmed desorption.

Project Status

Since molybdena catalysts are known to possess hydrogenation activity in addition to hydrodesulfurization (HDS) activity, 1-hexene was chosen to study the kinetics of the hydrogenation function. Hexene, diluted with n-heptane solvent, was fed over the same aged CoMo (Ketjen) catalyst previously used for HDS of benzothiophene. The experimental procedure is the same as described earlier.¹ Reaction products were analyzed by gas chromatography using a Flame Ionization Detector and a 6 ft column of n-octane on porosil C. Interestingly, apart from the hydrogenation reaction to give n-hexane, some

cracking to propylene also took place. Apart from the above two reactions, rapid isomerization of 1-hexene also occurred.

The kinetic series was carried out by a systematic variation of the partial pressures of hexene, H_2S , H_2 and He. Table 1 gives the partial pressures and rate data. Table 2 shows the rate equations used in fitting the data. It can be seen from the sum of squares that it is very difficult to differentiate between rate equations and even between dual and single site mechanisms. But some interesting conclusions may be reached: (1) hexene hydrogenation follows a Langmuir-Hinshelwood type mechanism and (2) reaction is inhibited by H_2 , hexene and to a small extent by H_2S . Comparing the H_2S inhibition for hydrodesulfurization¹ and hydrogenation, HDS of benzothiophene is inhibited to a much greater extent than hydrogenation of hexene. The relatively low values for H_2S adsorption (K_S in Table 2) for hydrogenation compared to HDS argues for different active sites for the two reactions, as has been previously suggested by Owens and Amberg.²

Rates of hexene cracking increased with an increase in H_2S partial pressure. Goudriaan et al.³ and Satterfield⁴ observed, during hydrodenitrogenation of pyridine, an enhancement of the hydrocracking activity of a CoMo/Al catalyst by H_2S . Increase in the cracking activity with H_2S may be due to the following: It was reported earlier¹, on the basis of TPD experiments using H_2S as the adsorbate, that part of the H_2S adsorbed on the catalyst is adsorbed dissociatively with release of H_2 . However, some of the H_2 may remain on the catalyst in the form of protons, increasing catalyst acidity. These protons can then participate in carbonium ion cracking reactions. According to this view, an increase in H_2S pressure should lead to an increase in proton concentration and consequently to an increase in cracking activity. Figure 1 shows the cracking to vary linearly with H_2S partial pressure and indicates a very low intrinsic cracking activity in the absence of H_2S .

Temperature programmed desorption (TPD) experiments were also continued during this period using thiophene (TP) as the adsorbate. The experimental set-up is the same as described earlier.⁵ The experimental sequence consisted of (1) sulfide the catalyst using 10% H_2S in H_2 at 400°C for 2 hours, (2) flush in He at 400°C for 1 hour, (3) cool to 100°C in He, (4) adsorb/desorb TP in He at 100°C, (5) TPD in He to 350°C, (6) cool to 100°C in He and (7) temperature programmed reduction (TPR) in H_2 to 350°C. Also, the above sequence was repeated replacing H_2 with D_2 in Step 7.

Figure 2 shows the above sequence of experiments with a Mo/Al₂O₃ catalyst. During the TPD run, TP desorbed along with butene, a desulfurization product, leaving some hydrogen deficient coke on the catalyst. But H_2S , another desulfurization product, was not observed. During the subsequent TPR in H_2 , butene, H_2S and TP were observed. Even though the catalyst was heated to 350°C during the TPD in He, TP desorbed around 160°C during the TPR, indicating that the TP came from a reactive polymer. As in the case of H_2S adsorption, during the TPR in H_2 , H_2S desorbed around 210°C indicating that this H_2S may be from S chemisorbed on the catalyst during the TPD in He. The butene which desorbed around 200°C may be due to HDS of the desorbing TP, while that around 280°C from hydrogenation of residual coke. Companion experiments in a flow microbalance confirmed the presence of a residue remaining after the TPD in He, which was completely removed in the subsequent H_2 step.

Figure 3 shows the TPR experiment in D_2 . Apart from the butene and thiophene, D_2S was also observed. The low temperature TP was completely deuterated, indicating two possibilities, viz., (1) the thiophene polymer is totally devoid of hydrogen or (2) the hydrogen remaining in the polymer exchanged with D_2 at low temperature. A separate TPR experiment in D_2 on adsorbed TP showed exchange to occur as low as $120^\circ C$; thus, either explanation remains a possibility, although a polymer without hydrogen seems unlikely. The butenes were observed around $200^\circ C$, mainly as C_4D_8 , and around $280^\circ C$, as C_4D_8 and $C_4H_2D_6$. The $200^\circ C$ portion of C_4D_8 may be due to the HDS reaction of C_4D_4S while the $280^\circ C$ portion may be from the coke, as explained above. Since some $C_4H_2D_6$ was always observed, the coke may have about 2 hydrogens per C_4 unit. Lower molecular weight products were not observed, indicating that the C_4 units must preserve their structural integrity in the coke.

The results of these desorption studies have some bearing on the mechanism of thiophene desulfurization. It is significant that some thiophene was so strongly chemisorbed on the catalyst, that it underwent decomposition to coke when temperature programmed in He. The hydrogen released in this polymerization was surprisingly active, forming butene below $200^\circ C$, either by an HDS reaction with adsorbed thiophene or hydrogenation of a portion of the coke. Two additional points are important, viz., butadiene and H_2S were not observed in the reaction products below $300^\circ C$. These facts appear to be in conflict with reaction mechanisms proposed by Owens and Amberg² and by Kolboe.⁶ The former postulates butadiene as a reaction intermediate, which should have been the most favored product in the absence of gas phase H_2 . The latter proposes direct formation of H_2S from an intramolecular hydrogenolysis reaction, which should have been detected based in previous results on H_2S adsorption-desorption.

Insight into the nature of the coke species left after TPD in He is provided by the subsequent TPR experiments in H_2 and D_2 . The release of thiophene at low temperature almost certainly indicates a portion of the coke exists as a hydrogen-deficient thiophene polymer. Addition of gaseous H_2 then causes hydrogenation of the polymer with formation of discrete thiophene molecules. Another portion of the coke is more resistant to hydrogenation and evolves as butene at higher temperature. This coke is also hydrogen-deficient, but appears to contain two hydrogens per C_4 unit. It may also contain sulfur, since an H_2S peak corresponded with the butene peak. Because of the integrity of the C_4 structure in this coke, it may consist of strongly chemisorbed, hydrogen-deficient thiophene units, in contrast to the apparently weakly adsorbed thiophene polymer. Under HDS conditions, the polymer form would not be stable, but the coke form could be an intermediate in the HDS reaction.

The above results were obtained on an 8% Mo/Al_2O_3 catalyst. To investigate the effect of cobalt, a sample of this catalyst was impregnated to give 3% Co and recalcined at $500^\circ C$. The catalyst was sulfided and TPD-TPR experiments were performed as above for the Mo catalyst.

Figure 4 compares TPD of thiophene for the two sulfided catalysts. The CoMo/Al catalyst gave two TP desorption peaks, the low temperature one similar to Mo/Al and an additional high temperature one. Evolution of H₂S and butene corresponded with the second TP peak, indicating a high temperature decomposition was occurring as well as the low temperature decomposition observed with both catalysts. The TPR in H₂, Fig 5, showed less H₂S for the CoMo/Al catalyst, and the high temperature H₂S peak found with Mo/Al was missing. These results show some similarities and some differences in catalyst adsorption sites when cobalt is present. If it is assumed that vacancies associated with Mo are the predominant sites for thiophene adsorption, it then appears that Co has affected the adsorption energetics of some of these sites while some retain their original character. Thus, the promotional effect of Co in HDS may be due to an electronic influence on the active sites, the effect increasing with Co content. This is in agreement with recent findings.

Future Work

A kinetic series of experiments will be carried out using BT-hexene mixtures to study their possible interaction. Also experiments on the poisoned and coked catalysts will be carried out to study their effect on HDS activity. The TPD and TPR experiments will be continued on aged and poisoned catalysts.

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Table 1. Hexene hydrogenation kinetic data.

$P_I \times 10^4, \text{ atm}$	$P_S \times 10^2, \text{ atm}$	$P_H, \text{ atm}$	$R_I \times 10^2, \text{ cm}^3/\text{min g}$
7.24	1.54	0.84	9.03
7.51	3.73	0.82	8.91
7.52	5.75	0.80	8.60
7.53	7.14	0.78	8.60
7.24	1.59	0.84	9.34
7.23	1.57	0.84	9.21
7.71	1.63	0.55	7.19
7.38	1.58	0.84	9.28
7.53	1.60	0.65	7.74
7.63	1.60	0.55	6.88
7.19	1.57	0.84	9.09
5.10	1.70	0.84	6.51
11.89	1.44	0.84	13.76
8.49	1.36	0.84	10.44
5.95	1.63	0.84	7.74
7.32	1.61	0.84	9.09
7.40	4.57	0.81	8.78

Table 2. Correlation of hexene hydrogenation kinetic data.

Case #	a	b	c	d	$\frac{SSQ}{DF} \times 10^6$	$k_I \times 10^2$, cc/m g at	$K_I \times 10^2$ at ⁻¹	K_S , at ⁻¹	K_H , at ⁻¹
<u>Dual Site</u> *									
1	1	1	1	1	2.17	2.62	2.18	1.23	0.58
2	1	2	1	1	2.17	2.59	0.98	0.56	0.57
3	1	2	1	0	12.25	1.82	1.12	0.58	--
4	1	1	0	1	4.49	2.53	1.90	--	0.59
5	1	2	0	1	4.50	2.51	0.88	--	0.59
<u>Single Site</u> †									
6	1	1	1		2.10	2.78	3.43	1.9	0.68
7	1	2	1		2.13	29.85	3.72	2.13	3.31

$$* R_I = \frac{k_I P_I P_H^a}{(1 + K_I P_I + K_S P_S)^b [1 + (K_H P_H)^c]^d}$$

$$† R_I = \frac{k_I P_I P_H^a}{[1 + K_I P_I + K_S P_S + (K_H P_H)^c]^b}$$

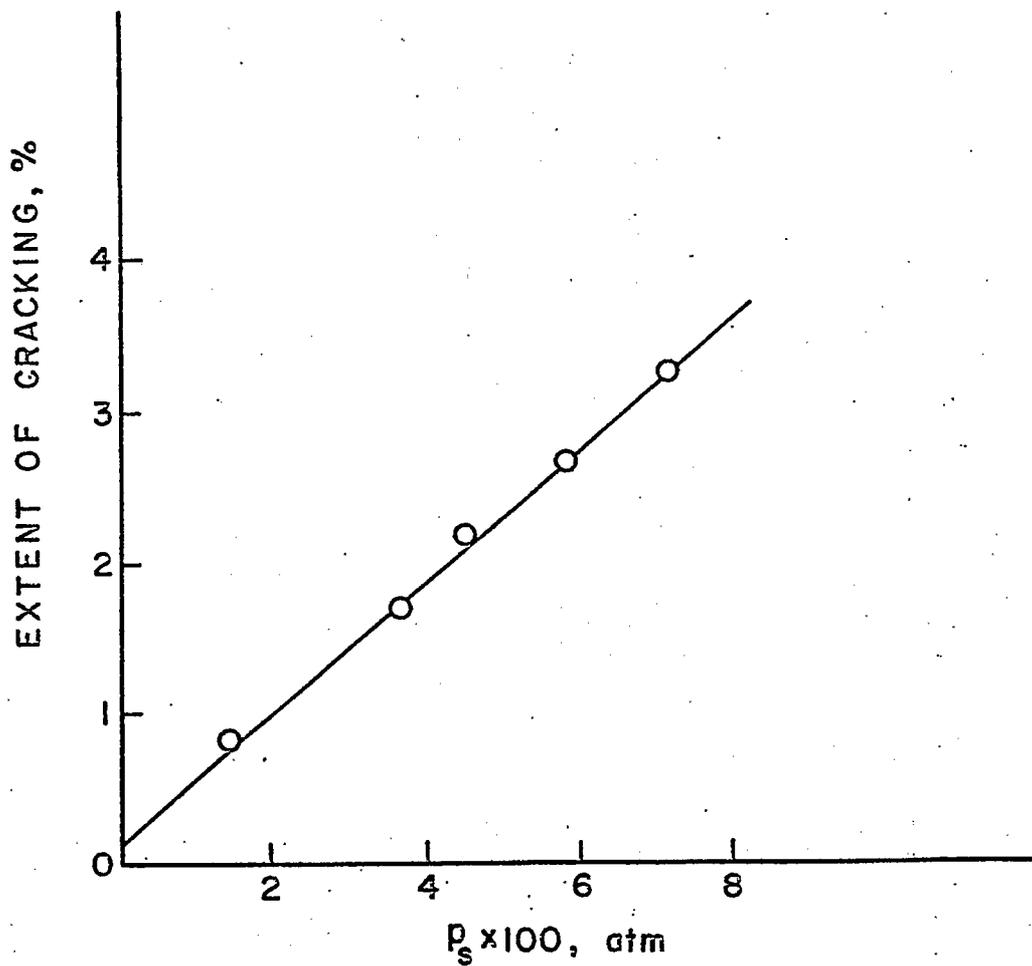


Fig. 1

Effect of Hydrogen Sulfide on Cracking Activity.

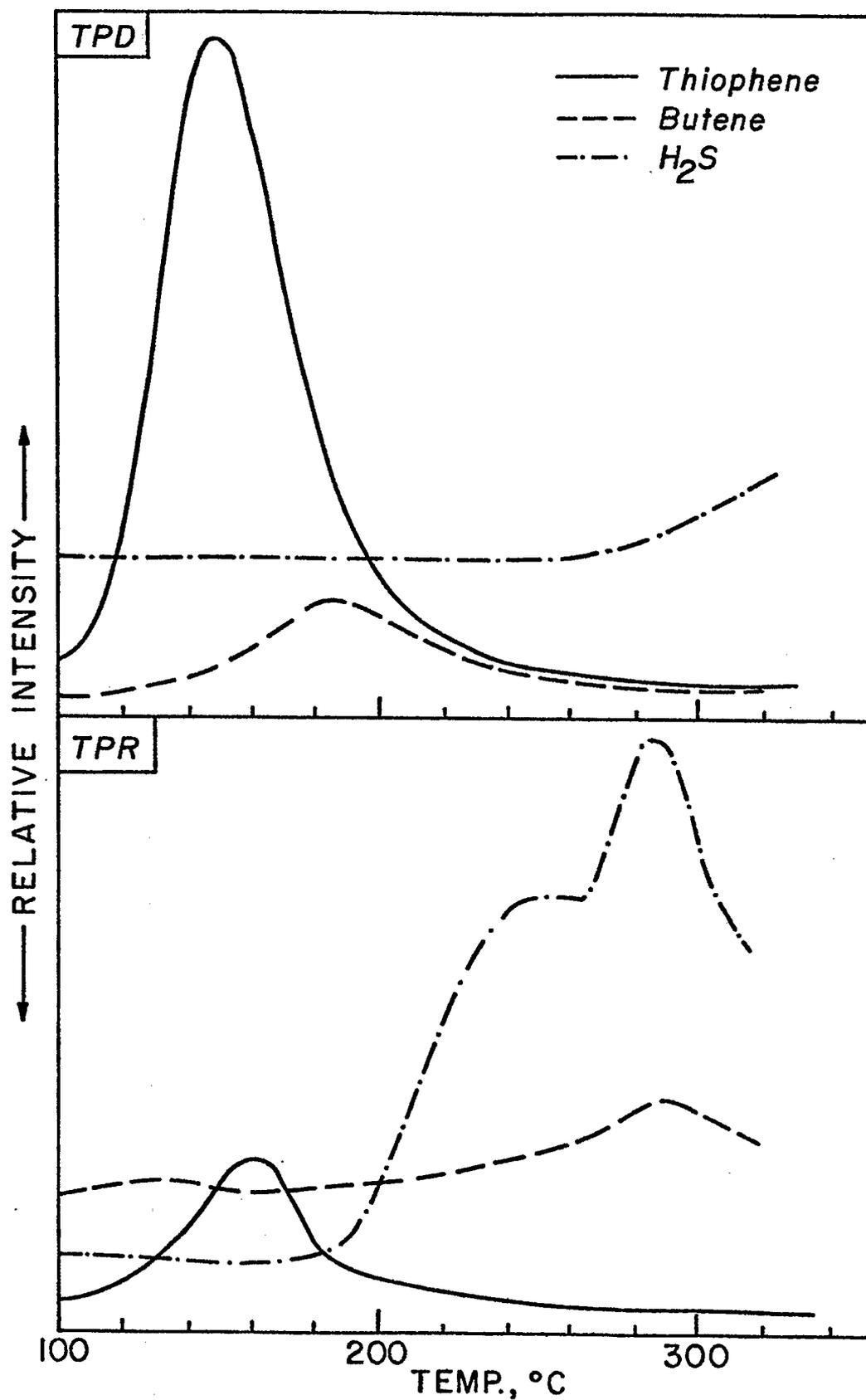


Figure 2. Fresh sulfided Mo/Al₂O₃ - thiophene adsorption

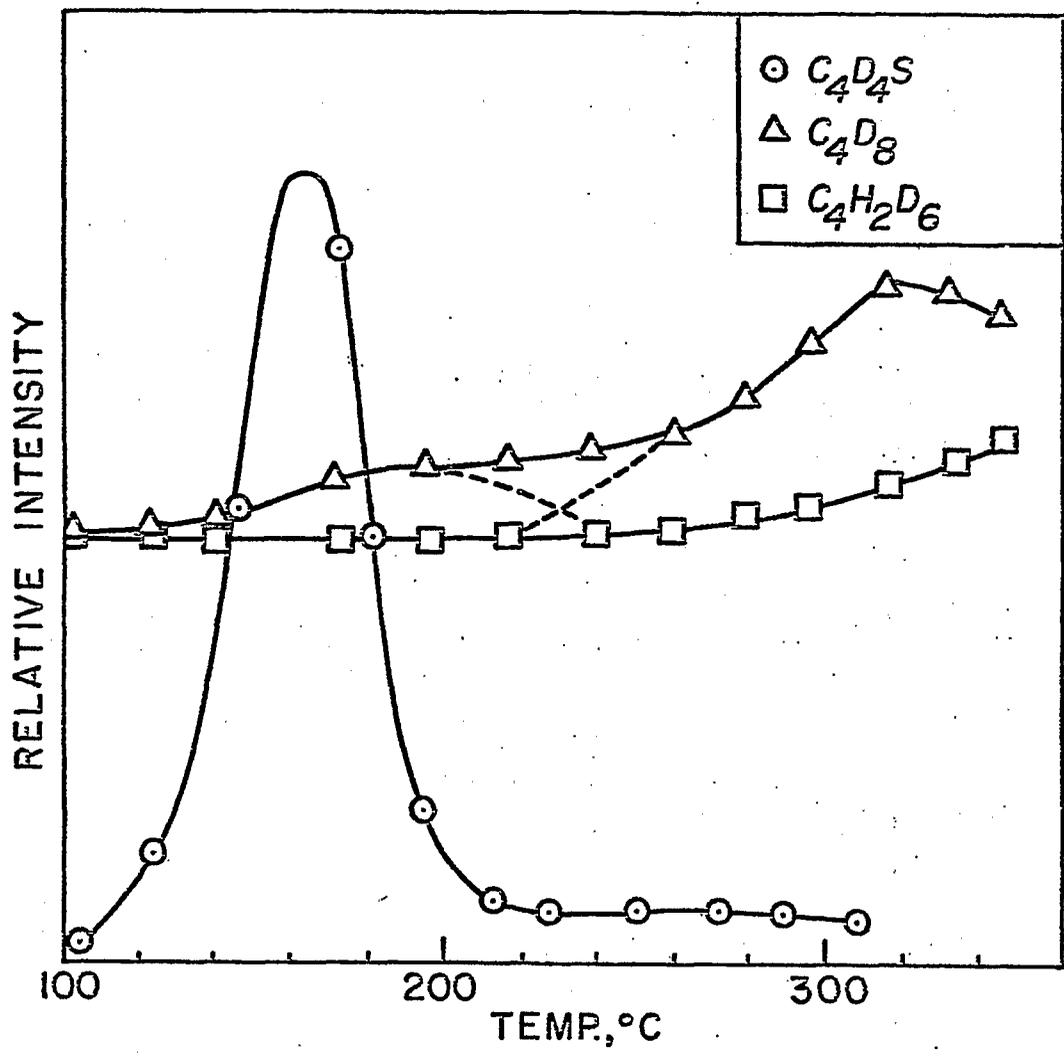


Figure 3. Sulfided Mo/Al₂O₃ - thiophene adsorption

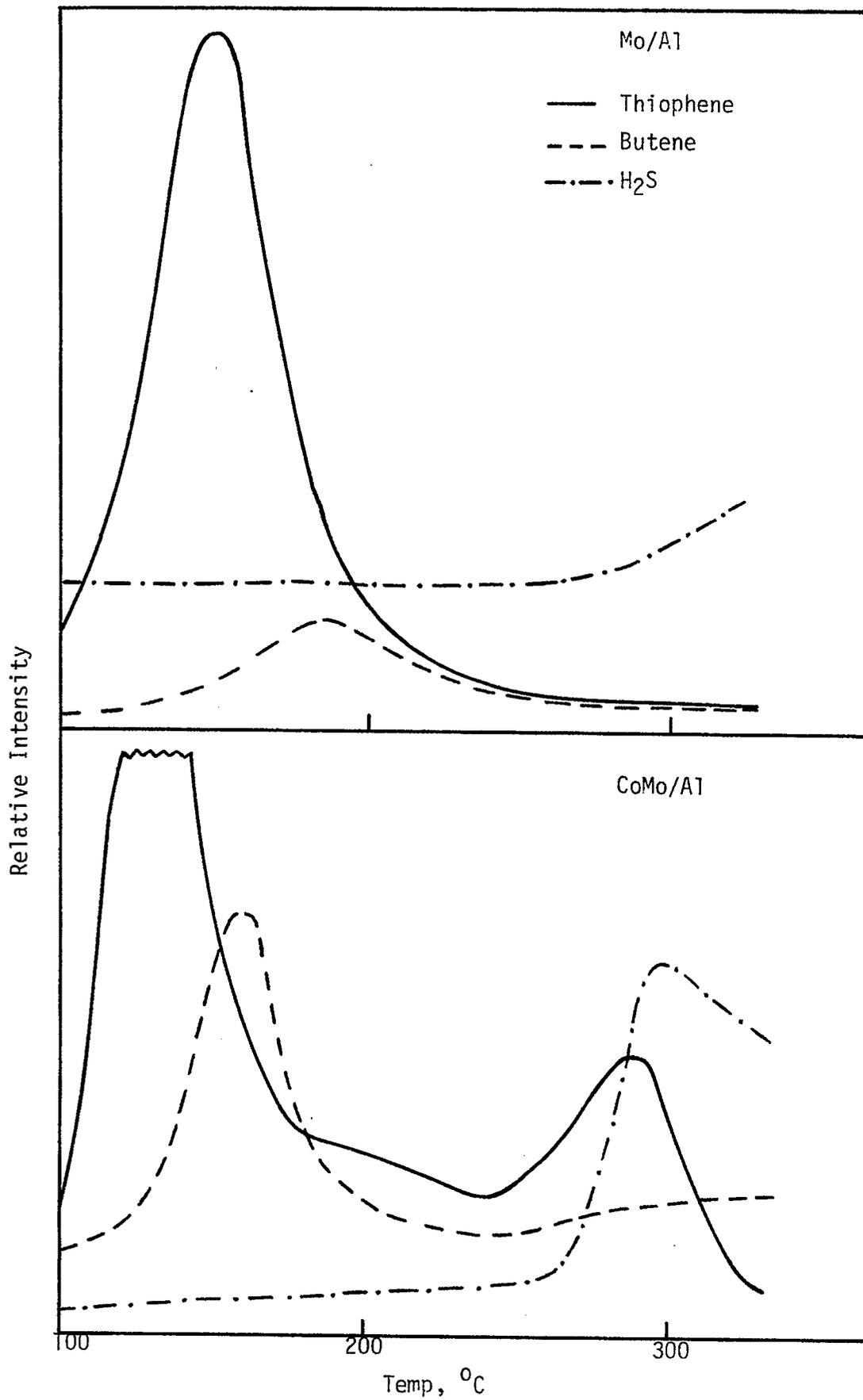


Figure 4. Sulfided Catalysts-Thiophene Adsorption-TPD.

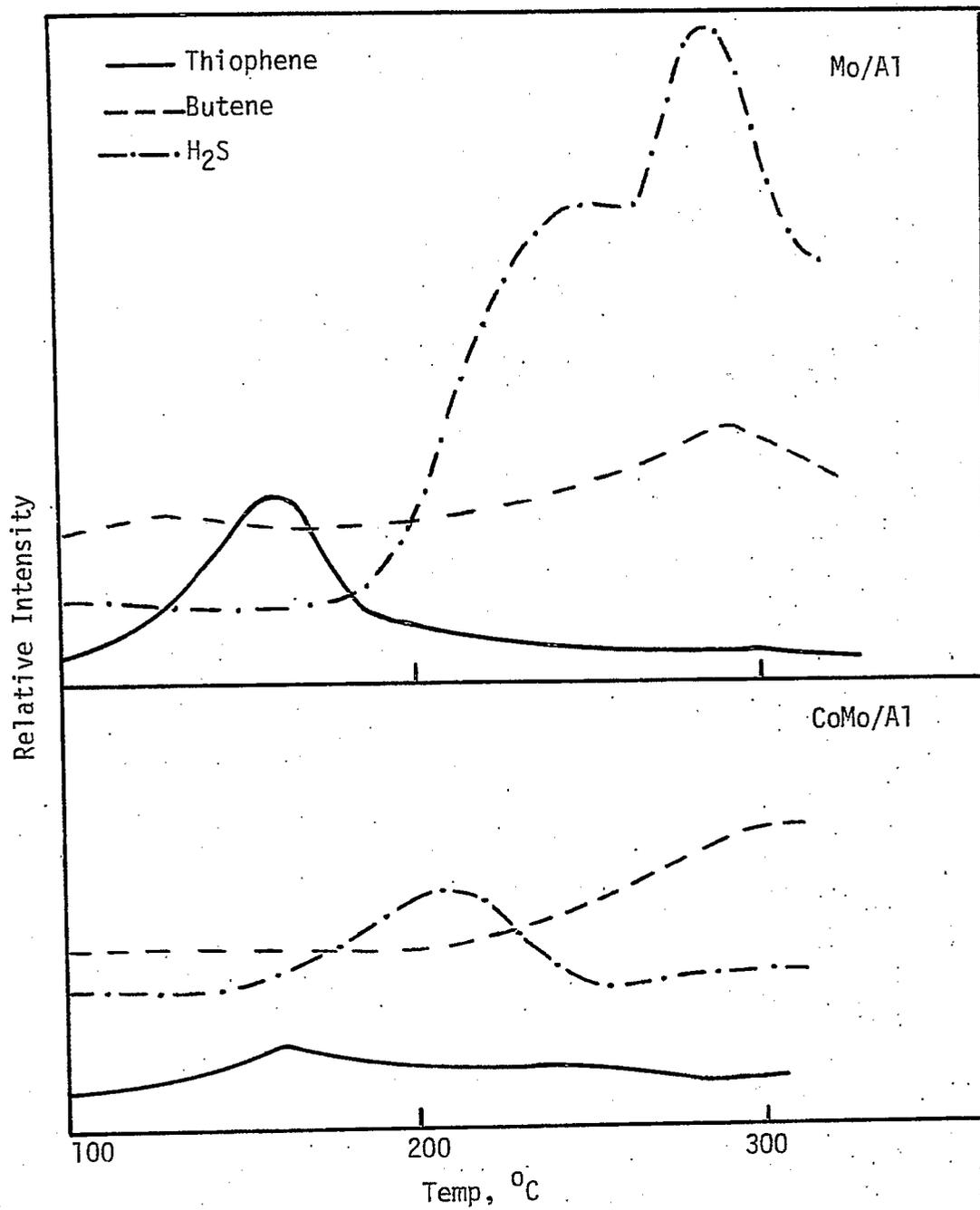


Figure 5. Sulfided Catalysts-TPR in H₂ following TP ads/des and TPD in H₂.

Diffusion of Polyaromatic Compounds in Amorphous Catalysts Supports

Faculty Advisor: F.E. Massoth
Graduate Student: A. Chantong

Introduction

This project involves assessing diffusional resistances within amorphous-type catalysts. Of primary concern is the question of whether the larger, multiring hydro-aromatics found in coal-derived liquids will have adequate accessibility to the active sites within the pores of typical processing catalysts. When molecular dimensions approach pore size diameters, the effectiveness of a particular catalyst is reduced owing to significant mass transport resistance. An extreme case occurs when molecular and pore sizes are equivalent, and pores below this size are physically inaccessible.

The project objective can be achieved through a systematic study of the effect of molecular size on sorptive diffusion rates relative to pore geometry. Conceptually, the diffusion of model aromatic compounds is carried out using a stirred batch reactor. The preferential uptake of the aromatic from the aliphatic solvent is measured using a UV spectrometer. Adsorption isotherms are determined to supplement the diffusion studies.

Initial work entailed development of a suitable reactor, measurement techniques and methods of data analysis. These demonstrated that adsorption was diffusion-controlled. Effective diffusivities were larger than predicted for pore diffusion and a surface diffusion contribution was postulated. Subsequent studies were extended to other multiaromatic compounds and aluminas with similar results. The fractional surface diffusion contribution was appreciable and about the same in all cases. Because of this, restrictive diffusion effects could not be properly evaluated. However, for the largest size compound (20Å) and smallest average pore size alumina (50 Å) tested, a markedly lower diffusivity was obtained, indicative of a restrictive diffusion effect.

Project Status

Adsorption data of naphthalene in cyclohexane with catalyst L (γ -alumina) at high concentrations are shown in Fig 1. The data show a highly nonlinear isotherm. Prasher and Ma report a linear isotherm for 1-methylnaphthalene in cyclohexane solution with alumina pellets.¹ Their data are compared with the data in Figure 1. The differences in the results obtained from the two sets of data may be explained by differences in the aluminas used. Not much difference in behavior between naphthalene and 1-methylnaphthalene would be expected.

The adsorption data at high concentration fit a Freundlich isotherm very well but not a Langmuir isotherm, as shown in Fig 2. In the low

concentration region (5-40 mg/l), the data fit both Freundlich and Langmuir isotherms. The Freundlich isotherm plot for the low concentration region is also shown in Fig 2. At about the 40-60 mg/l region, there is a discontinuity in the isotherm between the low and high concentration ranges.

The equilibrium curve for the Freundlich isotherm is represented by the following equation:

$$M_f = kC_f^{1/n}$$

where M_f is the final solute uptake in mg/cc catalyst, C_f is the final solute concentration in mg/l, and k and n are constants for a given solute and catalyst. Values of k and n are 0.212 and 1.49 in the low concentration range and 0.852 and 2.10 in the high range.

Additional diffusion runs were carried out at moderate concentrations. Results are given in Table 1, together with earlier data at low concentration. Calculated effective diffusivities are lower at the higher concentration. This apparent concentration effect may be due to the use of a linear isotherm assumption in the calculations, which is clearly not valid from the recent isotherm data obtained. A numerical solution to the diffusion equations incorporating the Freundlich isotherm is being developed.

Future Work

Additional diffusion runs will be made at other concentrations. Effective diffusivities for all runs will be redetermined using a mathematical model involving a Freundlich adsorption isotherm in an attempt to reconcile the concentration effect.

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TABLE 1

Effective diffusivities of naphthalene in cyclohexane with Catalyst L.

Final Conc. C_f (mg/l)	Final Uptake M_f (mg/cc)	Ads. Equil. Const. K (l)	$D_e \times 10^6$ (cm^2/sec)
367	13.0	35.5	3.9
345	12.9	37.4	4.9
345	12.6	35.3	3.7
10.5	1.4	137	7.7
7.5	1.0	139	7.1

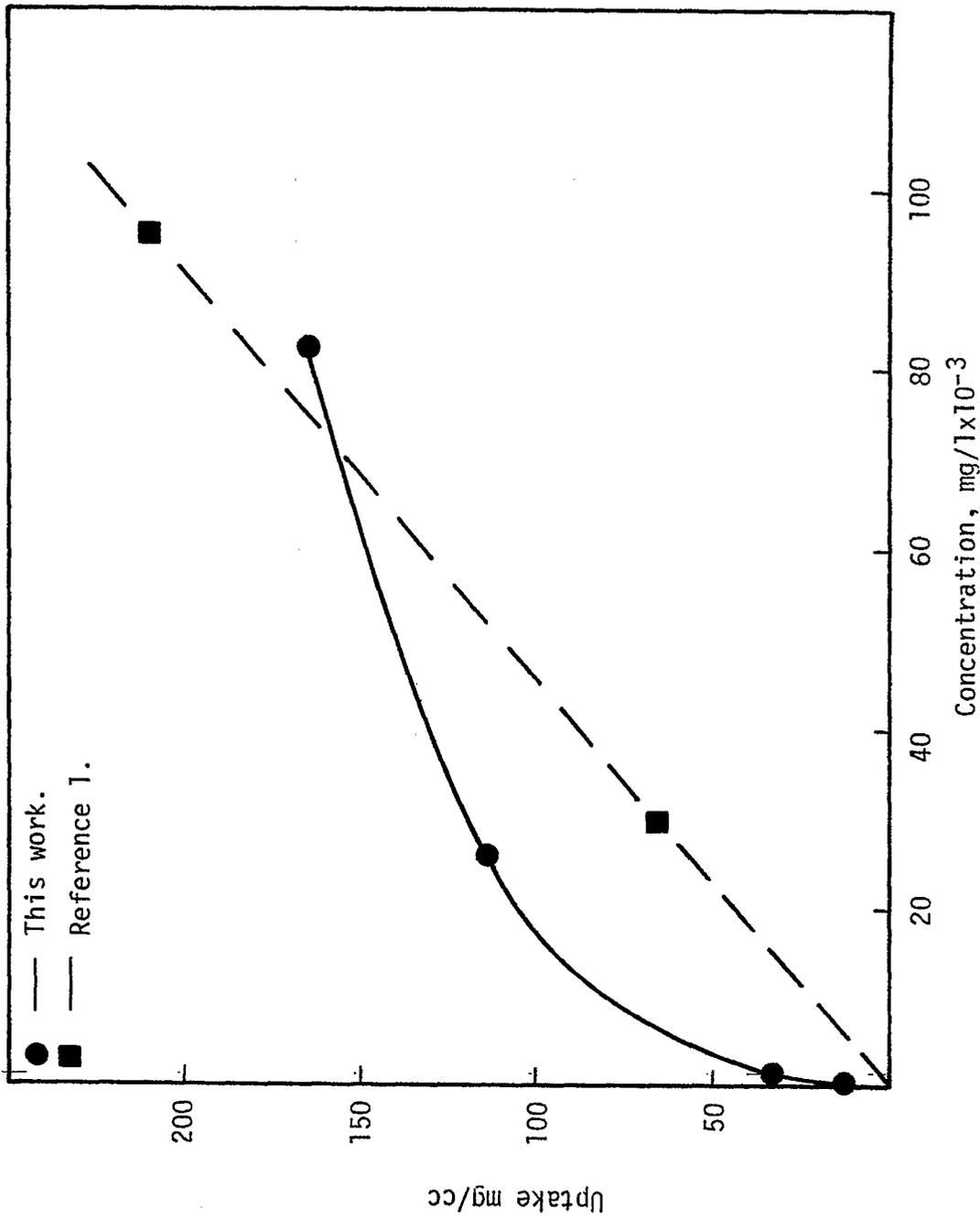


Figure 1. Adsorption Isotherm for Naphthalene in Cyclohexane with Catalyst L.

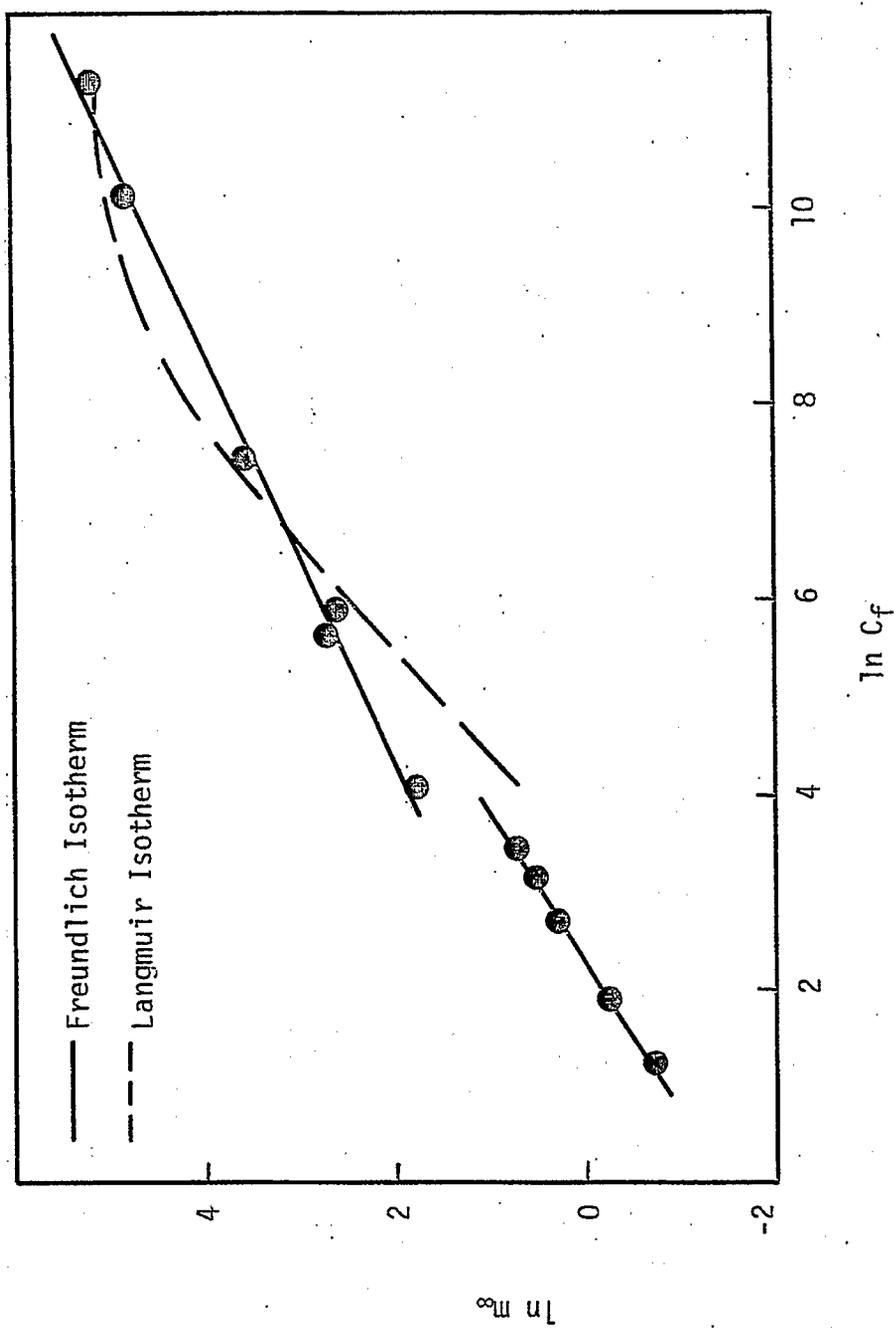


Figure 2. Freundlich Isotherm Plot for Naphthalene in Cyclohexane with Catalyst L.

Catalyst Research and Development

Faculty Advisor: A.G. Oblad
F.V. Hanson
Graduate Student: C.S. Kim

Introduction

The objectives of this project are to develop a preparation technique for a Raney type catalyst (particularly Raney iron-manganese catalyst) and to find the optimum operating process variables for the maximum production of C₂-C₁₀ hydrocarbons via hydrogenation of carbon monoxide. Previous work has shown that promoted iron catalysts particularly those promoted with manganese are very promising for the production of C₂-C₁₀ hydrocarbons. The objectives of this investigation can be subdivided as follows:

1. Preparation of Raney type catalyst of various compositions, particularly Fe-Mn catalyst.
2. Establish catalyst characterization procedures which can be correlated with yield and selectivity parameters. The characterization procedures will include atomic adsorption, X-ray diffraction, BET surface area measurement, chemisorption, TGA and surface spectroscopic analysis such as ESCA, Auger, etc.
3. Investigate the effect of fixed bed process variables such as temperature, pressure, space velocity and H₂/CO ratio on yield and selectivity.
4. Study the interactions between the major catalyst component and promoters in terms of yield and selectivity to C₂-C₁₀ products.
5. Study the overall kinetics of carbon monoxide hydrogenation process.

A fixed bed reactor system was designed and set up to find optimum operating process variables and to study the overall kinetics of hydrogenation of carbon monoxide over Raney type catalysts.

A tubular type electric furnace was designed to make Fe-Mn-Al alloys. All the necessary parts were ordered. Since the Raney type catalysts are pyrophoric when exposed to air, an apparatus for in-situ activation of Raney alloys was designed.

Project Status

As a first step to prepare a Raney type catalyst, a few attempts were made to make Fe-Al alloys according to the information reported in the literature. Equal weights of aluminum pellets and iron chips, of which diameters are about 1/8 inch and which were contained in separate crucibles, were placed in a box type electric furnace. The original door of the furnace was opened and firebricks were attached to the openings firmly to prevent intrusion of air into the hot box. A stream of argon gas was introduced into the hot box

and was allowed to flow just over the crucibles to exclude the remaining air in the furnace and to keep a positive pressure of argon gas in the hot box.

The furnace was heated to 900°C. The crucible containing the aluminum was removed from the furnace first and then the crucible containing the iron chips. Obviously the aluminum was completely melted and the iron chips were heated to bright red. The aluminum melt was poured into the crucible containing the iron and this mixture was mixed with a carbon stirring rod. The above procedure was done as quickly as possible to minimize the temperature drop and oxidation of two metals.

Although it is reported in the literature that enough heat of reaction is evolved to melt the iron and to form an alloy, there was no indication of alloy formation. The color of the surface of iron chips was changed to black from the shiny metal color of iron, which indicates an oxide film formation on the surface of iron, which in turn prevents the attack of aluminum onto the surface of iron to form an alloy. A further heating of this metal mixture to 1350°C, which is above the equilibrium temperature (1150°C) of liquid and solid aluminum-iron alloy at that composition (50/50 wt, %), did not show any alloy formation. Therefore a box type electric furnace is not adequate to make these alloys. Using an induction or arc furnace under vacuum or inert gas atmospheres may be a good choice to make the alloys, but the equipment is not available at the present time.

A tubular electric furnace was designed to make the alloys. This furnace consists of Kanthal Super 33 heating elements and a Mullite tube with one end closed. The other end of the tube will be connected to a copper sealing unit to make the tube gas tight. A vacuum or an inert gas atmosphere condition will be applied to this tube to prevent oxidation of metals.

Future Work

All the necessary parts for construction of the furnace has been ordered and will be available shortly. An apparatus for in-situ activation of Raney alloys will also be constructed. As soon as all the equipment is assembled, a Raney Fe-Mn catalyst will be made and hydrogenation of carbon monoxide will be carried out in the fixed bed reactor.

Task 14

Characterization of Catalysts and Mechanistic Studies

Faculty Advisor: F.E. Massoth
Graduate Student: K.B. Jensen

Introduction

This phase of the project is intended to supplement the high pressure reactor studies by detailed examination of the catalyst properties which enhance catalyst activity and selectivity. This is accomplished by characterization studies performed on fresh catalysts and on the same catalysts which have been run in the reactor. Of particular interest are metal areas, phase structure, catalyst stability and surface characteristics. Also, variables in catalyst preparation and pretreatment are examined to establish their effects on catalyst properties. Finally, in-situ adsorption and activity are studied under modified reaction conditions with a number of well-characterized catalysts to obtain correlating relationships.

The catalysts under present investigation are iron based catalysts promoted with manganese oxide.

Project Status

One of the characteristics of iron-based catalysts is the formation of iron carbide during Fischer-Tropsch synthesis.¹ In seeking the rôle of manganese oxide in altering the selectivity of iron catalysts, an investigation of its effect on the carburization reaction was undertaken. Initial study focused on the pure iron catalyst to provide a base case for comparison with mixed Mn-Fe catalysts. A flow microbalance was used to follow carbide formation in the presence of a CO/H₂ mixture.

Figure 1 shows a carburization-reduction cycle performed on the iron catalyst (T1). The catalyst sample was first prereduced in H₂ overnight at 500°C. The temperature was then lowered to 250°C and CO added to the H₂ flow to give a CO/H₂ ratio of about three. The sample rapidly gained weight, far exceeding monolayer coverage of CO (about 0.7%), and continued to gain weight at a slower rate. At 100 hr, the CO flow was discontinued and the subsequent weight loss monitored until an approximate approach to constant weight was achieved. Following, the catalyst was heated to 500°C in H₂, where upon the catalyst weight returned to its original reduced value. The weight loss was slow in both temperature regimes. These results show that carburization is slow under these conditions. The weight gain after 100 hr corresponds to a state between Fe₃C and Fe₂C, although some coke may also be present. Reduction in H₂ removed an appreciable portion of the weight gain, but a substantial amount remained at 250°C. The latter may be residual coke or a less-reactive carbide phase. An X-ray analysis of the sample at this point will be undertaken to clarify this issue.

The results of additional carburization runs at several temperatures are shown in Fig 2. Generally, the catalyst underwent a rapid weight pick up followed by a slow continuous gain. Attempts to linearize the data with a parabolic relationship (wt gain vs. square root time) were unsuccessful, although this form has been reported for carburization of iron catalysts under similar conditions.² However, an Elovich plot (wt gain vs. log time) gave a good fit of the data as shown in Fig 3. Two reactivity regimes are clearly indicated by the breaks in the lines, which is in qualitative agreement with previous findings.² An approximate activation energy of 3.5-4 kcal/mole from the initial slopes are also in agreement with previous work,² although the latter was derived from parabolic plots. To account for the two reaction regimes, reaction has been postulated to involve formation of a dilute iron carbide phase in iron followed by formation of iron carbide.²

The carburization run at 300°C was continued for 65 hr and the catalyst then analyzed by X-ray diffraction. The X-ray pattern was not nearly as sharp as for freshly reduced catalyst. However, the presence of at least one carbide phase was apparent; the peaks most closely matched α -Fe₂C (Hagg), although this phase did not account for all the peaks present. Hagg iron carbide is the predominant phase at carburization temperatures up to 325°C.

Future Work

Carburization studies will continue on the iron-manganese oxide catalysts.

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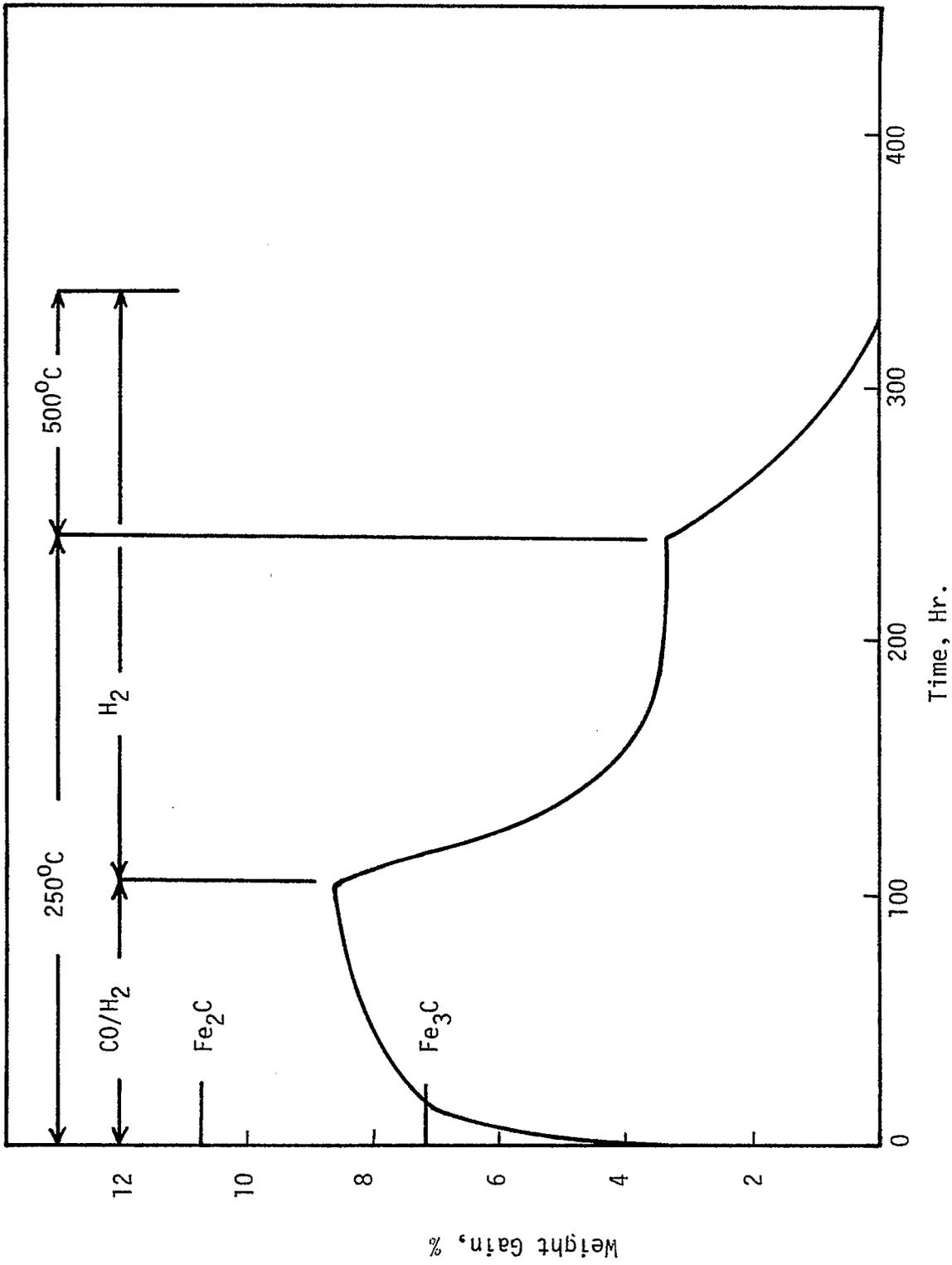


Figure 1. Carburization - Reduction Weight Profile for Iron Catalyst (T1).

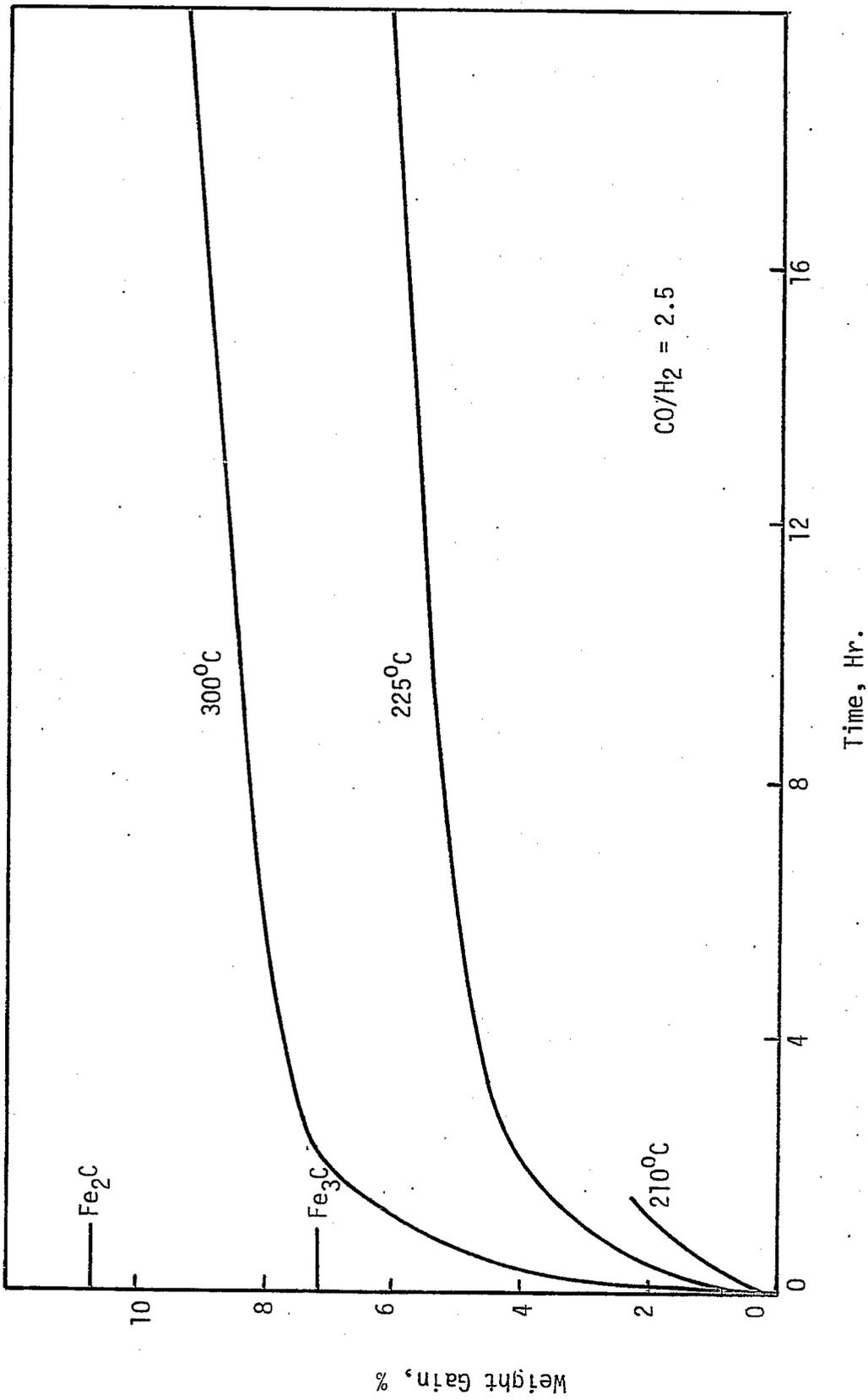


Figure 2. Carburization Weight Profiles for Iron Catalyst (TI).

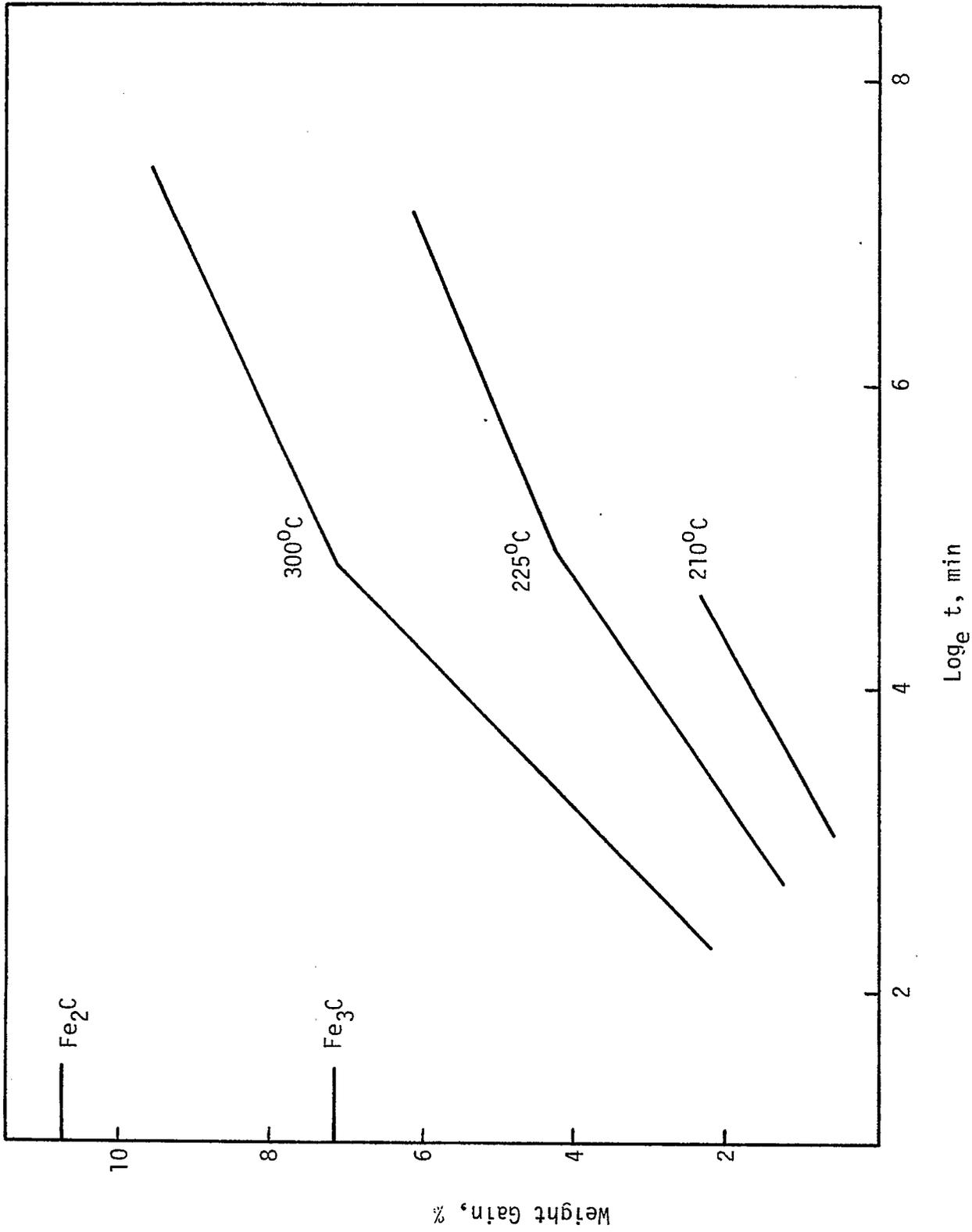


Figure 3. Elovich Plots for Carburization of Iron Catalyst (T1).

V. Conclusions

Detailed conclusions are included in the reports for each task. Task 1 is temporarily inactive, awaiting a student. Tasks 9 and 11 have not been initiated as yet. No work was done under Task 15.