APPLIED RESEARCH AND EVALUATION OF PROCESS CONCEPTS FOR LIQUEFACTION AND GASIFICATION OF WESTERN COALS. QUARTERLY PROGRESS REPORT, APRIL-JUNE 1979

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

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Applied Research and Evaluation of Process Concepts for Liquefaction and Gasification of Western Coals

Quarterly Progress Report
for the Period Apr - June 1979

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II. OBJECTIVE AND SCOPE OF WORK

The research reported herein is all of fundamental importance in support of either a process for development of liquefaction of coal, catalysis or some related research. The information which will be gained by research on this contract should materially assist the application of coal in the solution of the energy problems now facing the United States and the world. In particular, the projects reported herein are intended to apply the expertise developed by the coal research team at the University of Utah to problems in four general areas:

a) Evaluation of process concepts in relation to liquefaction and gasification of coal,
b) Catalysis studies of fundamental importance in liquefaction and gasification of coal,
c) Studies of fundamental principles involved in processes for liquefaction and gasification of coal,
d) Properties of coal and coal conversion products of significance in liquefaction and gasification of coal.

A-1 Coal will be gasified by direct catalytic hydrogenation to produce a high-BTU gas. A liquid will be produced in a first stage reaction at 400-450°C. This product will be further hydrogenated to produce a high-BTU gas. Catalysts and reaction conditions for each stage will be studied.

A-2 Kinetics, yields and optimum reaction conditions for extraction of coal will be determined. Hydrogen donor solvents, ultrasonic energy, hydrogen pressures and catalysts will be employed. Extraction products will be analyzed and characterized.

A-4 Aromatic liquids derived from coal hydrogenation or extraction will be considered as feedstocks for steam reforming to make a high-BTU gas. Optimum conditions for the production of hydrogen or high-BTU gas, optimum catalysts, the effects of poisons and the degree of coke formation will be determined.

A-6 The gasification of coal char will be studied at 2000-3000 psi to produce hydrogen for coal hydrogenation. Steam and oxygen will be used for gasification. The thermal efficiency of producing hydrogen at the pressure at which it will be used will be studied.

A-7 Thermal hydrogenolysis of coal slurried with recycle solvent will be studied as such or in the presence of a vapor-phase catalyst to determine the extent of upgrading.

A-8 Fischer-Tropsch synthesis of C_2-C_4 hydrocarbons will be studied. New catalysts will be developed and a continuous test unit for long-term catalyst testing will be constructed.

A-9 The capacity and durability of a previously developed high-pressure gas recycle pump will be increased. A goal of 3000 psi operating pressure at 500°C is desirable.

B-1 Adsorption properties and penetration of aromatic molecules on typical cracking catalysts will be determined. These properties will be used to evaluate the ability of such catalysts to crack the large molecules present in coal-derived liquids.

B-2 (alternate) The mechanism of deactivation of molybdena hydrodesulfurization catalysts by coal-derived liquids will be studied. Kinetic studies involving the model compound benzothiophene will be employed.

B-3 Hydrogen transfer by metal halide catalysts during coal hydrogenation will be studied. Deuterium labled hydrocarbons will be used to elucidate reaction mechanisms.

B-4 The mechanism of catalytic hydrogenation of coal by metal halide catalysts will be investigated. The nature of active catalyst sight will be studied. Changes in properties of the reacting coal will be determined and the nature of reaction products will be determined. Catalyst regeneration will also be studied.

C-1 The mechanism of pyrolysis of coal will be studied by the use of isotopically labled model compounds. Products of pyrolysis will be examined to determine their precursors in coal.

C-2 Fluid mechanics and heat transfer studies involving gas-solid suspensions in vertical downward cocurrent flow systems will be conducted to obtain information on the effect of these variables in the University ot Utah coal hydrogenation reactor.

D-1 The effect of coal and catalyst properties and pretreatment on the hydrogenation of western coals will be studied in the University of Utah short-residence-time, entrained-flow reactor.

D-2 The effect of coal structure on reactivity to hydrogenation, pyrolysis and dissolution will be studied. Pretreatment of the coal by specific reactions will be used to obtain samples with special structural features.

D-4 Liquid products from coal hydrogenation in the University of Utah reactor will be separated and characterized. Coal pyrolysis and hydrogenation mechanisms and model compound reactions will be studied.

Research Highlights

A reaction pathway for hydrodeoxygenation of oxygen-containing species is proposed based on studies of model compounds. Reaction pathways that can lead to coke formation and catalyst deactivation are identified.

Studies on the hydrodesulfurization of thiophene support the Kolboe mechanism.

Preasphaltenes produced at low conversions have been characterized. The heteroatom content is similar to that of the original coal and less than that of asphaltenes and oils. The carbon aromaticity is 0.6-0.7, but the molecules contain only 1-2 aromatic rings per condensed ring system.

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L. Veluswamy, J. Shabtai and A.G. Oblad, "Catalytic Hydrogenation of Coal Liquids with Sulfided Ni-Mo and Ni-W/Al$_2$O$_3$," Fuel Chem. Div., American Chemical Society, Vol. 24 No. 1, 280 (1979).

J. Shabtai, R. Sunder and A.G. Oblad, "Catalytic Cracking of Hydrotreated Coal Liquids and Related Polycyclic Naphthenes," Preprints, Petro. Chem. Div., American Chemical Society, Vol. 24, 653 (1979).

J. Shabtai and R. Lazar, "Catalytic Cracking Properties of Novel Cross-Linked Smectites," Preprints, Petro. Chem. Div., American Chemical Society, Vol. 24, 622 (1979).

Project A-1

Catalytic Gasification of Coal to High BTU Gas

Single Stage Coal Gasification

Faculty Advisor: Wendell H. Wiser
Graduate Student: Ted J. Ajax

Introduction

Single stage catalytic coal gasification has attracted
a great deal of interest as a direct method of producing
high BTU synthetic gas from coal. This process involves
the introduction of a coal-solvent slurry and hydrogen into
a single fixed bed catalytic reactor to produce a combustible
gas containing high yields of methane. Thermodynamic cal-
culations show this process to be essentially autothermal,
which offers significant energy savings over a similar multi-
stage approach.

The primary objective of this research is to optimize the
process variables for the reactions involved and to develop
suitable catalysts for the process. These catalysts must
have both hydrogenation and cracking activity to produce high
yields of methane from the feed coal slurry. The -200 mesh
coal is slurried in a hydrogen donor solvent, tetralin, and
a ratio of 2 parts solvent to one part coal is employed.
Previous work utilized a solvent to coal ratio of 4 to 1.

The process conditions have been tentatively set as

temperature $400 - 550^{\circ}C$

pressure ~ 1500 psi

residence time $10 - 30$ min

Initially, $Ni-Mo/SiO_2-Al_2O_3$ and $Ni-W/SiO_2-Al_2O_3$ catalysts
will be used.

Project Status

A new reactor and feed system is being designed. This system,
constructed of 316 stainless steel, will be more versatile than
the previous version to accommodate the 2:1 solvent-coal slurry
as well as operate at higher pressure. A special slurry pump
has been ordered. A schematic of the single stage catalytic
coal gasification apparatus was shown in the previous report.

Nickel-tungsten and nickel-molybdenum catalysts supported
on silica-alumina have been ordered. These catalysts will be
one of the focal points of this research.

Future Work

The apparatus will be assembled as the necessary equipment arrives. Several pressure testing and shakedown runs will then be made.

Project A-2

Dissolution of Coal in Hydrogen Donor Solvents
with Application of Catalysts and
Energized Conditions to Produce Clean Fuels

Solvent Treatment of Coal-Derived Liquids (CDL)

Faculty Advisor: L.L. Anderson
Graduate Student: Kwang Eun Chung

Introduction

The objective of this investigation is to separate CDL
into chemically different fractions of potential commerical
value. Major developments have included (1) the isolation
of paraffinic material, (2) the separation of CDL into highly
H-bonded and less H-bonded fractions, (3) the observation of
free -OH bonds in the infrared spectra of CDL fractions in
dilute solutions, (4) a new activity expression in liquid
solutions, (5) a new procedure for molecular weight deter-
mination by vapor phase osmometry and (6) a characterization
scheme for CDL. The data from the characterization work are
being further examined to relate these to the structure of
coal and its liquefaction behavior.

Project Status

Experimental work has included testing of an acetylation
method for hydroxyl group determination and reproducing results
on the solubilization of coal. The acetylation method was
not reproducible with coal and its solubilization products as
reported by Ruberto and Cronauer.[1]

More solubilization experiments were carried out to
reproduce and refine previous results. One run was performed
at 320°C, and two were made at 300°C. In NMR analysis, dioxane
was used as an internal standard to correct the residual
protons in the solvent, pyridine-D_5. Some of the previous
data were refined through the correction of a simple arithmetic
error and the better handling of the residual protons in
pyridine-D_s. Data from the 300°C experiments provided additional
support for the previous interpretations. Other interesting
features of coal structure were also determined based on the
structural parameters of the liquid products. A summary of
these findings has been submitted and will be presented at the
September American Chemical Society Meeting, Division of Fuel
Chemistry, in Washington, D.C., 1979.[2] Also a paper on a new
procedure for molecular weight determination by vapor phase
osmometry has been accepted for publication in Fuel.[3]

Future Work

Experimental work is completed, and a final report is in
preparation.

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2. K.E. Chung, L.L. Anderson and W.H. Wiser, Preprints, American Chemical Society, Fuel Chemistry Div., Washington, D.C., Sept 1979, Vol. 24, No. 3, pp 243-250.

3. K.E. Chung, L.L. Anderson and W.H. Wiser, Fuel, in press.

Project A-7

The Study of Thermal and Vapor Phase Catalytic Upgrading of Coal Liquids

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

Faculty Advisors: J. Shabtai
and A.G. Oblad
Graduate Student: G. Haider

Introduction

Coal-derived liquids are characterized by a high proportion of oxygen-containing compounds. Therefore, a systematic catalytic hydrodeoxygenation (HDO) study of coal-derived liquids 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 liquids, but also on the role of oxygen-containing compounds in the primary coal liquefaction process.

Project Status

The detailed HDO study of isochroman (1; ⬡O⬡) was continued. The change in product composition as a function of experimental conditions, e.g., catalyst type, reaction temperature and reaction time, was investigated.

Figures 1 and 2 summarize the change in product composition from HDO of compound 1 as a function of temperature, using sulfided Ni-W/Al$_2$O$_3$ and sulfided Co-Mo/Al$_2$O$_3$ catalysts, respectively. The Ni-W/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$ catalyst precursors used were Sphericat 550 (1/16") and Nalcomo 471 (1/32"), respectively; both were supplied by Nalco Chemical Co.

As seen from Figure 1 the main products from 1 at temperatures below 170°C are the dibenzyl ether 2 and the alcohols 3 and 4. Extrapolation to temperatures below 170°C indicates that the main product under such conditions is ether 2. With a gradual increase in temperature above 170°C, there is a gradual decrease in the concentration of 2, while the concentration of 3 and 4 sharply increases. After reaching a maximum of ca. 70 mole % at a temperature near 230°C, the concentration of alcohols 3 and 4 decreases at a higher temperature, while that of the final deoxygenated product, i.e., methylethylbenzene (5) correspondingly increases. At this higher temperature range (230-290°C), there is also formation of some of the unsaturated alcohols 6 and 7. Similar trends are also observed

with a sulfided Co-Mo/Al$_2$O$_3$ catalyst (Figure 2), although there are also some significant differences. In particular, a markedly lower rate of hydrodeoxygenation with the Co-Mo catalyst is observed, as reflected in the much lower extent of formation of the final product 5 at temperatures above 230°C. Further, there is only a negligible extent of formation of 6 and 7, apparently due to the lower acidity of the sulfided Co-Mo/Al$_2$O$_3$ catalyst. However, the lower hydrodeoxygenation activity of the latter catalyst may also be due to faster poisoning by some of the intermediate oxygen-containing products.

Figure 3 shows the change in product composition from HDO of 1 as a function of reaction time, at a temperature of 290°C, keeping a constant pressure of 1550 psig and using the sulfided Ni-W/Al$_2$O$_3$ catalyst.

The change in product distribution in Figure 3 shows that the concentration of 3 and 4 first increases with time and then, after a period of 5 min gradually decreases, while the concentration of the final product 5 first decreases and then (after a period of about 5 min) gradually increases. This behavior is obviously due to the instability and apparent over-activity of the fresh catalyst. After formation of some water by hydrodeoxygenation, the catalyst is quickly stabilized, and at reaction times longer than 5 min, the change in composition follows the anticipated pattern, viz., gradual decrease in the concentration of the intermediate alcohols 3 and 4, and corresponding gradual increase in the concentration of the final HDO product 5. At the relatively high temperature employed (290°C), the extent of the competing formation of ether 2 is lower than that of forming 3 and 4.

The results in Figures 1-3 can be rationalized by considering the mechanism outlined in Figure 4. In the first reaction step the isochroman (1) could form a surface alkoxide intermediate by chemisorption and associated cleavage of the heterocyclic ring. Subsequent reaction of such alkoxide species could involve either protonation to yield alcohols 3 and 4 or etherification, viz., interaction of two chemisorbed species, to yield compound 2. At low temperatures the protonic acidity of the sulfided catalyst is low and, consequently, protonation of the postulated alkoxide species to yield alcohols 3 and 4 proceed at a lower rate, as compared with the etherification reaction which can easily proceed by a concerted mechanism. On the other hand, at higher temperatures protonation of the alkoxide species is fast, resulting in preferential formation of 3 and 4. Formation of ether intermediates in HDO of alcohols over sulfided catalysts has been indicated in some previous studies.[1-3]

In the present case the indicated preferred pathway of deoxygenation in the range of 200-290°C involves hydrogenolysis of the intermediate alcohols 3 and 4. However, at temperatures below 200° C hydrogenolysis of the ether intermediate 2 becomes competitive. Formation of methylstyrenes (9) via hydrogenolysis

of the unsaturated alcohols 6 and 7 also contributes to the overall HDO process. Indeed formation of methylstyrenes (9) as indicated above, or by dehydration of 4, may be responsible for the gradual deactivation of the sulfided catalyst, since such reactive monomers can be expected to undergo fast polymerization (coking) under the experimental conditions. The systematic study of 1, therefore, indicates for the first time certain reaction pathways by which oxygen-containing compounds may produce reactive poison precursors leading to coke formation in conventional sulfided catalysts.

Identification of products from HDO of isochroman (1) was carried out by gas chromatography/mass spectrometry and by comparison with reference samples. Typical gas chromatograms of products from HDO of isochroman (1) are shown in Figures 5 and 6. The column used consisted of 3% Dexsil 410 on Anakrom Q 90/100. Quantitative analyses were carried out with the same column.

Future Work

Systematic HDO studies are being presently carried out with condensed polycyclic ketones as feedstocks.

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3. O. Weisser, S. Landa, K. Pecka, Chem. Tech. (Berlin), 16, 463 (1964).

Figure 1. Change in Composition of Liquid Product From Hydrodeoxygenation of Isochroman as a Function of Temperature (Pressure:1550 psig; Reaction Time: 30 min; Catalyst: sulfided $Ni-W/Al_2O_3$).

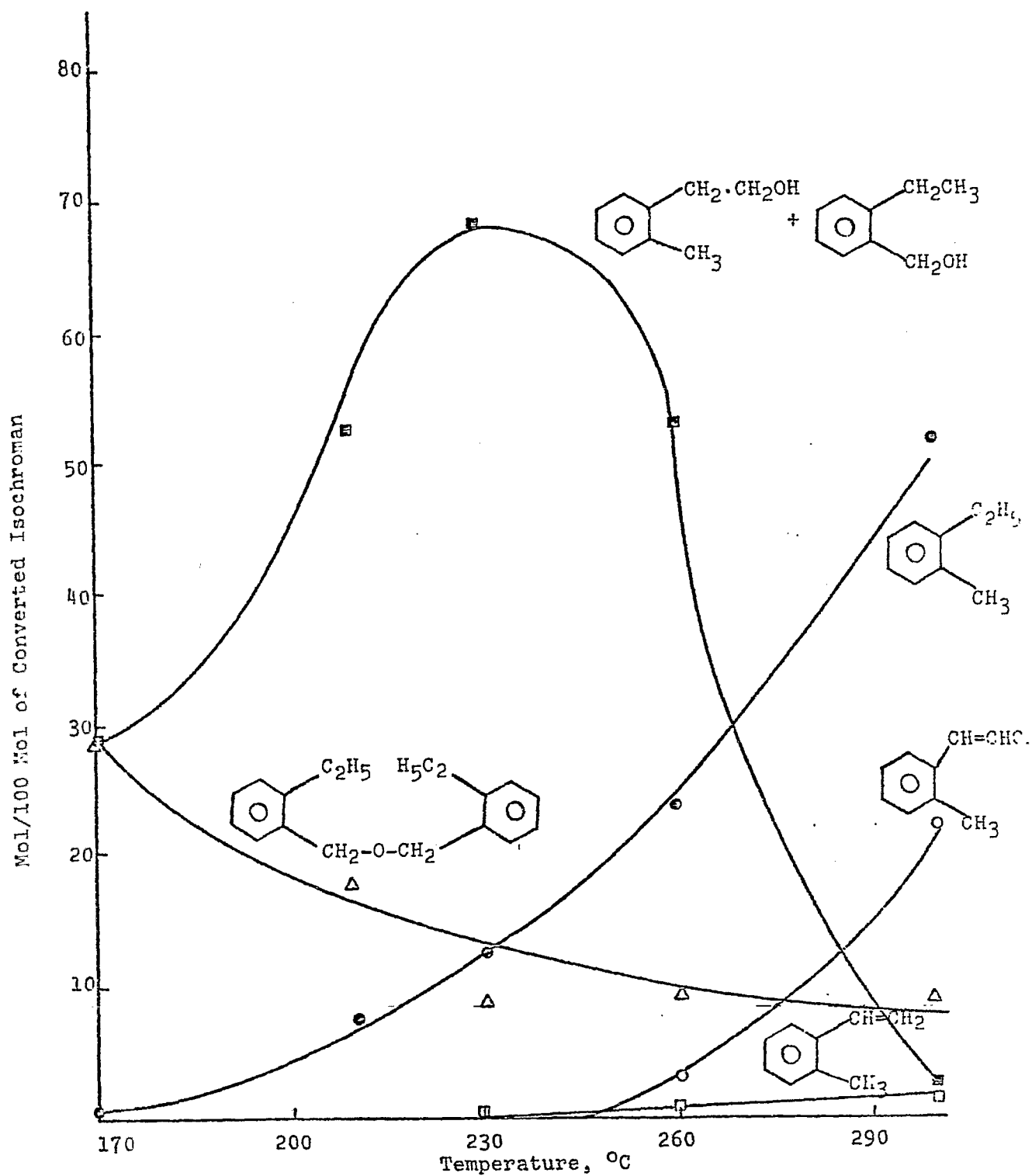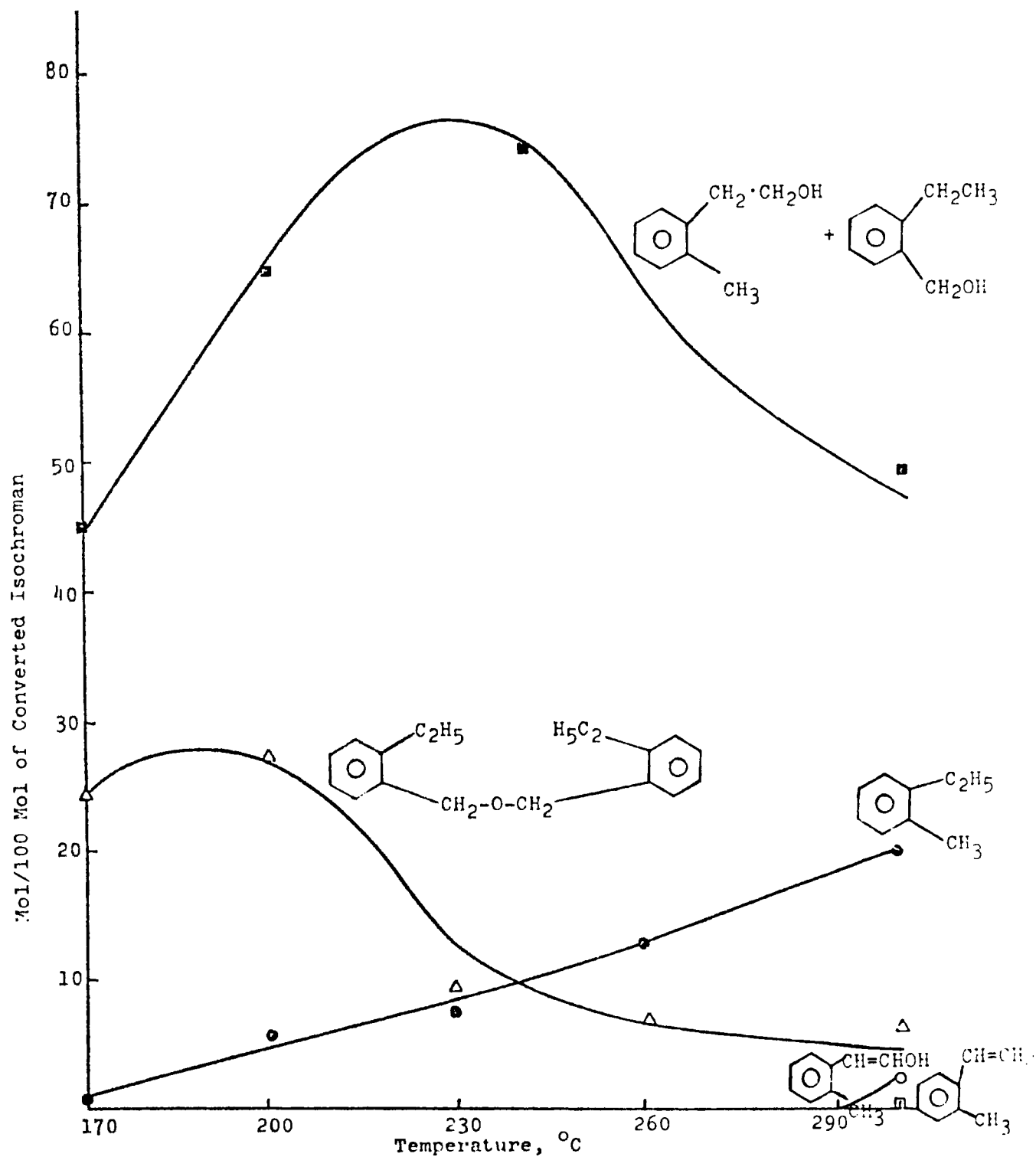Figure 2. Change in Composition of Liquid Product From Hydrodeoxygenation of Isochroman as a Function of Temperature (Pressure: 1550 psig; Reaction Time: 30 min; Catalyst: Sulfided Co-Mo/Al$_2$O$_3$).
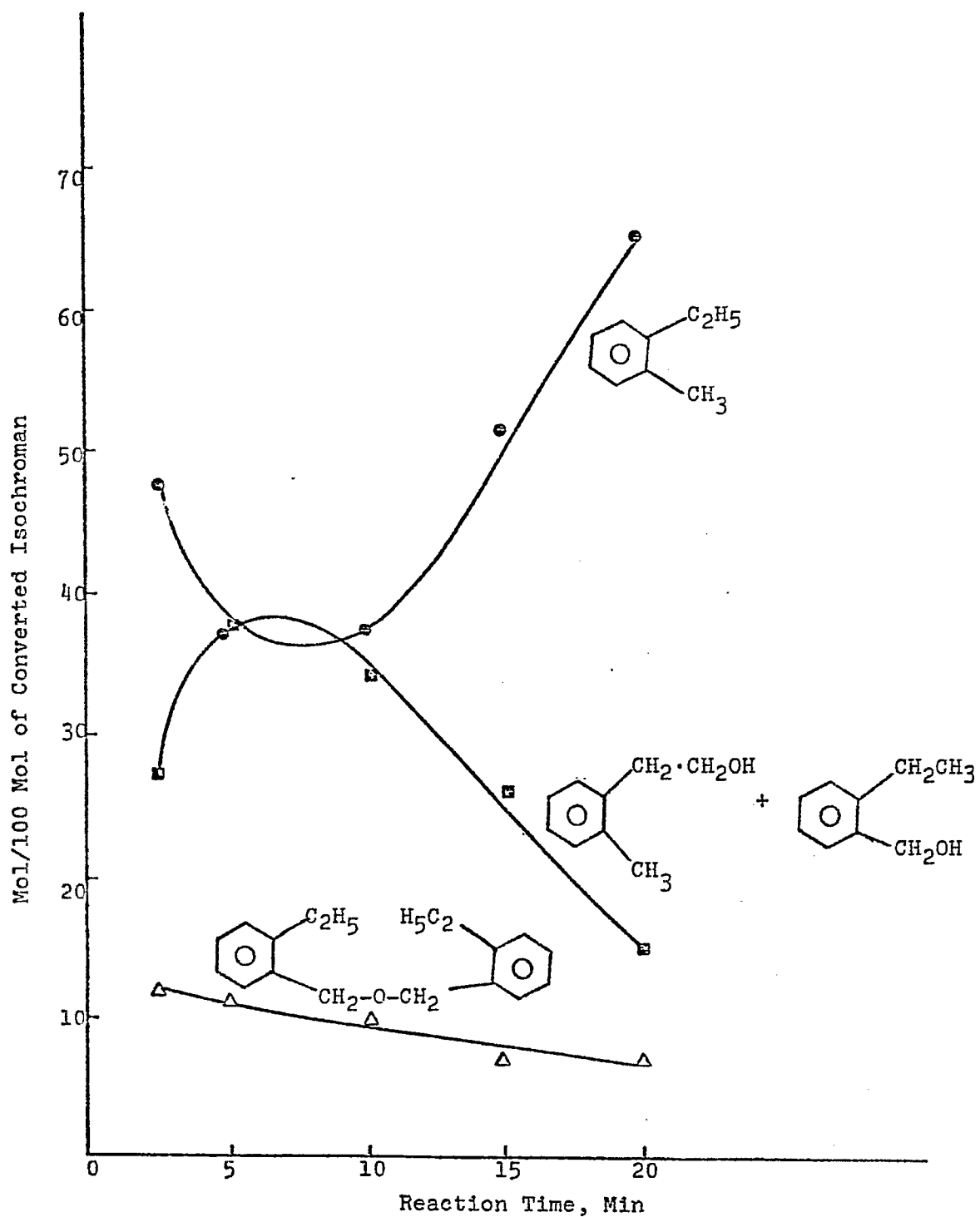
Figure 3. Change in Composition of the Liquid Product From Hydrodeoxygenation of Isochroman as a Function of Reaction Time (Pressure: 1550 psig; Temperature: 290°C; Catalyst: Sulfided Ni-W/Al$_2$O$_3$).

1) Chemisorption
2) Etherification
   (2 moles of 1)

CH_2CH_3 H_3CH_2C

CH_2-O-CH_2

2

$CH_2 \cdot CH_3$

CH_2OH

3

$CH_2 \cdot CH_2OH$

CH_3

4

1

[2H]

[2H]

$CH_2 \cdot CH_3$

CH_3

(Plus m and
p isomers)

5

(-H_2)

8

$CH=CHOH$

Cis & Trans
(Plus m & p isomers)

6

[2H]

$CH=CH_2$

CH_2OH (Plus m and
              p isomers)

7

$CH=CH_2$

CH_3

9

Figure 4.   Suggested Mechanism of Isochroman Hydrodeoxygenation.

Figure 5. Typical Gas Chromatogram of Liquid Products From Hydrodeoxygenation of Isochroman.

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Figure 6.   Typical Gas Chromatogram of Liquid Products From Hydrodeoxygenation of Isochroman.

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Project A-7

Study of Thermal and Vapor Phase Catalytic Upgrading
to Coal Liquids

Hydrogenation of Coal-Derived Liquids and Related
Model Polycyclic Arenes in the Presence of Sulfided
Catalysts

Faculty Advisor: J. Shabtai
Postdoctoral Fellow: Chris Russell
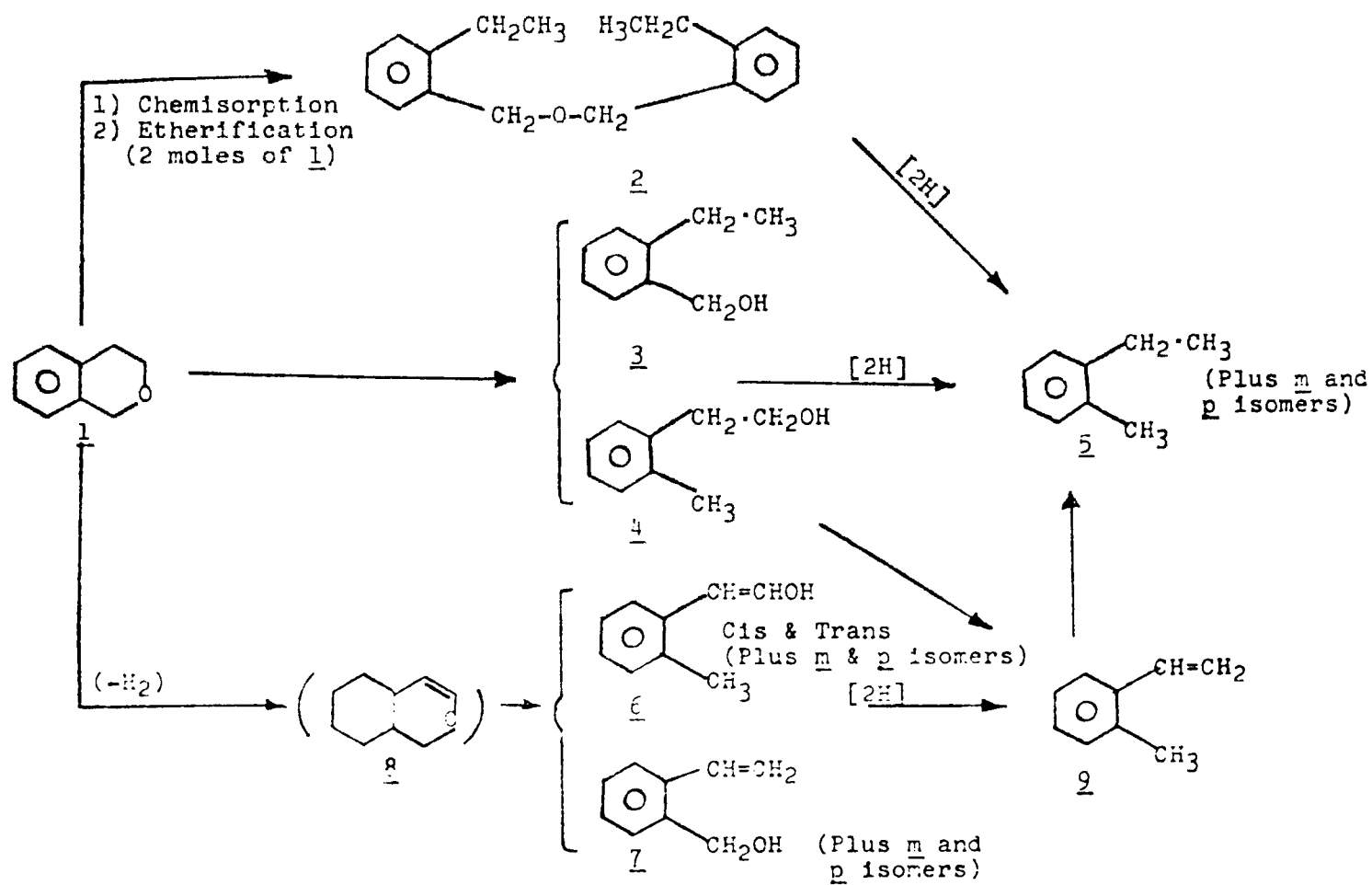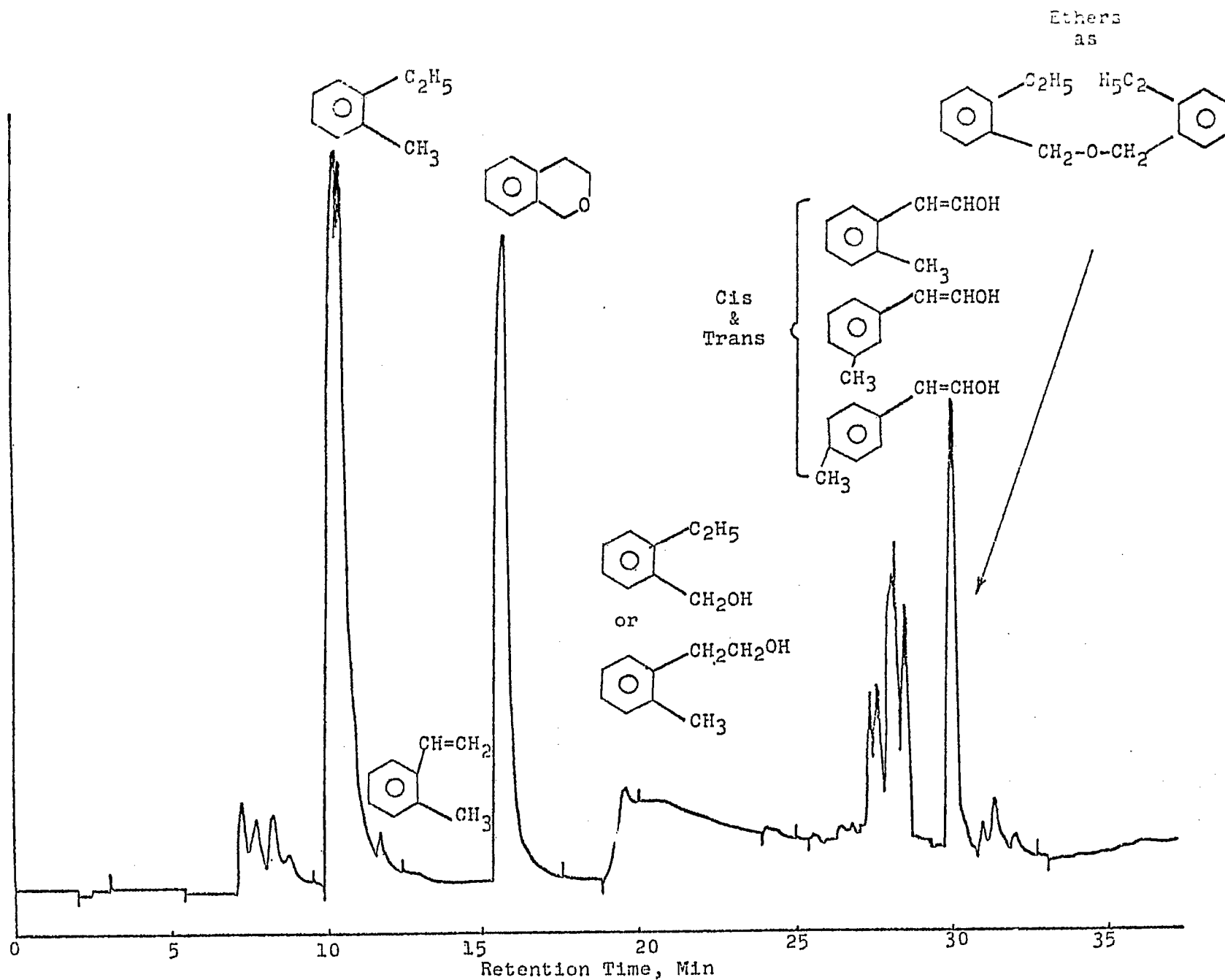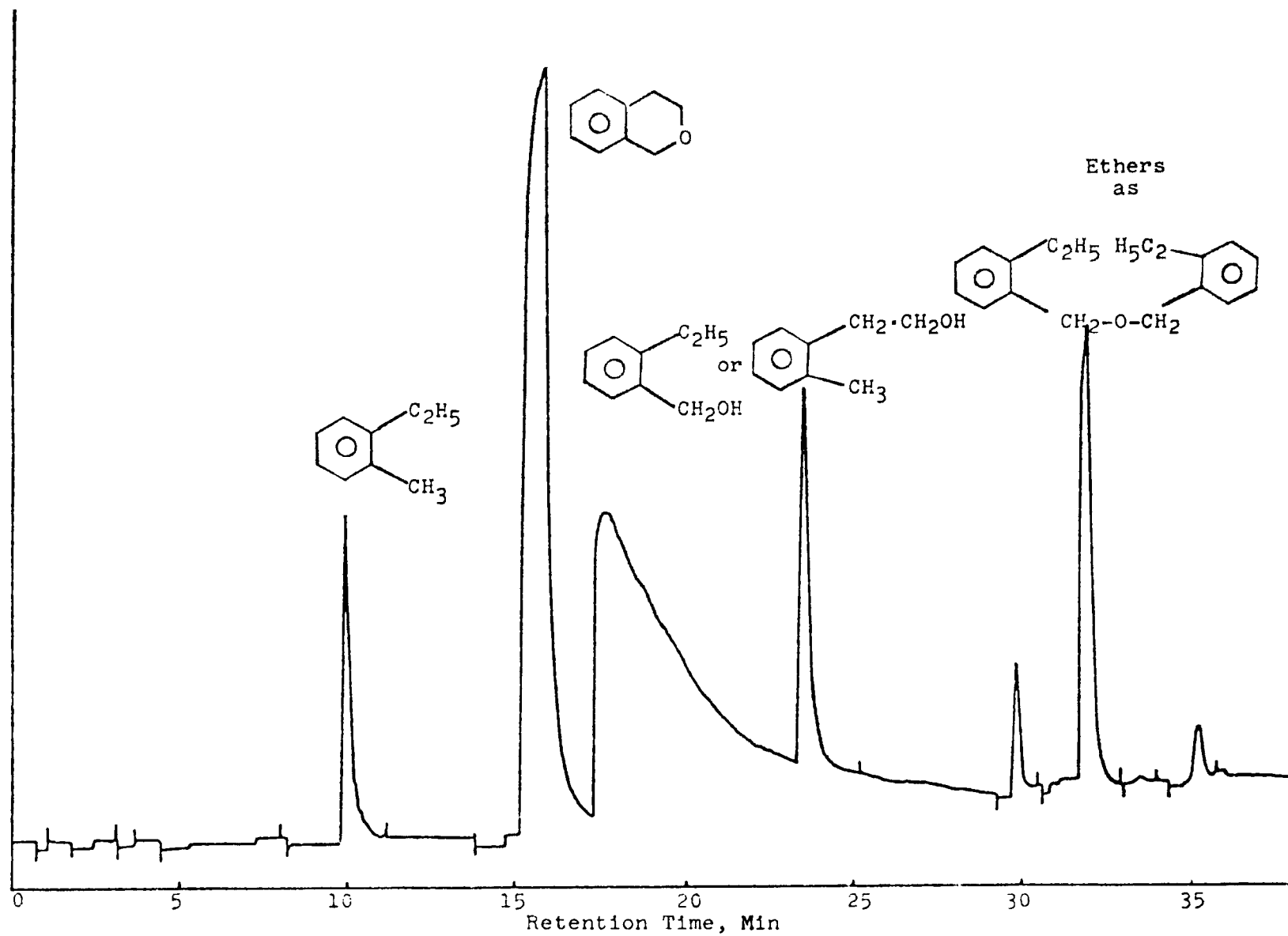
Introduction

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 rela-
tive 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.[1,2] 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.

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 is concerned with the hydrogenation
reactions of anthracene ($\underline{1}$) over a sulfided Ni-W/Al$_2$O$_3$ catalyst.
Hydrogenation experiments were carried out in an autoclave
system described elsewhere.[3-5] The experimental procedure
adopted by Veluswamy was used in this work as well.[3-5] Hydro-
genation products were identified by a combination of gas
chromatography, mass spectrometry and comparison with pure
reference compounds.

With anthracene ($\underline{1}$) as feedstock, changes in product
composition as a function of temperature and pressure were
investigated. Results on product composition changes in the
range of 200-380°C (at 2900 psig) are given in Figures 1A and
1B.

As seen from Figure 1A, the main hydrogenation product from 1 at low temperature is 9,10-dihydroanthracene (2). This primary product is accompanied by smaller amounts of 1,2,3,4-tetrahydroanthracene (3), the anticipated alternative first-step product. With an increase in temperature from 200° to 350°C, there is a sharp decrease in the concentration of 2, while the concentration of compound 3 first slightly increases and, after passing through a maximum around 300°C, quickly decreases at higher temperature. Parallel to this there is a rapid build up in the concentration of 1,2,3,4,5,6, 7,8-octahydroanthracene (4). After reaching a maximum around 325°C, the concentration of compound 4 slowly decreases at higher temperatures, while the concentration of the final hydrogenation product, viz., perhydroanthracene, slowly increases (Figure 1B). The change in concentration of 1,2,3,4, 9,10,11,12-octahydroanthracene (5), which is formed in markedly lower amounts as compared with the symmetric isomer 4, indicates that this intermediate compound also participates to some extent to the overall hydrogenation process.

To examine the possibility that the first-step intermediate 2 serves as a precursor of 1,2,3,4-tetrahydroanthracene (3), a comparative series of experiments, with 2 as feedstock, were also carried out. Results obtained showed that 2 is hydrogenated at a higher rate as compared with anthracene (1) under identical experimental conditions. Further, the fast increase in the concentration of the sym-octahydro derivative 4 with temperature, was consistent with a fast hydrogenation-rearrangement step of 2 into 3, which precedes the hydrogenation of 3 to 4. Results obtained indeed provide evidence that the rate at which the 9,10-dihydroanthracene (2) converts to 1,2,3,4-tetrahydroanthracene (3) is faster than the rate at which compound 3 converts to the sym-octahydroanthracene (4). Between 300°C and 325°C, compound 4 increases sharply while 1,2,3,4-tetrahydroanthracene (3) decreases sharply. This suggests that the sym-octahydroanthracene (4) is formed entirely from 3 as an intermediate.

At higher temperatures (Figure 1B), the sym-octahydro-anthracene (4) slowly decreases while the perhydroanthracene increases and the unsymmetric-octahydroanthracene remains essentially unchanged. This suggests that hydrogenation of the unsymmetric-octahydroanthracene (5) to perhydroanthracene is even slower than hydrogenation of sym-octahydroanthracene (4) to perhydroanthracene. Under these same conditions, Veluswamy obtained almost 100% perhydrophenanthrene from the hydrogenation of phenanthrene.[3-5] This shows that the hydrogenation of sym-octahydrophenanthrene to perhydrophenanthrene is much faster than the hydrogenation of sym-octahydroanthracene to perhydro-phenanthrene over the sulfided Ni-W catalyst used. This information is very important, since it indicates that in linear polycyclic naphthenoaromatic components of coal liquids, any aromatic ring flanked by two naphthenic rings (as in compound 4) may show considerable resistance to hydrogenation.

The change in composition of hydrogenation products from 1 as a function of hydrogen pressure in the range of 250 to 3000 psi (temperature, 341°C) is summarized in Figures 2A and 2B. The patterns are generally consistent with those in the study of the temperature effect, although the above mentioned slow rate of hydrogenation of 4 into perhydroanthracene is more clearly seen (Figure 2B).

The data in Figures 1A and 1B indicate that the sulfided Ni-W/Al$_2$O$_3$ catalysts causes some skeletal isomerization of sym-octahydroanthracene (4) or its precursors into hydrogenated phenanthrene derivatives. This was confirmed when sym-octahydroanthracene was reacted at 300°C over the same catalyst under a nitrogen atmosphere, P=600 psig, for 2 hours. The ratio of sym-octahydrophenanthrene to sym-octahydroanthracene in the product was 0.3.

The results obtained in the hydrogenation study of 1 can be rationalized by a mechanism as outlined in Figure 3. Kinetic studies are presently underway to confirm this mechanism.


Future Work

An autoclave has been modified allowing determination of kinetic rate constants for hydrogenation of coal liquids and of model polycyclic compounds. This autoclave system (Figure 4) is presently being used in kinetic studies of condensed arenes, as well as of condensed heterocyclic-aromatic compounds. The stereochemistry of hydrogenation of model compounds is also being investigated.

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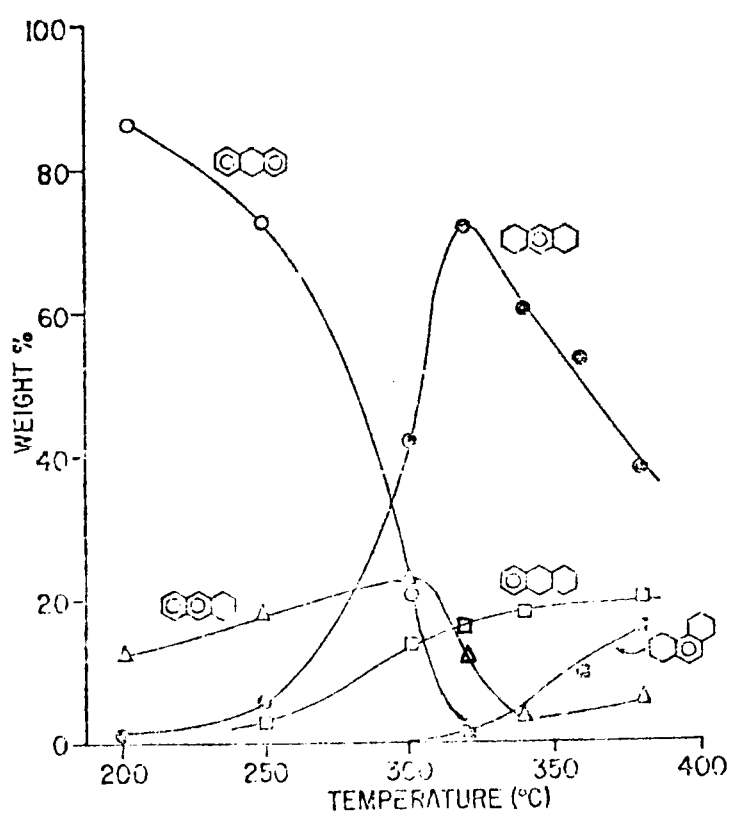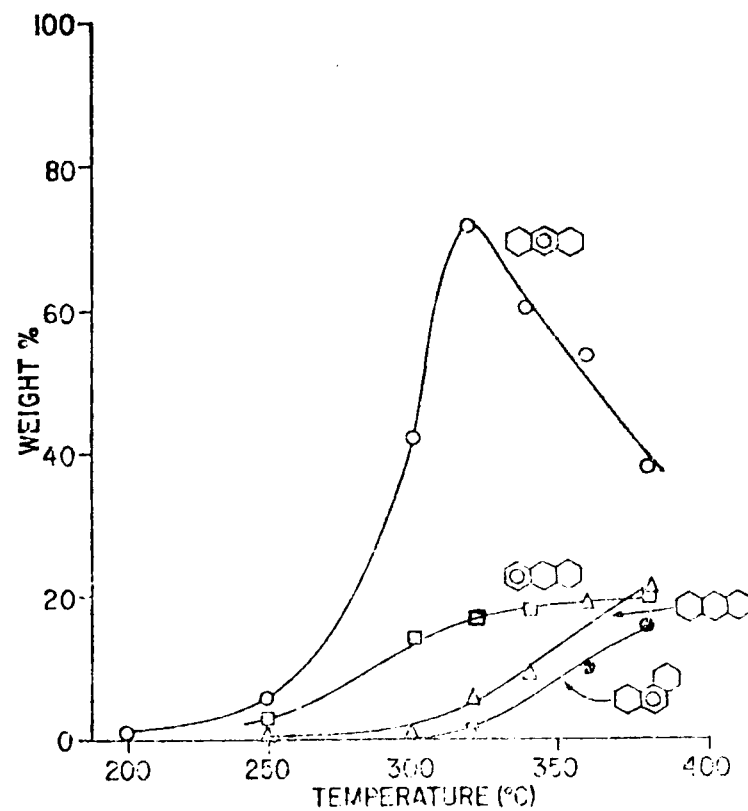
FIGURE 1.   Change in product composition from hydrogenation of
anthracene as a function of temperature.   Pressure: 2900 psig
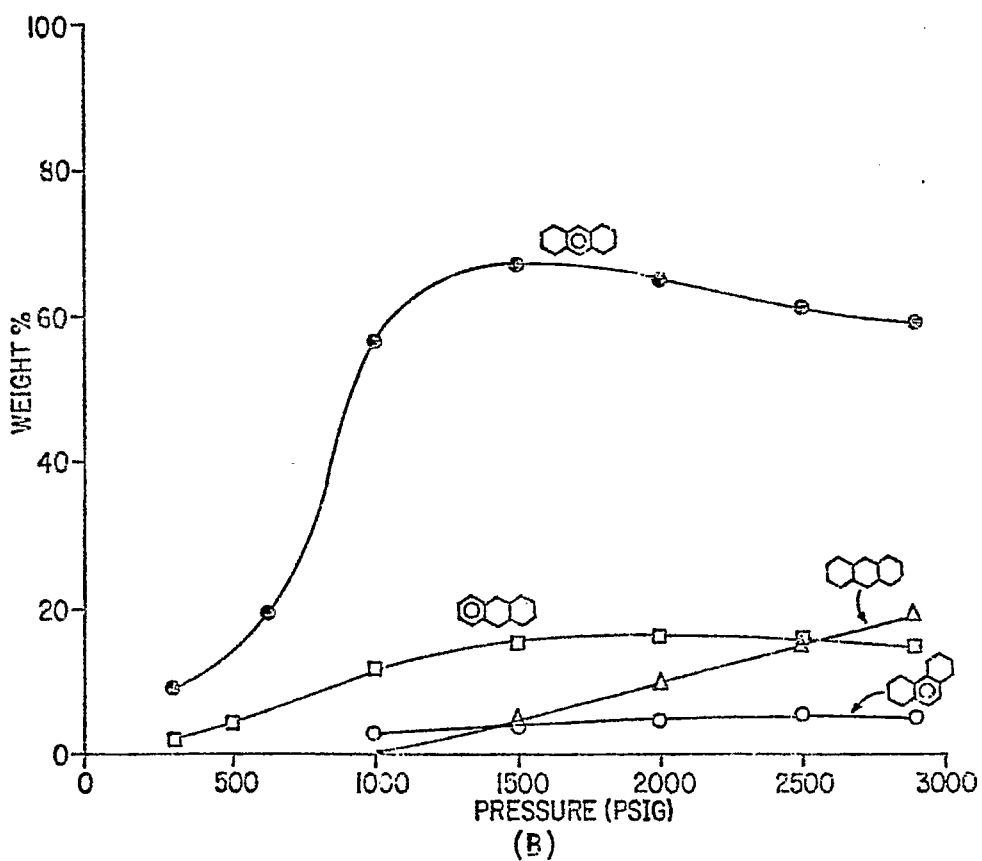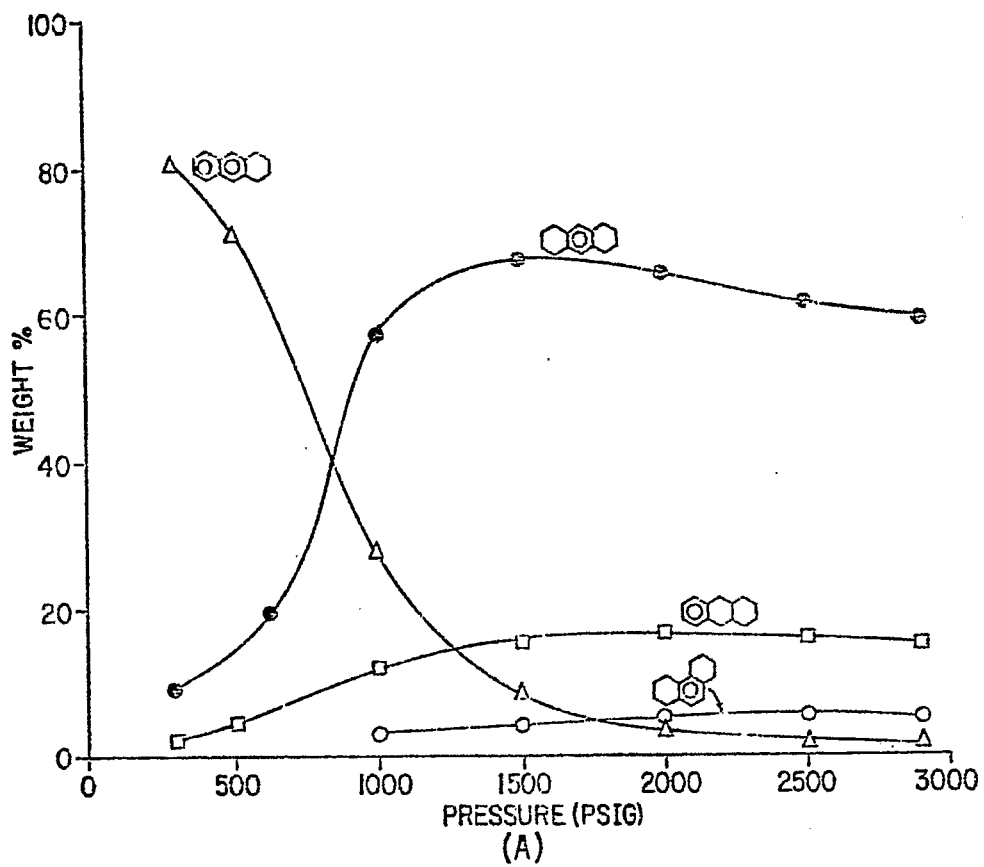
FIGURE 2.   Change in product composition from hydrogenation
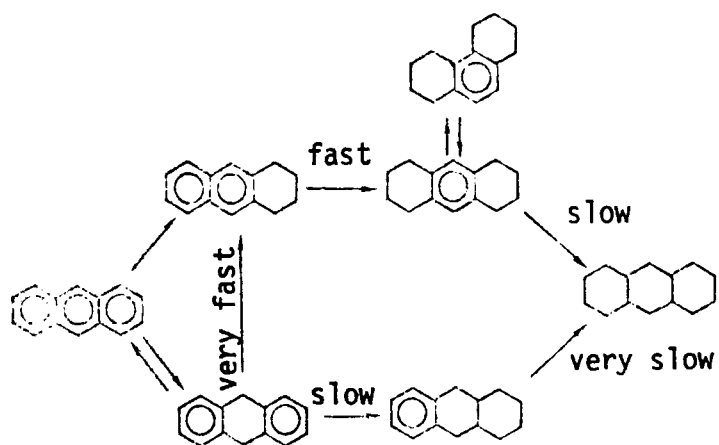of anthracene as a function of pressure.   Temp: 341°C.

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FIGURE 3. INDICATED MECHANISM OF ANTHRACENE HYDROGENATION
(CATALYST: Ni-W-S/Al$_2$O$_3$)

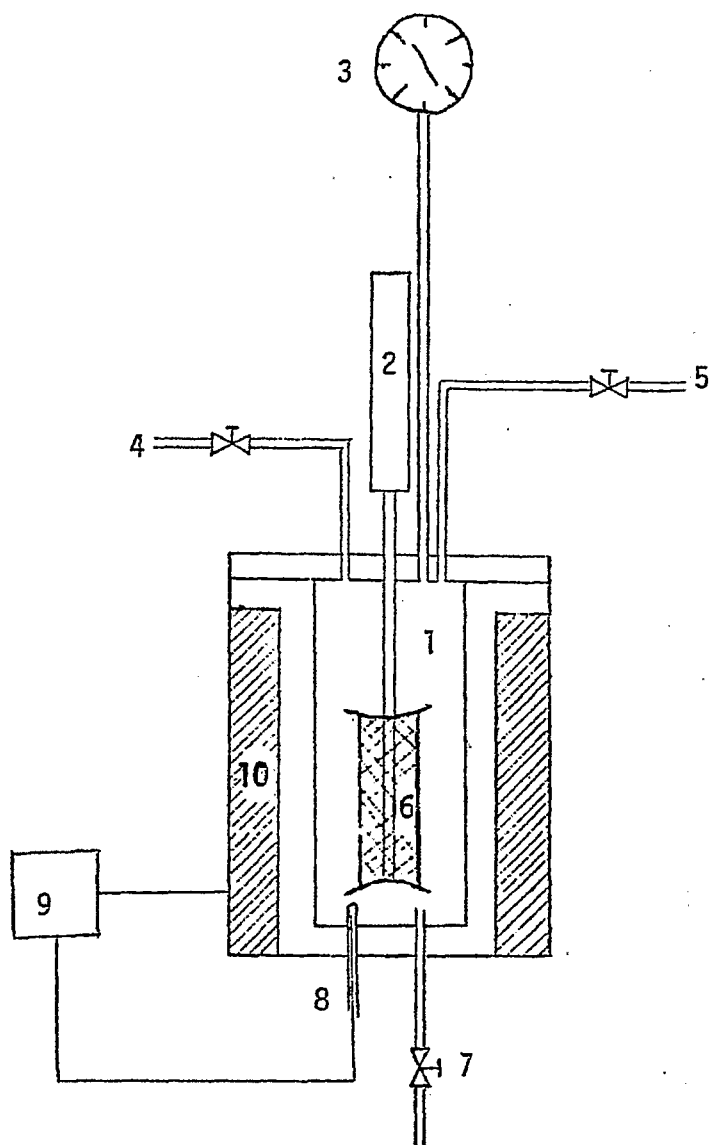FIGURE 4. Modified Autoclave for Kinetic Studies

1. 150cc Autoclave
2. Magnadash Agitator
3. Pressure Gauge
4. H_2 Inlet
5. Vent

6. Wire Catalyst Holder
7. Sample Valve
8. Thermocouple
9. Temperature Controller
10. Heater Jacket

Project A-7

Study of Thermal and Vapor Phase Catalytic Upgrading
to Coal Liquids

Catalytic Cracking of Coal-Derived Liquids

Faculty Advisor: F.V. Hanson
Graduate Student: Jay Dorius

Introduction

The catalytic cracking of coal-derived liquids may
provide a viable means of upgrading these liquids to a
marketable product. Previous studies have demonstrated that
short residence time, high temperature fluid catalytic
cracking of petroleum derived heavy gas oils to fuel oil and/
or gasoline is feasible. The objective of the present in-
vestigation is to extend this work to coal-derived liquids.

Project Status

Fabrication of the new regenerator-catalyst-hopper has been
completed. The hopper has been pressure tested and installed
in the system. The performance of the heating system for the
regenerator is now being evaluated.

The new regenerator-catalyst-hopper will be calibrated for
catalyst delivery rate after the installation of more accurate flow
meters in the fluidizing gas lines. The heated burette for
the liquid feed system has arrived and is being installed.

Future Work

After the equipment modifications are completed, initial
experiments will be conducted using gas oils from Altamont
and Rangely crude oils and a Mobil Durabead-9 fluid catalyst.
These experiments will provide a reference point for the
data obtained in the catalytic cracking of synthetic crude oils.

Project A-8

Synthesis of Light Hydrocarbons From Carbon Monoxide and Hydrogen

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

Introduction

The hydrogenation of carbon monoxide for the production of low molecular weight olefins (C_2-C_4) has been investigated over a variety of metallic catalysts. Although Raney type catalysts have been used extensively in various chemical synthesis processes involving hydrogenation, only a few investigations have been carried out using these catalysts for the hydrogenation of carbon monoxide.

The objectives of this research are 1) to prepare Raney type catalysts with various compositions, particularly Fe-Mn catalysts; 2) to establish catalyst characterization procedures that can be correlated with yield and selectivity parameters (characterization techniques will include chemisorption, thermal analysis and BET surface area in conjunction with surface spectroscopic analyses such as ESCA, AUGER, etc.); 3) to assess process variable effects using an isothermal fixed-bed reactor; 4) to study the interaction between the major component and promoters or modifiers in terms of yield and selectivity of products and 5) to study the over-all kinetics of the carbon monoxide hydrogenation process based on the data obtained in the fixed-bed isothermal studies.

Project Status

The fixed-bed reactor system has been designed and the components have been ordered. A preliminary literature survey on the preparation of Raney type catalysts and their use in carbon monoxide hydrogenation reactions has been completed.

Future Work

Raney iron catalysts will be prepared and evaluated. The catalytic properties of these laboratory catalysts will be compared to the catalytic properties of a commercially available catalyst. The preparation and activation techniques will be investigated for the Raney type Fe-Mn catalyst. The chemisorption apparatus and the fixed-bed reactor system will be fabricated.

Project A-8

Synthesis of Light Hydrocarbons From CO and H_2

Faculty Advisor: F.V. Hanson
Graduate Student: Y.S. Tsai

Introduction

The hydrogenation of carbon monoxide for the production of low molecular weight olefins (C_2-C_4) has been investigated over a variety of metallic catalysts. In particular, iron-manganese catalysts have exhibited significant selectivity for low molecular weight olefins. The initial catalyst screening data indicated that an iron-manganese catalyst composed of 2.2 parts of manganese per 100 parts of iron (atomic basis) would be the preferred composition with which to conduct a process variable investigation. The standard operating conditions for the iron-manganese catalyst screening studies were 500 psig, 1.06 g g^{-1} s^{-1} WHSV, H_2/CO ratio of 2/1 and 7-9% conversion (single pass).

Project Status

The process variable response of three additional catalysts was investigated. The catalyst compositions were 8.4 Mn/100 Fe, 63.0 Mn/100 Fe and 278 Mn/100 Fe. The range of process variables investigated were as follows:

pressure	200 – 750 psig
space velocity	0.53 – 2.12 cm^3 g^{-1} s^{-1}
H_2/CO ratio	1/1 – 3/1

The reaction temperature was adjusted to give a constant CO conversion. Thus the correlation between hydrocarbon selectivity and the process variables was made at constant conversion. The effect of the H_2/CO ratio on hydrocarbon selectivity for these three catalysts is presented in Figures 1-3. The correlation between the hydrocarbon selectivity and space velocity is presented in Figures 4-6. Finally, the correlation between hydrocarbon selectivity and reactant pressures is presented in Figures 7-9.

The following conclusions were drawn from this phase of the investigation:

1) The yield of C_2-C_4 hydrocarbons (50±5% based on total

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hydrocarbons) was relatively insensitive to catalyst composition and process parameter variation.

2) The olefin/paraffin ratio decreased with increasing H_2/CO ratio for the three catalysts tested. However, the trend was more pronounced for the lower Mn/Fe ratio.

3) The olefin/paraffin ratio appeared to increase with increasing space velocity, but may have attained a limiting value at a space velocity of 1 for the lower Mn/Fe ratio.

4) The olefin/paraffin ratio generally increased with increasing pressure at a hydrogen/carbon monoxide ratio of 2 which was not expected.

Future Work

The influence of catalyst preparation pretreatment and in-situ activation will be investigated. The fixed bed reactor apparatus will be modified to improve isothermality of the reactor and to improve the material balance.

5.5∿8.0% CO Conversion, Atomic 278.0 Mn/100 Fe, 1.06 cc/g/sec, 500 psig
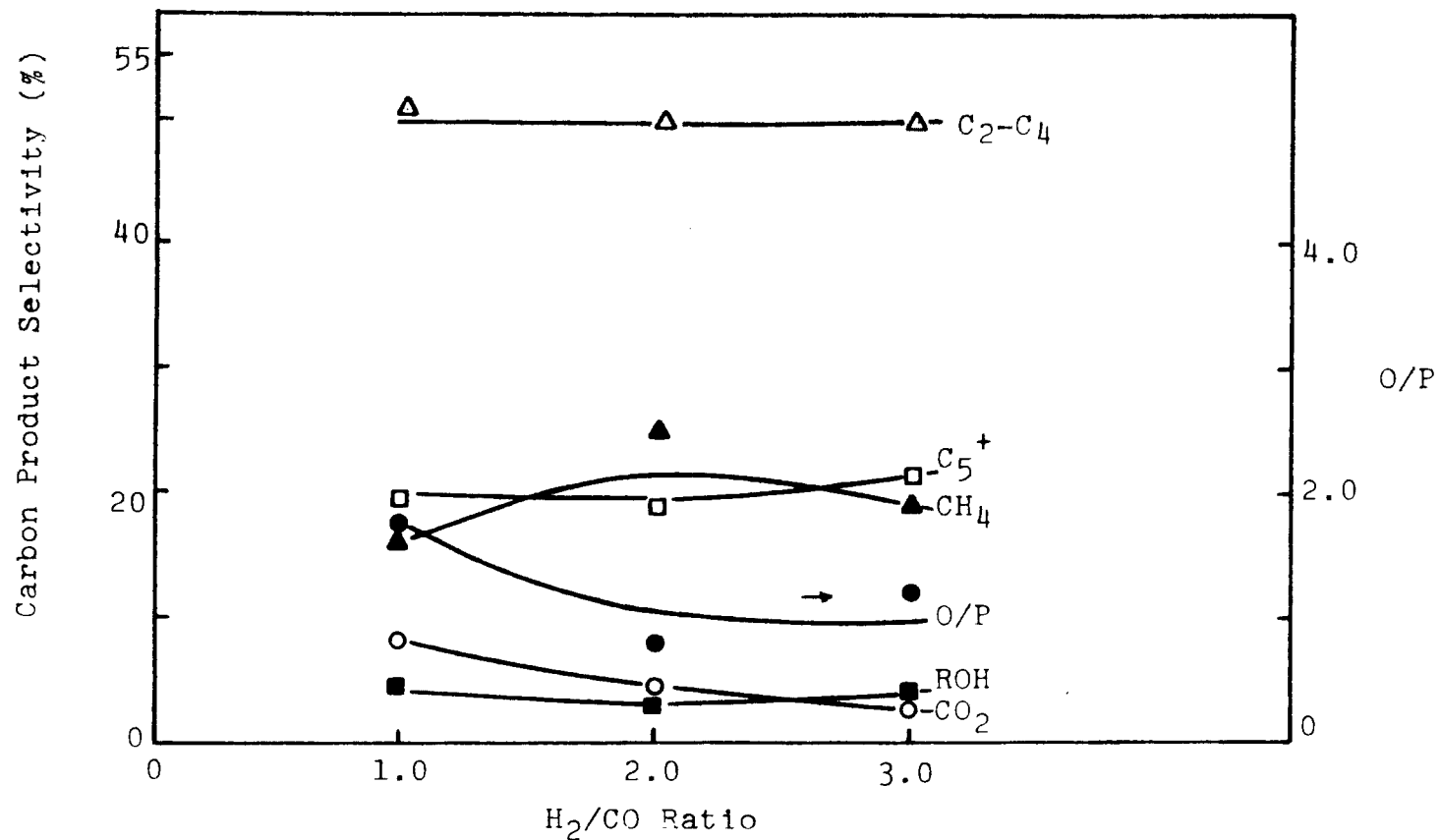
Figure 3. Effect of H_2/CO Ratio over 278.0 Mn/100 Fe Catalyst.

5.4~6.1% CO Conversion, Atomic 63.0 Mn/100 Fe, 1.06 cc/g/sec, 500 psig
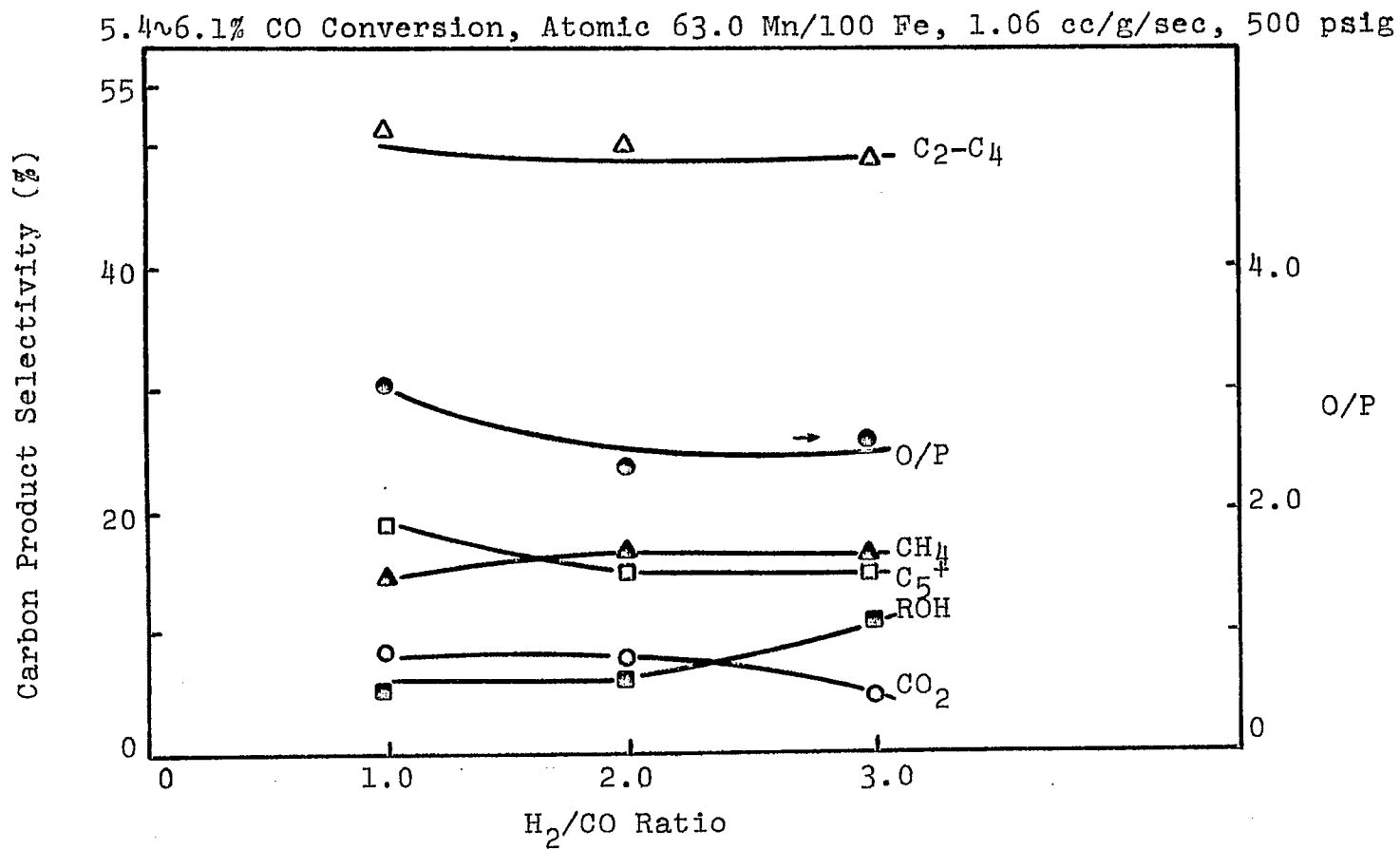
Figure 2.   Effect of H_2/CO Ratio over 63.0 Mn/100 Fe Catalyst.

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6.0∿8.5% CO Conversion, Atomic 8.4 Mn/100 F3, 1.06 cc/g/sec, 500 psig
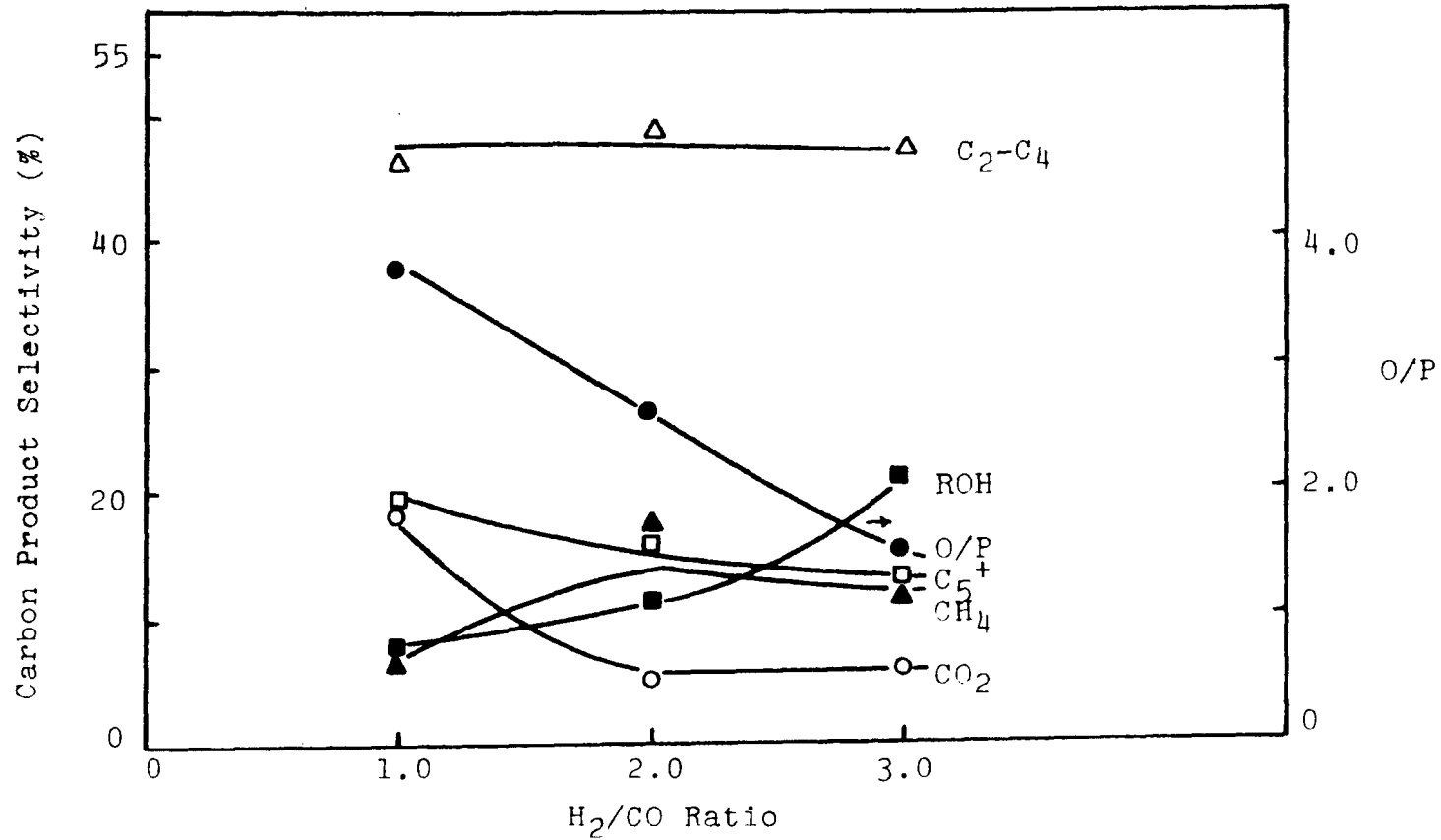
Figure 1. Effect of H_2/CO Ratio over 8.4 Mn/100 Fe Catalyst.

8.0~9.0% CO Conversion, Atomic 8.4 Mn/100 Fe, 500 psig, $H_2/CO=2/1$
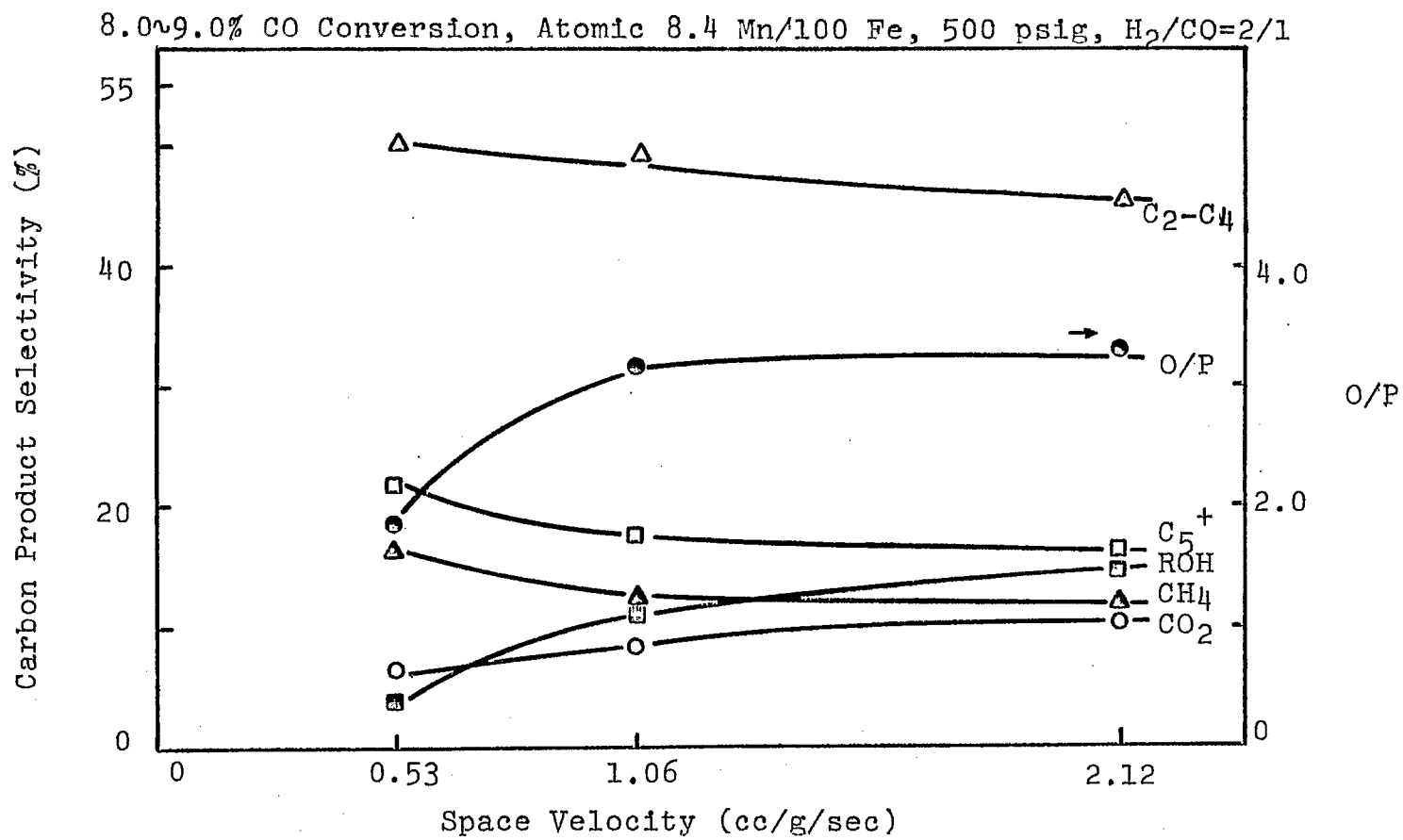
Figure 4.   Effect of Space Velocity over 8.4 Mn/100 Fe Catalyst.

5.7~7.0% CO Conversion, Atomic 63.0 Mn/100 Fe, 500 psig, $H_2/CO=2/1$
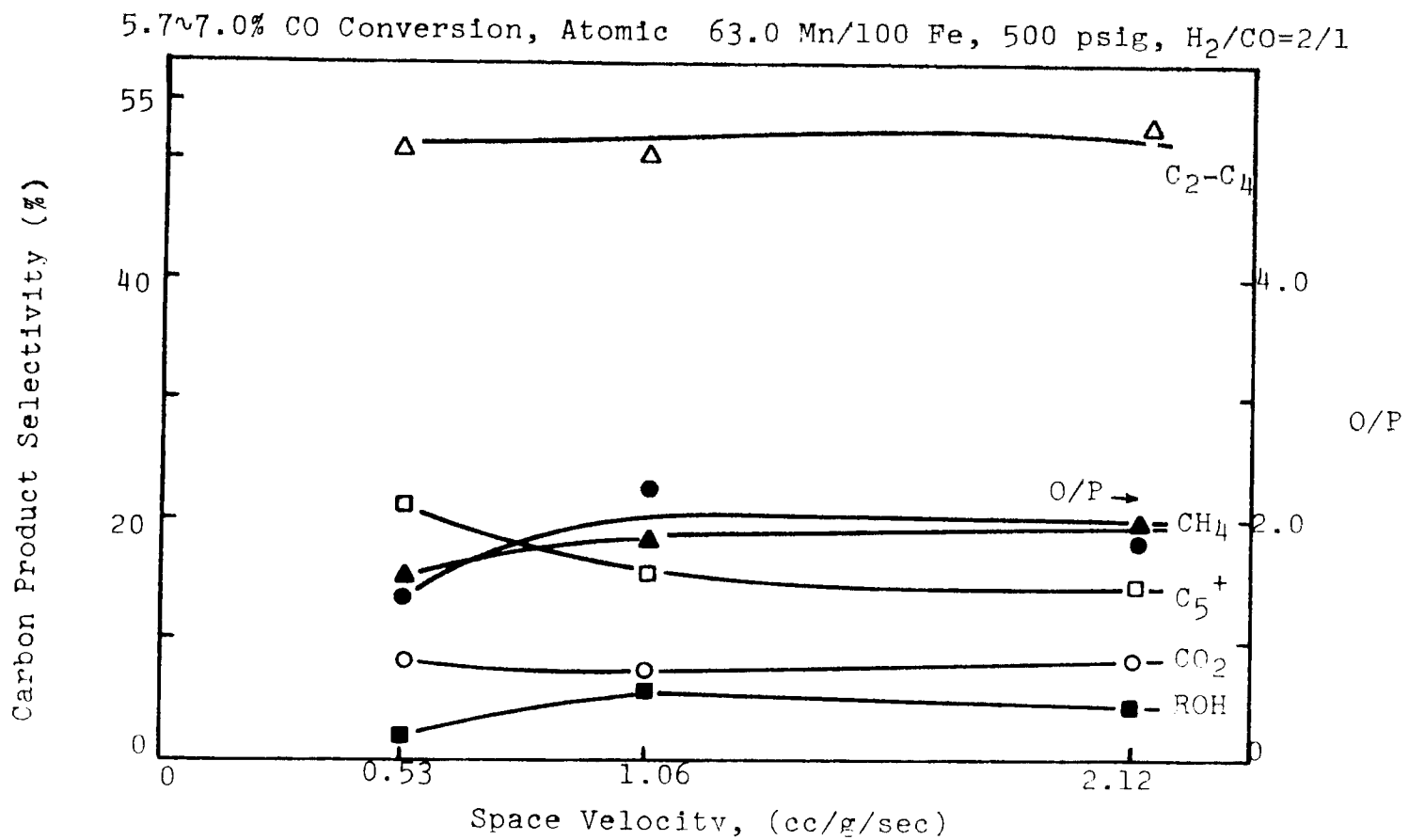
Figure 5. Effect of Space Velocity over 63.0 Mn/100 Fe Catalyst.
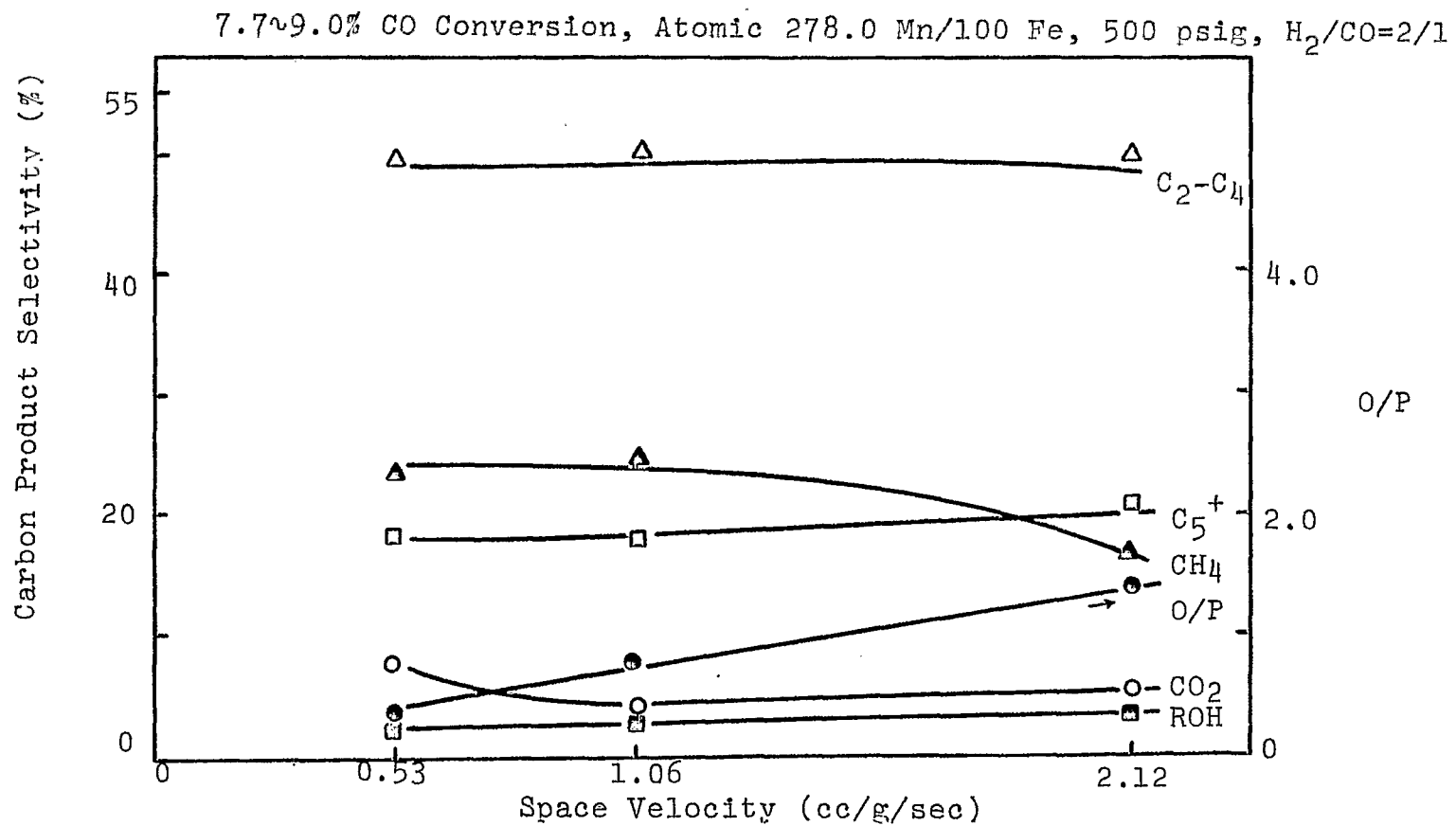
Figure 6.   Effect of Space Velocity over 278.0 Mn/100 Fe Catalyst.

7.0~7.7% CO Conversion, Atomic 8.4 Mn/100 Fe, 1.06 cc/g/sec, $H_2/CO=2/1$
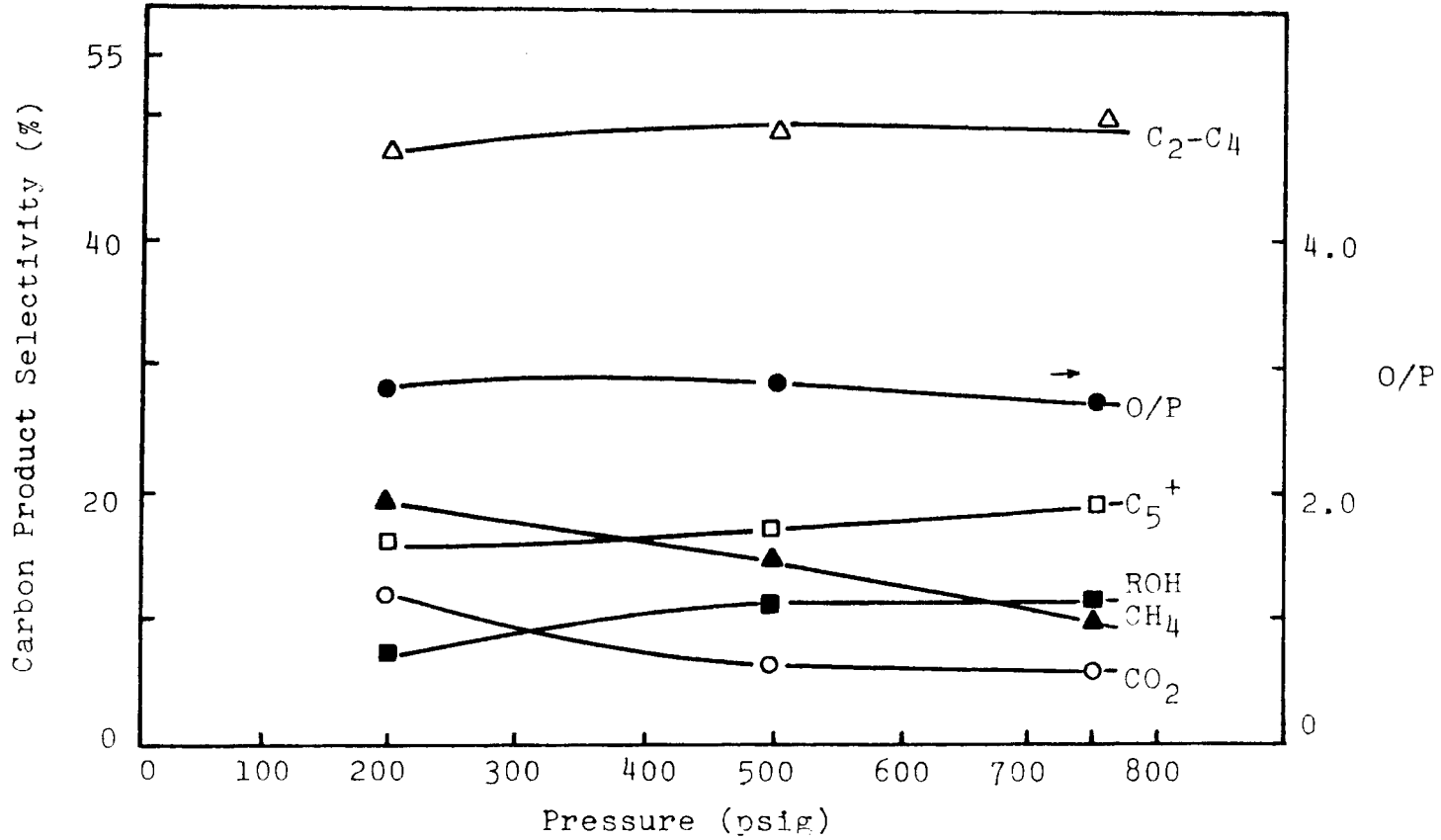
Figure 7. Effect of Pressure over 8.4 Mn/100 Fe Catalyst.

5.8~7.6% CO Conversion, Atomic 63.0 Mn/100 Fe, 1.06 cc/g/sec, $H_2CO=2/1$
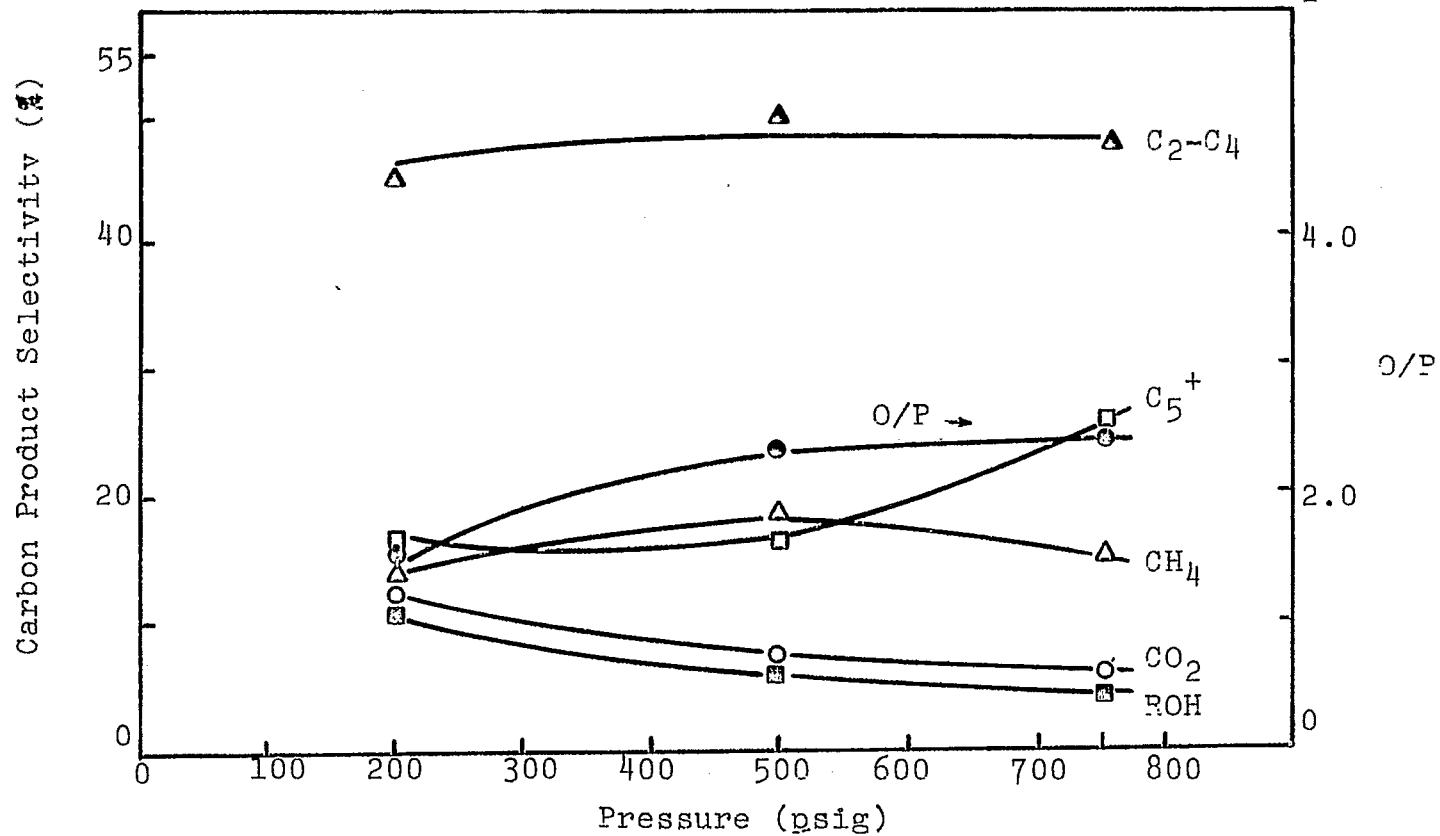
Figure 8. Effect of Pressure over 63.0 Mn/100 Fe Catalyst.

6.1~7.7% CO Conversion, Atomic 278.0 Mn/100 Fe, 1.06 cc/g/sec, H_2/CO=2/1

Figure 9.   Effect of Pressure over 278.0 Mn/100Fe Catalyst.

Project A-8

Synthesis of Light Hydrocarbons from
CO and H_2 (Continued)

Carbon Monoxide Hydrogenation in a Slurry Reactor

Faculty Advisor: F.V. Hanson
Graduate Student: W.P. Tai

Introduction

The exothermic nature of the carbon monoxide hydrogenation reaction severely limits the conversion level that can be attained in a fixed-bed reactor. The "hot spot" observed in fixed-bed operation ac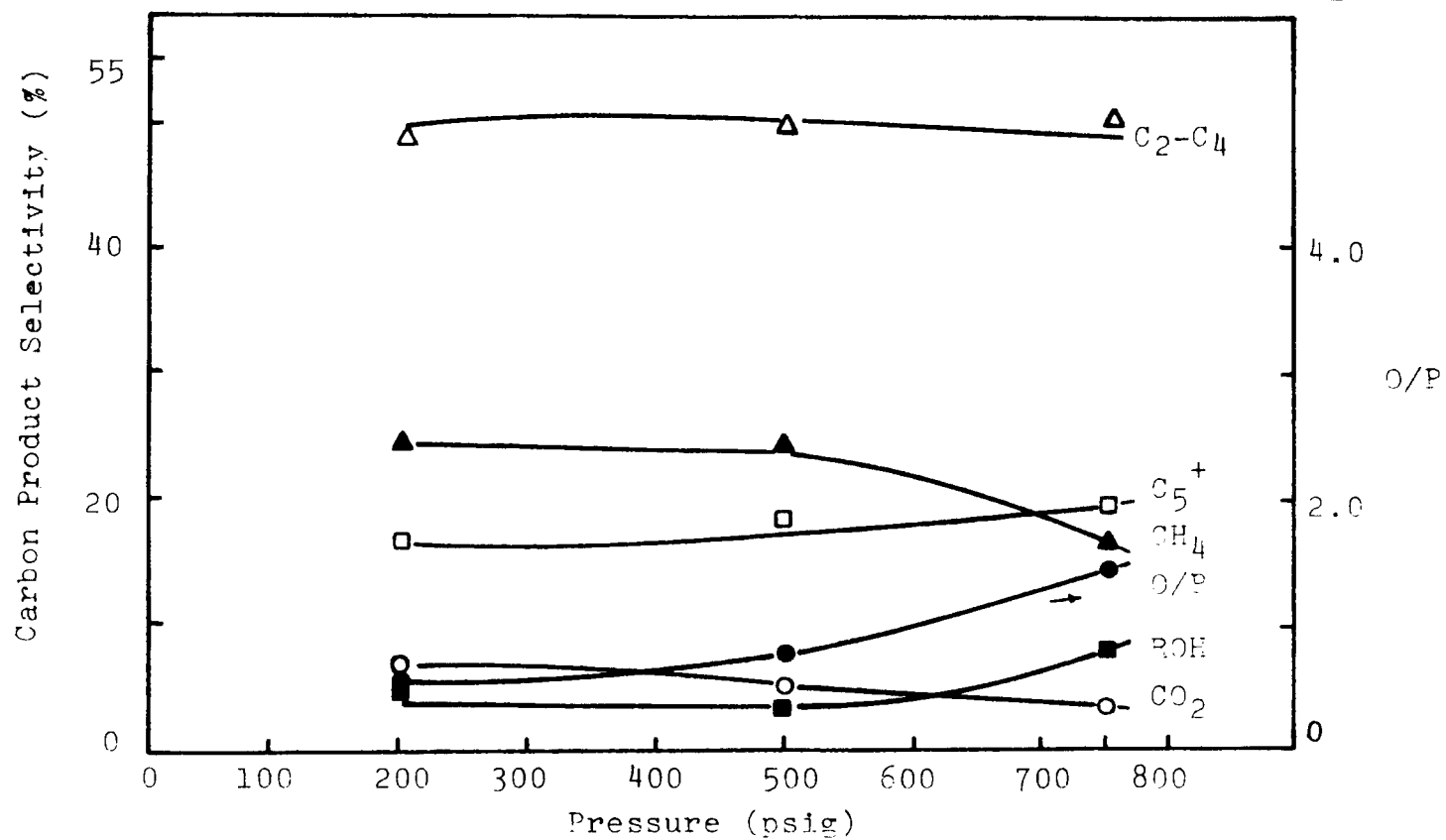celerates the Boudouard reaction (disproportionation of CO to CO_2 and carbon) with the concomitant fouling of the catalyst and shifts the selectivity in the direction of methane. Thus, the global heat release must be dissipated to suppress these undesirable side reactions. The objective of this investigation is to explore the potential of the slurry reactor for the dissipation of the heat generated during reactions, thereby maintaining the catalyst activity and selectivity.

Project Status

The fixed-bed slurry reactor system has been assembled and preliminary testing has been completed. A schematic of the apparatus is presented in Figure 1. The reactant gas mixture (CO + H_2) is passed through a bed of activated charcoal (B) to remove metal carbonyls. The flow is controlled by means of a metering valve (K), and the flow rate is monitored with a mass flow meter (D). The reactant gas and the liquid heat transfer medium are mixed in line, and the mixture is brought to a predetermined temperature in the preheater (E) prior to contacting the catalyst in the reactor (F). The catalyst bed temperature is monitored by a moveable thermocouple in a thermowell located on the centerline of the reactor. A water-cooled condenser (Q) cools the reaction products and the liquid heat transfer medium. The light gases are separated from the liquid products (at the reaction pressure) and the heat transfer liquid in the high pressure separator (G-M). The system pressure is maintained by a Grove 91-W back pressure regulator (L). The liquid passes from the high pressure separator to a low pressure separator (H-M) through a control valve where the heavy gases are separated from the heat transfer liquid. The heat transfer liquid is returned to the preheater inlet by means of the liquid circulation pump (J). The liquid circulation and the gas-liquid separation system have been tested and performed quite acceptably.

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Future Work

A control panel is being fabricated. All of the valves, pressure gages, temperature controllers, separator liquid level indicators, variacs, temperature indicator, switches and pressure regulators will be mounted on the control panel. A commercially available ammonia synthesis catalyst will be tested initially, followed by unsupported iron-manganese catalysts prepared in this laboratory. Process variables such as temperature, pressure, catalyst-slurry ratio, H_2/CO ratio, gas hourly space velocity and heat transfer medium will be studied.
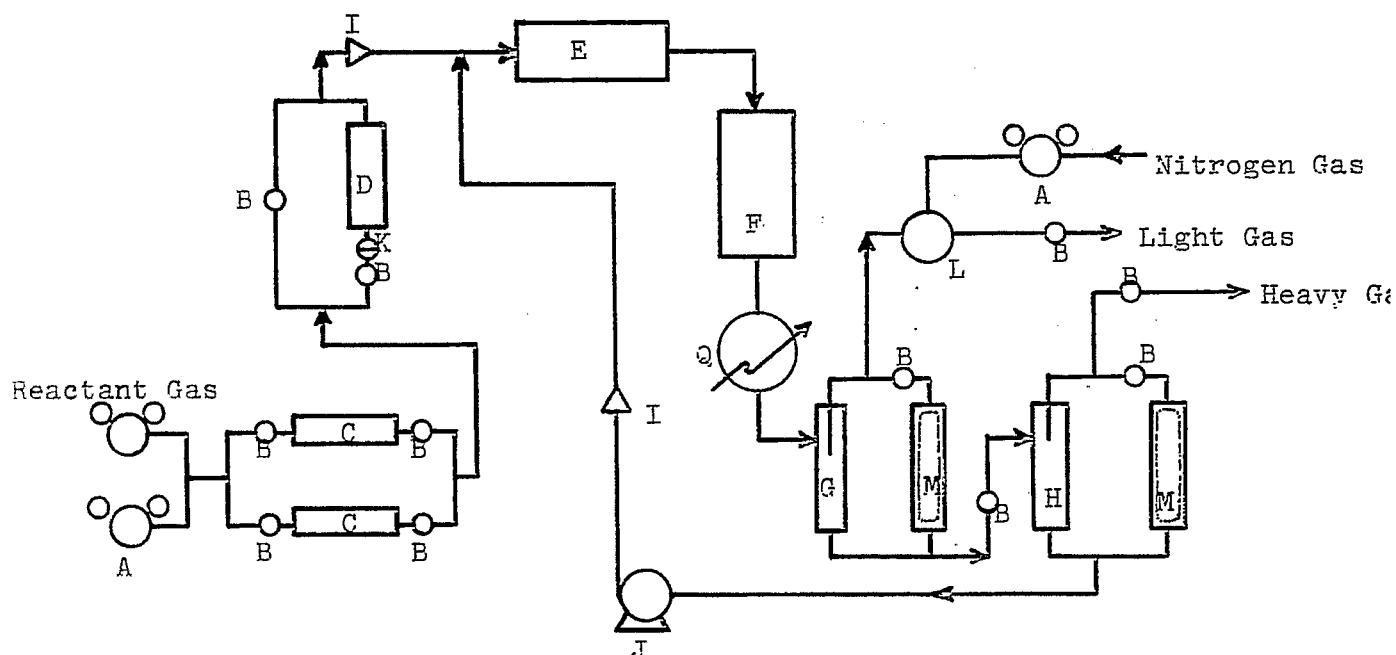
Figure 1. A Schematic of the Slurry Reactor.

A. In-line pressure regulator

B. On-off valve

C. Activated carbon purifier

D. Mass flow meter

E. Gas-liquid feed preheater

F. Reactor (fixed bed or rotating basket)

G. High pressure separator

H. Low pressure separator

I. Check valve

J. Heat transfer liquid circulating pump

K. Metering valve

L. Grove back pressure regulator

M. Jerguson liquid level indicator

Q. Condenser/heat exchanger

Project A-8

Synthesis of Hydrocarbons from CO and H_2
(Continued)

Catalyst Characterization 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 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.

Presently the catalyst under investigation are iron-based catalysts promoted with various amounts of manganese in the oxide form. Characterization techniques employed previously on the $Co-Cu-Al_2O_3$ catalysts are being applied to the iron catalysts along with some additional techniques.

Project Status

Work this period concentrated on X-ray diffraction studies of iron-manganese oxide catalysts prepared and used in the reactor studies and on the assembly and preliminary testing of a new temperature programmed desorption apparatus. The X-ray studies included both unreduced and "used" (reduced) catalysts.

The temperature programmed desorption/reaction apparatus consists of three sections: 1) a gas purification section, 2) a reaction section and 3) a detection section. In Figure 1 a schematic of the present arrangement is given. The purification system consists of a gas purifier cartridge on the helium line along with two large oxygen and moisture removal systems followed by a molecular sieve/activated carbon trap, which can be cooled in liquid nitrogen.

The reactor section consists of a 1/2" by 28" Vycor tube whose temperature is monitored with a thermocouple placed in the glass wool support bed. The reactor tube is surrounded by

an electric furnace that is connected to a temperature programmer. The catalyst sample rests on the glass wool. The carrier gas or reactant gas passes through the reactor and into the detector system, using 1/4" plastic tubing.

The detection system consists of two GC thermoconductivity cells and a quadrapol mass spectrometer. The incoming stream to the catalyst bed passes through one side of the thermoconductivity detector while the outgoing stream passes through the other. Differences in the thermoconductivity of the passing gases are easily detected. The gas then goes to a molecular jet separator which concentrates the heavier product gases for the mass spectrometer by partially removing the lighter carrier gas. The mass spectrometer permits identification of the desorption products and also their relative concentrations. A bypass valve to a bubble meter is used when determining the space velocity of the gas in the system.

The TPD/TPR apparatus described promises to be a very useful tool in studying the interaction of the reactant gases with the catalysts of interest.

Presently X-ray diffraction spectra have been made on five unreduced catalyst preparations designated T1 (iron oxide), T3, T9, T13 and T15 (manganese oxide). The T1 and T15 were precipitated from iron nitrate and manganese nitrate, respectively. The X-ray diffraction patterns correspond to αFe_2O_3 (hematite) for T1 while the pattern from T15 corresponds to Mn_3O_4 (hausmannite). The unreduced T3 (low manganese) catalyst gives an X-ray diffraction pattern similar to that of T1. Minor differences can be seen and the only dominate phase appears to be αFe_2O_3. The T13 (high manganese) has an X-ray diffraction pattern whose major feactures correspond to those of T15 (hausmannite). However, evidence of a small amount of the αFe_2O_3 phase can be seen. The unreduced catalyst T9 (intermediate iron and manganese) showed no X-ray diffraction peaks. Evidently no crystalline phase exists in the unreduced catalyst. Other catalyst formulations similar to T9 must be examined by X-ray before attempting to explain this result.

X-Ray diffraction studies of the used catalysts, which were obtained from the reactor studies showed the main catalyst phases to be α-Fe and MnO. However, evidence of another phase was seen corresponding perhaps to an iron oxide, manganese oxide, or possibly an iron carbide. This will be investigated further.

Future Work

The X-ray diffraction studies will continue. The TPD/TPR equipment will also be used extensively to study the reactant surface interaction of these catalysts.
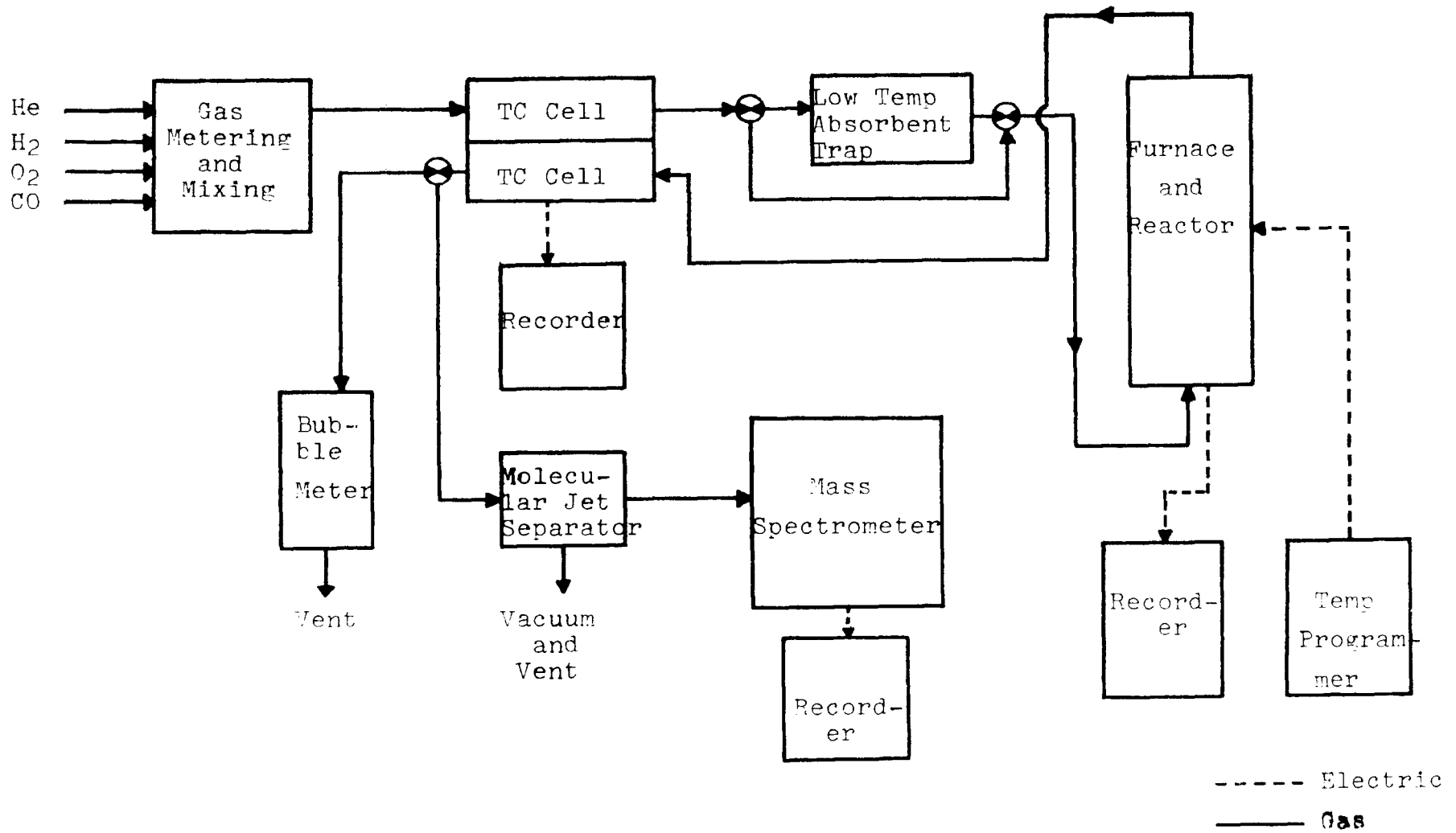
Figure 1. Schematic of Temperature Programmed Desorption/Reaction
Apparatus.

Project B-1

Development of Optimum Catalysts and 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, multirings aromatics found in coal-derived liquids will have adequate accessibility to the active sites 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 catalytically inactive.

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 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 (20 Å) and smallest average pore size alumina (50 Å) tested, a markedly lower diffusivity was obtained, indicative of a restrictive diffusion effect.

Project Status

The continuous flow reactor was used to measure the diffusion rate of meso-tetraphenylporphine (solute) in catalyst L with cyclohexane as a solvent.[1] The change in solute concentration was monitored by a UV detector. The solute concentration decreased with increased time (about 13 hr) until a steady state was obtained, i.e., no further change in solute concentration. Under these conditions the solute should have saturated the catalyst adsorption sites. However, it was discovered that complete saturation had not been achieved.

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Therefore, another method was used to insure the complete saturation of the catalyst.

Equal amounts of catalyst were added to fifteen bottles containing identical solutions of the solute and solvent. The bottles were placed in a shaker bath and the concentration change in each bottle was measured by UV. Preliminary runs show that 72 hours are required before complete saturation is acheived.

Future Work

The D_e values for meso-tetraphenylporphine with catalyst L will be measured.

Reference

1. W.H. Wiser et al., DOE Contract No. E(49-18)-2006, Quarterly Progress Report, Salt Lake City, Utah, Jan-Mar 1979.

Project B-2 (Alternate)

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 hydro-treating 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.

Initial tests with the flow microbalance reactor showed that perfect gas mixing was not achieved when injecting a liquid feed (gaseous at reaction temperature) directly into the reactor. Modifications were incorporated into a new reactor design which have eliminated the problem and improved the mechanical stability of the system.

Preliminary tests of the benzothiophene hydrodesulfurization reaction showed the rate to be proportional to benzothiophene and hydrogen and inhibited by benzothiophene and H_2S. Pyridine and quinoline were poisons for the reaction. Advantage of this finding was taken to develop a technique for assaying active catalyst sites by successive poisoning-activity measurements.

Adsorption of H_2S on the sulfided catalyst was reversible and could be correlated with the Langmuir adsorption isotherm. Chemisorption of pyridine lowered H_2S adsorption, indicating a competition for adsorption sites. Temperature programmed desorption studies of thiophene also showed quinoline to compete with thiophene for adsorption sites.

The temperature programmed desorption studies using FID and TCD detectors showed the presence of a high temperature peak which is completely inorganic in nature.

Project Status

Temperature programmed desorption (TPD) studies were continued using thiophene (TP) as the adsorbate on different

catalysts. The apparatus was modified by replacing the gas chromatograph with a quadrapole mass spectrometer for identifying the desorbing species. Figure 1 shows a schematic of the apparatus. Eventhough the experimental set-up is different, the results should be qualitatively comparable.

Experiments were carried out on $\gamma-Al_2O_3$, 8%-Mo/Al_2O_3 and 3%-Co 8%-Mo/Al_2O_3 catalysts. Each catalyst was 1) sulfided for 2 hours at 400°C and flushed for 1 hour at 400°C in He, and 2) cooled to 100°C. 3) Thiophene (TP) was adsorbed followed by desorption of the reversible portion in He at 100°C. 4) The irreversible portion was desorbed by TPD in He from 100°C to 350°C. 5) Each catalyst was aged using TP in H_2 at 350°C overnight. 6) Steps 2 thru 4 were repeated. 7) The catalyst was poisoned using pyridine in He at 350°C followed by desorption of the reversibly adsorbed poison in He for 1 hour. 8) Steps 2 thru 4 were repeated.

Figure 2 shows a series of runs with $\gamma-Al_2O_3$. Desorption of TP from the presulfided catalyst (bottom plot) showed the presence of TP, butene, H_2S and a trace of CO_2. The presence of butene was surprising and indicates that a significant amount of TP had undergone decomposition, confirmed by the presence of H_2S. The results show two distinctive peaks as observed earlier.[2] After poisoning (top plot), the high temperature peak totally disappeared and the low temperature peak diminished substantially indicating that TP and the poison compete for the same type of active sites. Hydrogen sulfide seems to adsorb more strongly than butene. In the case of the fresh catalyst, the H_2S peaks were not completely resolved. However, they show desorption maxima at temperatures close to that observed for the two butene peaks. Apparently, two kinds of sites are available for TP adsorption/decomposition.

Figure 3 shows the results of a series of runs with 3% Co 8%-Mo/Al_2O_3 catalyst (Ketjen fine 124-1.5 E HD catalyst). Desorption of TP from the presulfided catalyst (top plot) showed the presence of TP, butene, H_2S and CO_2. The presence of butene, signifies that some TP had undergone decomposition, as confirmed by the presence of H_2S. A composite of the two TP peaks and one butene peak resembles the FID peak #1.[2]

The presence of three different peaks may indicate the presence of several different adsorption sites for TP on this catalyst. The low temperature TP peak may be due to weak adsorption on Al_2O_3 or Mo/Al_2O_3 sites, since it was also observed on the Al_2O_3 support. The intermediate butene peak may arise from TP, which adsorbs on a moderately strong site and decomposes upon heating, or it may be due to readsorption of butene from the decomposition of TP on the first site and subsequent desorption of butene. The high temperature TP peak evidently involves a strong adsorption site, from which TP desorbs intact.

It may seem odd that this TP does not decompose to butene at
these higher temperatures. There may be some decomposition
to coke and H_2S, since the H_2S concentration rises steeply in
this region.

The H_2S curve resembles the high temperature portion of
the TCD Curve B indicating that the latter is mainly due to
H_2S from decomposition of TP.[2] Its evolution at high temper-
atures is probably due to the reaction of an adsorbed sulfur
atom with a surface hydrogen. The resulting hydrocarbon
portion remains as coke on the surface. The source of hydro-
gen for the formation of H_2S and butene may be from the
irreversible hydrogen held on the presulfided catalyst[3] or
from the thiophene molecule itself.[4]

A curious finding in the runs with Mo/Al_2O_3 and 3%-Co
8%-Mo/Al_2O_3 is the presence of appreciable amounts of CO_2
This was not observed with the Al_2O_3 support (Figure 2).
Therefore, the CO_2 formation is indigeneous to the presence
of Co and Mo in the catalysts. This might arise from the
reaction of butene or condensed hydrocarbon (coke precursor)
on the catalyst with an active oxide phase remaining on the
sulfided catalyst. To investigate this possibility, the
catalyst was allowed to react with TP in H_2 overnight at 350^oC
to remove the active oxygen by reaction. A subsequent thio-
phene TPD run in He now showed no CO_2 in the desorption pro-
duct (middle plots in Figures 3 and 4). This result indicates
that, even after presulfiding the catalyst at 400^oC, neither
TP nor its products are capable of reacting with the residual
oxide left on the catalyst.

The results of the $CoMo/Al_2O_3$ catalyst, Figure 3, show
a shift in the TP and butene peaks to higher temperatures.
The reacted state of the catalyst (after being exposed to TP/H_2
under catalytic reaction conditions for an extended period of
time) is considerably different from the original presulfided
state. The activity differences for these catalysts persist
for a considerable period of time before a constant, steady
state activity is achieved.[5] Apparently, this is due to
catalyst structural changes as well as coke formation during
this period. Similar structural changes have been reported
recently.[6]

The effect of subsequent pyridine poisoning on the reacted
catalyst is shown in the lower plot of Figure 3. Now, a
lowering of the temperature is observed in the TP and butene
peaks and the high temperature TP peak is absent. Thus,
poisoning has caused the loss of some active sites and a
decrease in the peak temperature when compared with the more
stable state or aged catalyst. However, the temperatures
are higher for the poisoned catalyst than for the presulfided
catalyst, as reported earlier.[2] The actual decrease in
temperature between the aged and poisoned states of the catalyst
represents a decrease in activation energy of desorption. The
poison adsorbs strongly on the stronger sites leaving the
weaker sites for future adsorption.

For the 8% Mo/Al_2O_3 catalyst (Figure 4) aging and poisoning do not change the energetics of the active sites although the number of active sites decreases, as observed previously.[2] Aging is observed to remove all the reactive oxygen in the catalyst after presulfiding at 400°C for 2 hours. The catalyst was sulfided at 400°C overnight to check whether the desorption of CO_2 was reduced, but the state of this catalyst was not much different from the one which was sulfided for only 2 hours. The TP in H_2 at 400°C sulfided the catalyst better than H_2S/H_2 mixture.

To determine the source of hydrogen for the formation of butene and H_2S from TP, TP in helium was passed over the catalyst at 400°C for 24 hours to titrate the surface hydrogen. The TP was adsorbed and desorbed, and then TPD was carried out in helium. The desorption profile of butene and H_2S did not change indicating that hydrogen for the formation of butene and H_2S probably came from the TP molecule itself and not from the catalyst. These results support the dehydrosulfurization mechanism of Kolboe.[7]

Also the initial runs of TP adsorption and TPD in helium on the deuterium exchanges catalyst surface did not indicate the presence of deuterium in butene and H_2S. This, too, supports the Kolboe mechanism.

Future Work

Benzothiophene (BT) desulfurization kinetic studies will be started. The catalyst will be aged using BT in H_2 before any kinetic measurements are made. The deuterium exchange experiment will be carried out the establish the source of hydrogen for the reaction.

References

1. W.H. Wiser et al., DOE Contract No. E(49-18)-2006, Salt Lake City, Utah, Quarterly Progress Report, Jan-Mar 1978.

2. ibid., Jan-Mar 1979.

3. F.E. Massoth, J. Catal., 36, 164 (1975).

4. R.J. Mikovsky, A.J. Silvesti and H. Heinemann, J. Catal., 34, 324-326 (1974).

5. O. Weisser and S. Landa, "Sulfide Catalysts-Their Properties and Application," Pergamon, New York, 1973.

6. D.H. Broderick, G.C.A. Schuit and B.C. Gates, J. Catal., 54, 94-97 (1978).

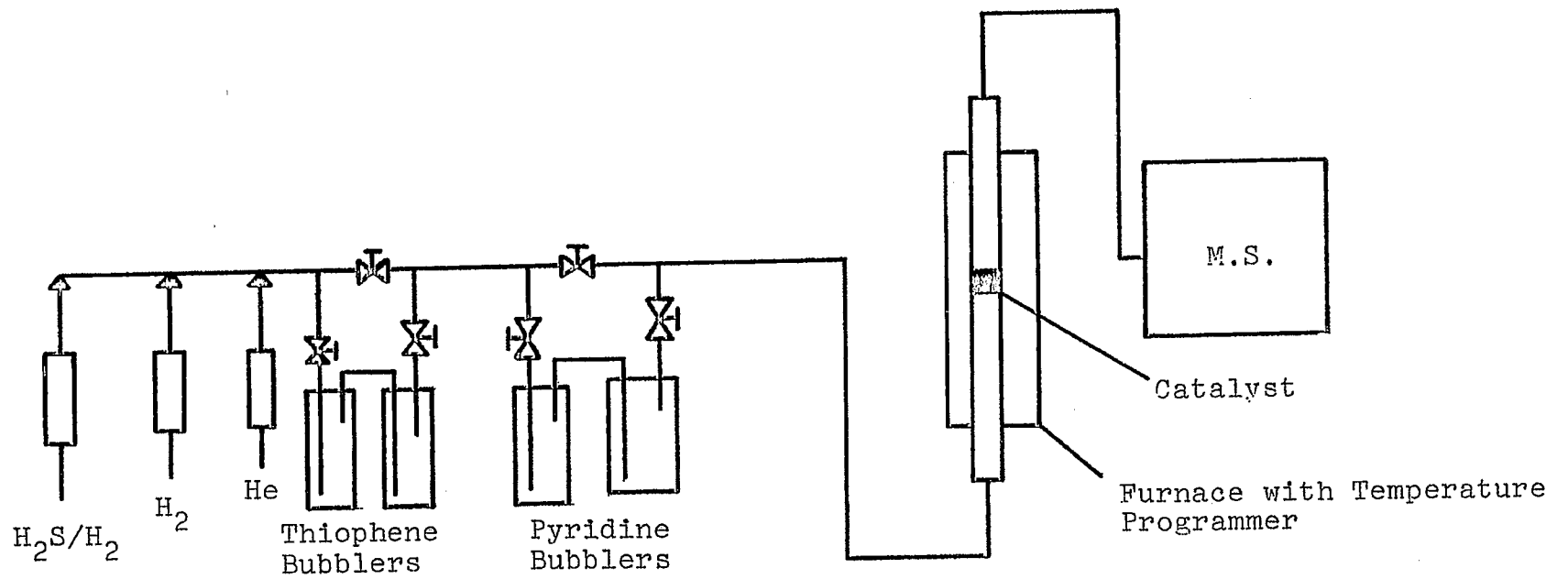7. S. Kolboe, Can. J. Chem., 47, 352 (1969).

Figure 1.   Temperature Programmed Desorption-Schematic.

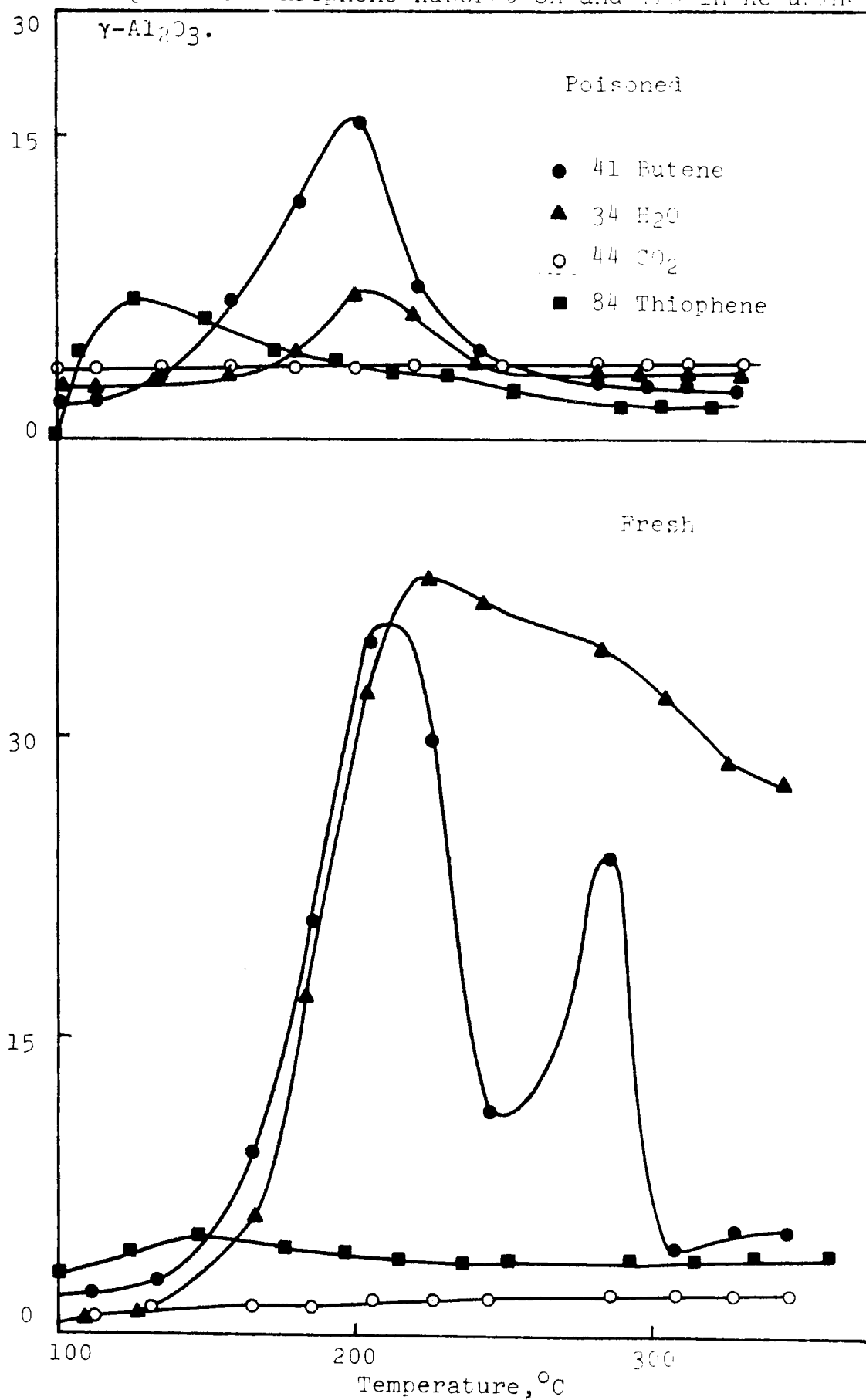Figure 2. Thiophene Adsorption and TPD in He using γ-Al₂O₃.

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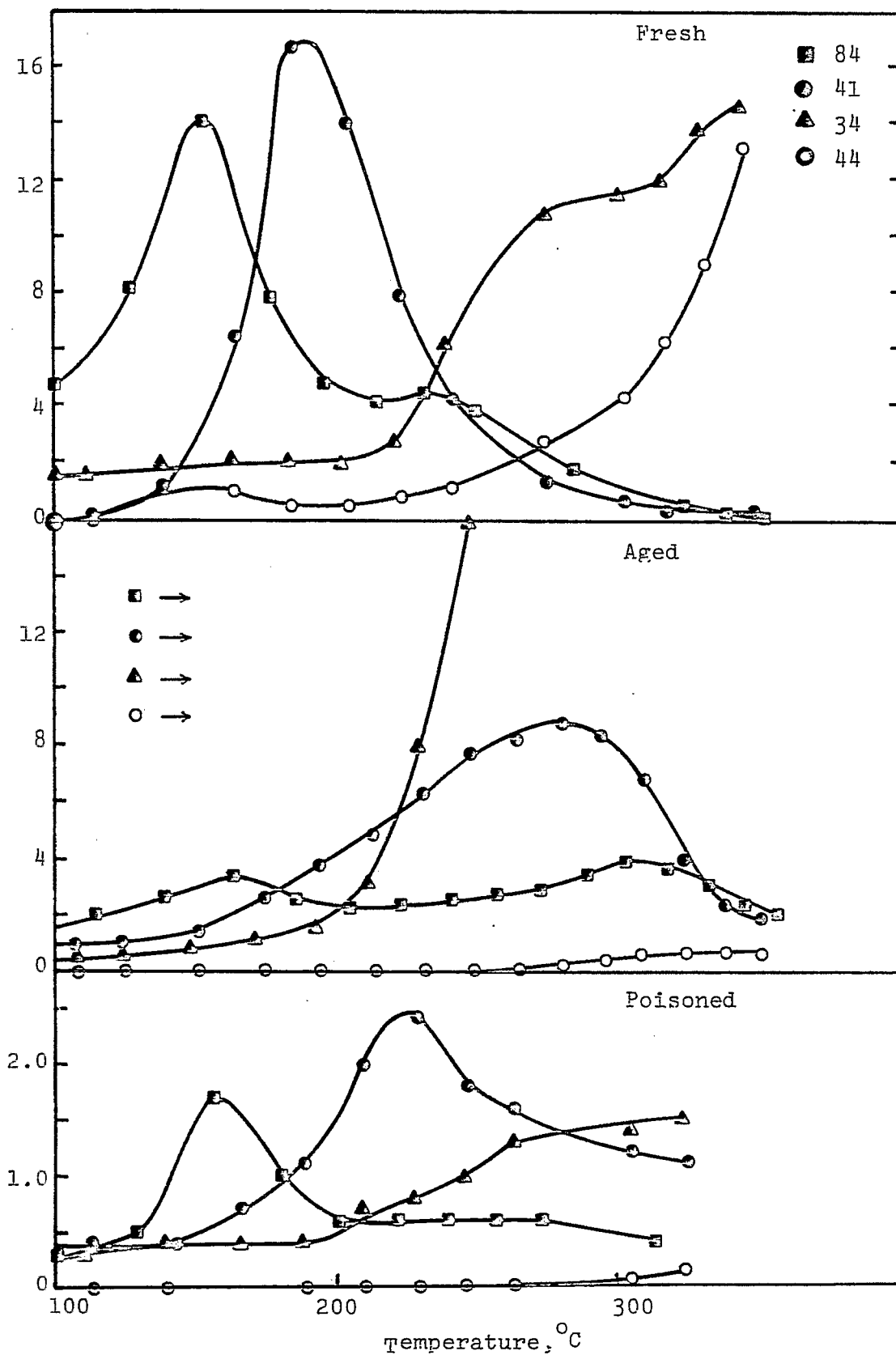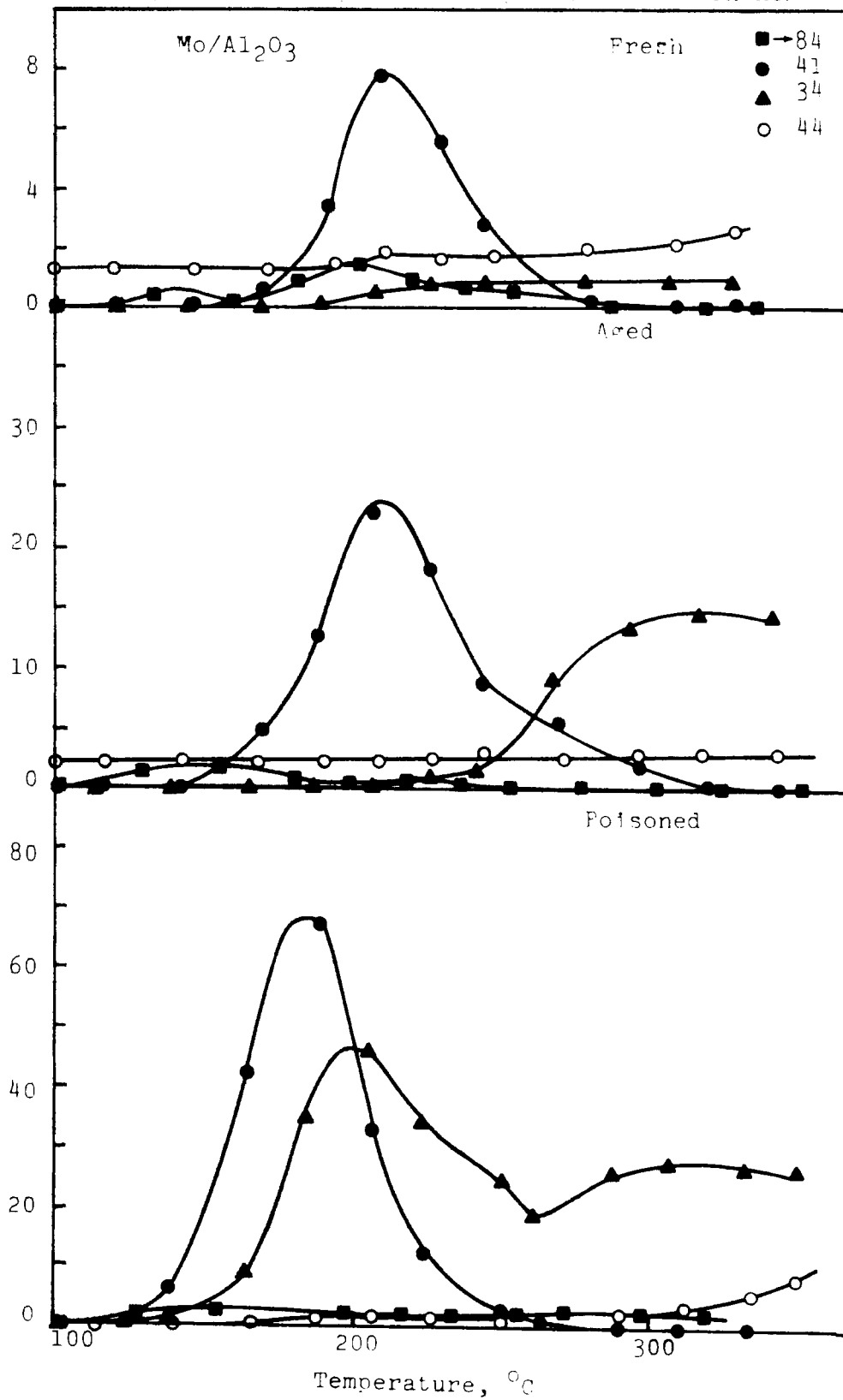Figure 3. Thiophene Adsorption and TPD in He using Ketjen CoMo Catalyst.

Temperature, $^{\circ}C$

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Figure 4. Thiophene Adsorption and TPD in He.

Project B-4

Mechanism of Catalytic Hydrogenation
by Metal Halide Catalysts

The Initial Stage of Coal Hydrogenation in the Presence of Catalysts

Faculty Advisor: D.M. Bodily
Postdoctoral Fellow: R. Yoshida

Introduction

Studies of the treatment of coal with hydrogen under mild reaction conditions indicate that the benzene-soluble products from the initial stages of the reaction are structurally different from the products obtained at longer reaction times. These products may originate from structurally different portions of the original coal. Kinetic studies of coal hydrogenation show that the reaction may be divided into two stages, an initial stage where the rate of reaction is rapid and a second stage where the reaction rate is comparatively slower.

The reaction rate of the initial stage is related to coal parameters such as volatile matter and fixed carbon content. These parameters are related to the thermal reactions which occur upon heating. The soluble products of the first stage are of relatively low molecular weight and could be attributed to the thermal reactions occurring in the initial stages of the reaction. The reaction rate of the second step is independent of coal rank. These results could also be interpreted in terms of a dual structural system in coal.

Hydrogasification of coal also occurs in two stages. The initial stage is very rapid while the second stage is much slower. Rate constants for the initial stage are proportional to the volatile matter of the feed coal, but at higher conversions the rate constants for all coals approach one another. Optimum conditions for the formation of organic liquid products during the initial stage have been determined.

Pyrolysis and dissolution of a high-volatile Utah coal have been discussed and compared with hydrogenation. These reactions involve an initial rapid process followed by a slower process. The original coal may contain considerable quantities of nonaromatic and low molecular weight aromatic constituents which can be liberated through purely thermal

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rupture and internal stabilization of bonds during the initial
stage. A recent study on flash heating of high volatile
coal indicates that coal is composed of at least two very
different structures, and the result of flash heating is
the evolution of smaller molecules less tightly bound. The
yield of these molecules is proportional to volatile matter
content.

The postulate of a dual structure in coal is consistent
with results of mass spectrometry and solvent extraction
experiments on coal.

When coal hydrogenation is considered in terms of a
dual structure model, the initial stage of the reaction is
of great importance in the design of a hydrogenation process.
The initial stages of coal hydrogenation will be studied
using several catalyst systems.

Project Status

The formation and chemical strucutre of preasphaltenes
were investigated. The toluene-insolubles were extracted
with 20 vol of pyridine per weight of toluene-insolubles at
room temperature (Preasphaltene-I). The residue was
further extracted with pyridine in a Soxhlet extractor at
the boiling point of pyridine (Preasphaltene-II).

In the short residence time process, preasphaltene is the
major product, and the yield increases with conversion of the
coal to pyridine-solubles and gases up to 65% conversion for
$ZnCl_2$ catalyst as shown in Figure 1. Beyond 65% conversion,
preasphaltenes decrease and hexane-soluble oils increase
rapidly. Asphaltene-II (hexane insoluble/toluene solubles)
also increases.

The oxygen, nitrogen and sulfur content of the preasphal-
tene is higher than that of the asphaltenes or oils and is
similar to that of the original coal as shown in Figure 2. The
hydrogen to carbon ratio of the preasphaltenes is less than
that of the asphaltenes and oils.

In Figure 3 changes of structural parameters with conver-
sion (1-pyridine-insolubles) are shown. These structural
parameters were calculated from 'H-NMR and elemental analysis
data by using the equation of Brown-Ladner. In calculating
the degree of substitution of structural units (σ) and the
aromatic hydrogen-to-carbon ratio of the hypothetical unsub-
stituted aromatic material (H_{au}/C_a) of Preasphaltene-I con-
taining high content of heteroatoms, two extreme cases were
assumed on heteroatoms.

1) All heteroatoms occur as phenols, amines (excluding

diphenyl- and triphenylamine) and thiophenols. In this case σ and H_{au}/C_a are defined as follows:

$$\sigma_1 = \frac{\frac{1}{x} \cdot \frac{H_\alpha}{H} + \frac{O,N,S}{H}}{\frac{1}{x} \cdot \frac{H_\alpha}{H} + \frac{H_{ar}}{H} + \frac{O,N,S}{H}}$$

$$\left(\frac{H_{au}}{C_a}\right) = \frac{\frac{1}{x} \cdot \frac{H_\alpha}{H} + \frac{H_{ar}}{H} + \frac{O,N,S}{H}}{\frac{C}{H} - \frac{1}{x} \cdot \frac{H_\alpha}{H} - \frac{1}{y} \cdot \frac{H_o}{H}}$$

2) All heteroatoms occur as heterocyclic types. In this case σ and H_{au}/C_a are defined as follows:

$$\sigma_2 = \frac{\frac{1}{x} \cdot \frac{H_\alpha}{H} + 2\left(\frac{O,N,S}{H}\right)}{\frac{1}{x} \cdot \frac{H_\alpha}{H} + \frac{H_{ar}}{H} + 2\left(\frac{O,N,S}{H}\right)}$$

$$\left(\frac{H_{au}}{C_a}\right)_2 = \frac{\frac{1}{x} \cdot \frac{H_\alpha}{H} + \frac{H_{ar}}{H} + 2\left(\frac{O,N,S}{H}\right)}{\frac{C}{H} - \frac{1}{x} \cdot \frac{H_\alpha}{H} - \frac{1}{y} \cdot \frac{H_o}{H}}$$

Actual values of σ and H_{au}/C_a for preasphaltenes are between σ_1 and σ_2, and $(H_{au}/C_a)_1$ and $(H_{au}/C_a)_2$. The range is shown by the bars in Figure 3. For preasphaltene-I, the aromaticity (f_a) and the degree of substitution of structural units are higher, and the length of alkyl substituents on the aromatic ring $(H_o/H_\alpha + 1)$ is shorter than those of oil and asphaltene. The number of aromatic rings per structural unit is 1-2 rings.

From these results preasphaltene-I is characterized by carbon aromaticities of 0.6 to 0.7, 1-2 aromatic rings per condensed aromatic ring system, 60~70% substitution of aromatic ring carbons and C_{2-3} aliphatic chains.

In the 'H-NMR spectra of preasphaltene-II, resonance lines are observed at 3.5 ~ 4.5 ppm and 9.3 ~ 9.9 ppm. These lines are not observed in the spectra of oil and asphaltene. The former is assigned to hydrogens bound to carbon atoms in β and γ positions relative to aromatic rings which are substituted by oxygen atoms, and β hydrogens of phenylcumarane type. The latter is assigned to phenolic protons. Consequently, the existence of ether, phenolic and alcoholic oxygen are intimated.
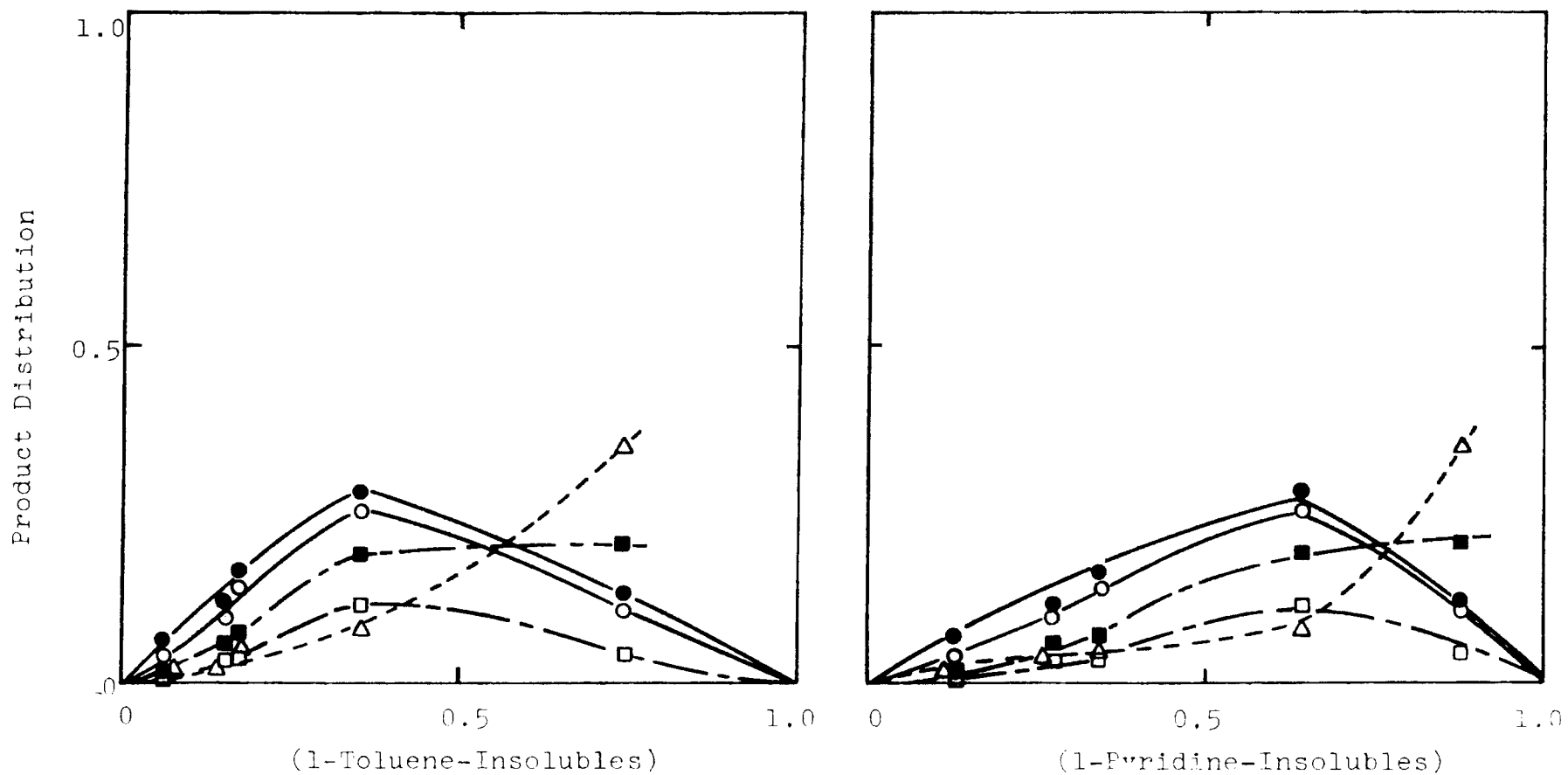
Figure 1.   Product Distribution Vs. Conversion with $ZnCl_2$.

—●— Preasphaltene-I + Preasphaltene-II
—○— Preasphaltene-I
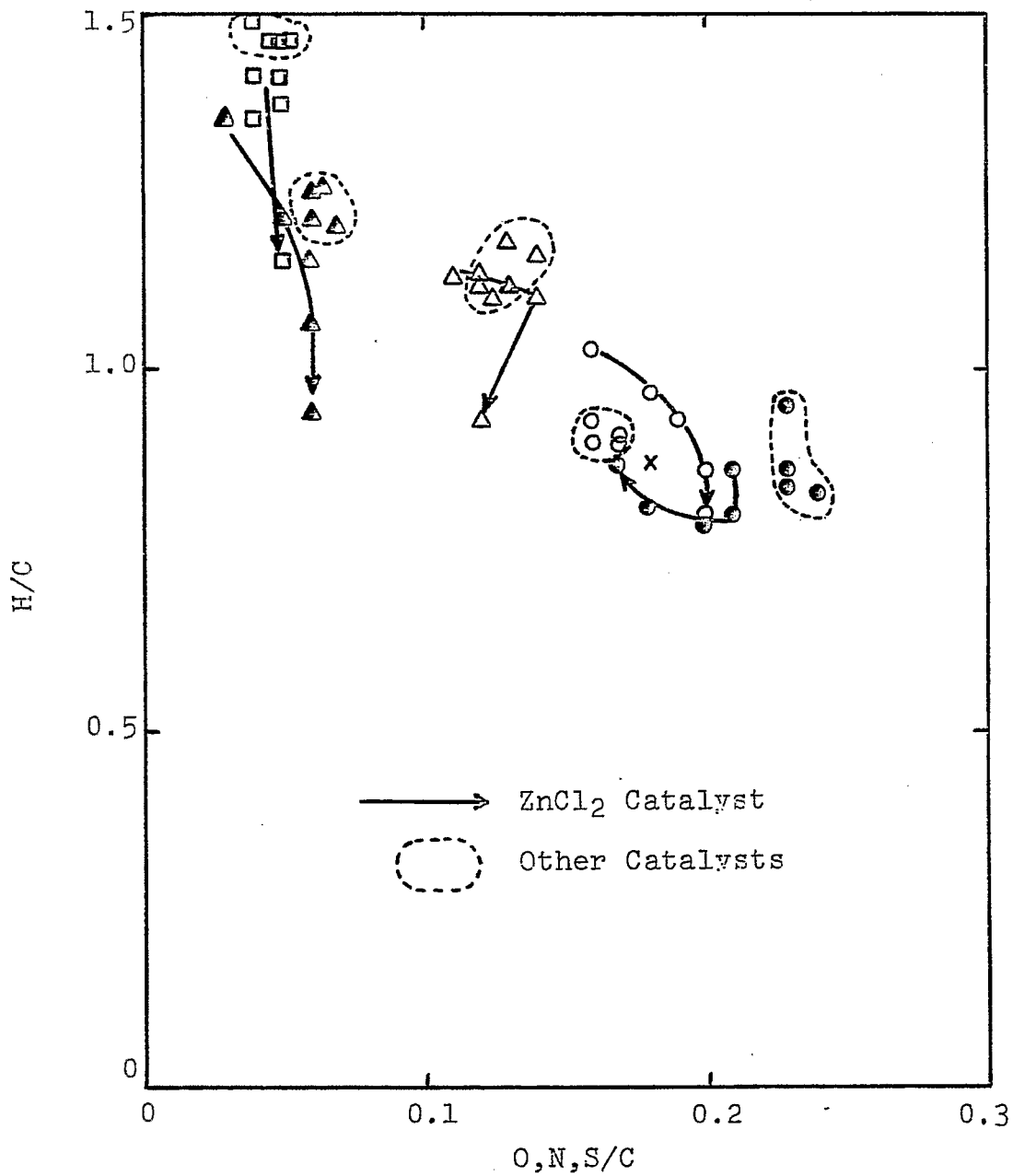—■— Asphaltene-I + Asphaltene-II
—□— Asphaltene-I
--△-- Oil

Figure 2. H/C-O,N,S/C in Parent Coal and Hydro-
Hydrogenation Products.

✕ Parent Coal
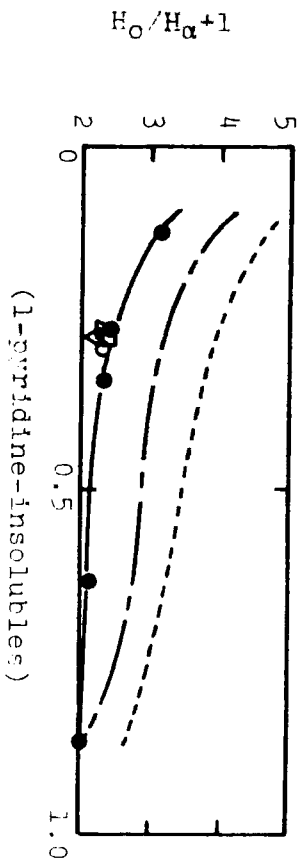○ Preasphaltene-I
◐ Preasphaltene-II
△ Asphaltene-I
▲ Asphaltene-II
▢ Oil

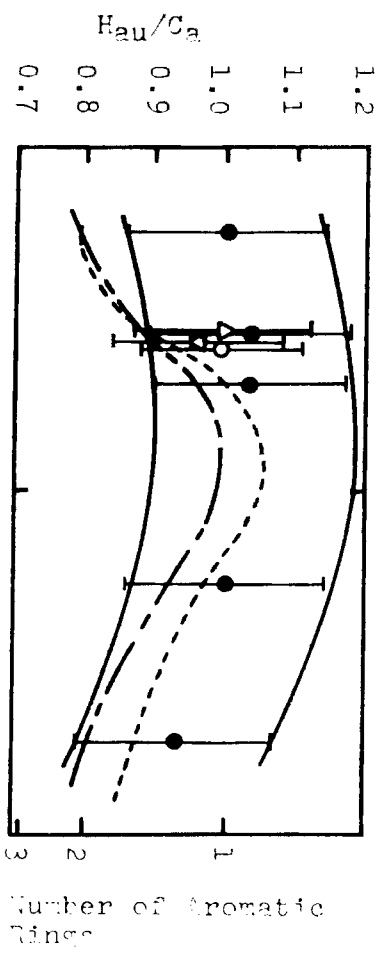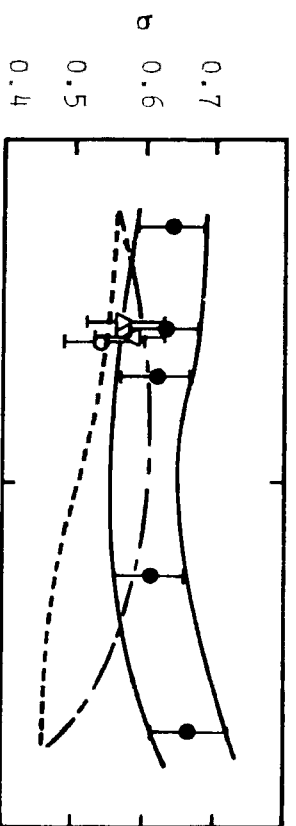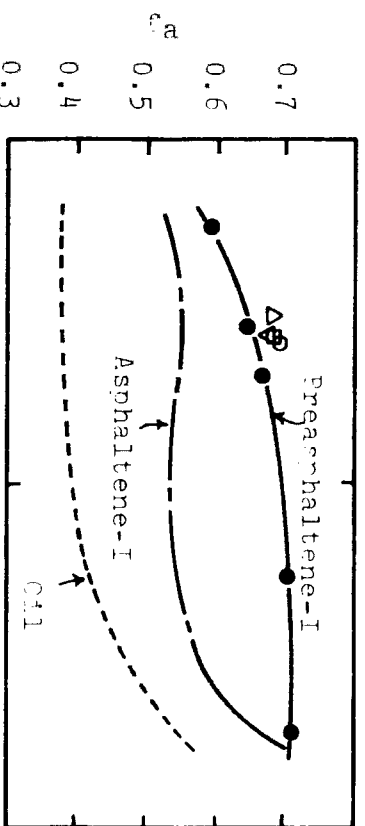Figure 3. Structural Parameters of Preasphaltene-I.
(1-pyridine-insolubles)

● ZnCl2
▲ Co-Mo
□ Presulfided Red-Mud
○ Red-Mud Plus Sulfur
▽ No Catalyst

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Mechanism of Catalytic Hydrogenation by
Metal Halide Catalysts

IR Studies of Coal Metal Salts Interactions

Faculty Advisor: R.E Wood
Graduate Student: Doug Stuart

Introduction

Coal catalyst interactions are being investigated using infrared spectroscopy. Various coal molecular bond structures have been associated with peaks in the IR spectrum. These peaks are being compared for different coals and chars to monitor change in the associated structure.

The potassium bromide pellet sample preparation procedure has been standardized and the coal and char spectra have been obtained.

Project Status

The IR spectra of the heavy liquids were useful in determining changes in structure. The heavy liquids are the liquid reaction product of the hydroliquefaction reaction that have an atmospheric boiling point greater than 300°F. Heavy liquid samples were available for 22 of the 24 coal samples studied. In most cases the heavy liquid was from the same run as the char.

The heavy liquid IR spectra were obtained under the same spectrometer conditions as the coal and char samples. These spectra were from a thin film of the heavy liquid between sodium chloride windows rather than from a potassium bromide pellet. The spectra are qualitative rather than quantitative because no effort was made to measure the sample film thickness nor to maintain a uniform thickness.

Future Work

The coal, char and heavy liquid spectra are now being compared both qualitatively and quantitatively (where possible), and a final report is being prepared.

Project C-1

The Mechanism of Pyrolysis of Bituminous Coal

Faculty Advisor: W.H. Wiser
Graduate Student: John Shigley

Introduction

In the present state of knowledge concerning the funda-
mental 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. Hence, the stabili-
zation involving abstraction of hydrogen from the hydroaromatic
structures by the free radicals, believed to be the predominant
means of yielding liquid size molecules in coal pyrolysis,
is of major importance in all coal liquefaction, except
Fischer-Tropsch variations. The objective of this research
is to understand the chemistry of this pyrolytic operation.

Project Status

Two model compounds are being synthesized by Parrish
Chemical Company of Provo, Utah.[1]

In linking the thermogravimetric system to a gas
chromatograph, certain problems have been foreseen, including
condensation of reaction products, free radical reactions
with the surfaces, etc. Several methods are being studied
to alleviate these problems.

An extensive literature search is being conducted to
collect any valuable information from previous work.

Future Work

The equipment will be assembled and calibrated. Several
test runs will be made to insure the consistency and integrity
of the system. The mechanism and kinetics of the model compounds
will be determined.

References

1. W.H. Wiser et al., DOE Contract No. E(49-18)-2006,
   Quarterly Progress Report, Salt Lake City, Utah, Jan-Mar 1979.

Project C-2

Heat Transfer to Gas-Solid Suspensions in
Vertical Cocurrent Downflow

Faculty Advisor: J.D. Seader
Graduate Students: J.M. Kim
B.S. Brewster

Introduction

This project is concerned with an investigation of the momentum and heat transport phenomena for gas-solids suspensions flowing vertically downward through a heated tube. Motivation for conducting this research comes from the lack of data or correlations in the literature pertaining specifically to the cocurrent configuration, which has recently found application to the coal conversion reactors. Studies with glass bead-air and coal particle-air suspensions are being conducted.

Project Status

Based on pressure drop and heat transfer results obtained for the study of downflow for suspensions of air and glass beads, the following conclusions have been drawn:

1. Both hydraulic and thermal entry lengths are extended by the addition of particles and are more dependent on the solids flow rate or loading than on the gas Reynolds number.

2. In downflow, a negative total pressure drop can occur; however, if the static head effect is accounted for by adding the weight of particles, the resulting frictional pressure drop becomes positive and is a weak function of solids-loading ratio.

3. The frictional pressure drop can be correlated in terms of the two-phase friction factor which is a function of gas Reynolds number and a dimensionless parameter, α, derived in this study from a similarity analysis of the equations of change and discussed in the previous report.

4. The presence of particles seems to have a stabilizing effect on suspension flow in the transition region.

5. The pressure drop through a packed bed can also be correlated in terms of the parameter α. Comparison of the correlations for dilute-phase transport and the packed bed indicate that the parameter α may find applicability in correlating the frictional pressure drop for the general gas-solids systems. Further study is necessary to confirm this conclusion.

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6. Particle size has a great effect on the particle temperature attained in a heated tube. The temperature of 329-micron particles is much lower than the gas temperature. For smaller-diameter particles, temperature differences will probably diminish.

7. Because of the above results, Nusselt numbers based on suspension mixed-mean temperature can give erroneous conclusions about heat transfer mechanisms for coarse-particle suspension.

8. At a gas Reynolds number of 9800, the asymptotic Nusselt number, based on the gas mixed-mean temperature, stays almost constant for solids-loading ratios up to 20. However, it decreases with an increase in the solids-loading ratio at high Reynolds numbers. This can be explained by considering the opposing effects of particles on the suspension heat transfer; boundary layer thinning, which enhances the heat transfer; and reduced turbulence near the wall, which inhibits the heat transfer.

9. Although no increase in Nusselt number with solids-loading ratio was found, as shown in Figure 1, the total heat transfer rate from the wall to suspension increases with solids loading because of increased thermal capacity.

10. A qualitative comparison of the present data with the upflow results in the literature shows that momentum and heat transfer processes of suspensions in downflow are weaker than in upflow.

For the coal particle-air studies, pressure drop and particle velocity measurements have been completed for the -28/+48 mesh coal sample. The results of the particle velocity measurements are shown in Figure 2 and compared with the particle velocity calculated for the glass beads from the experimental holdup data. The glass beads are seen to lag the gas by as much as 30 percent while the slip velocity with the coal particles is negligible. Since the coal particles are irregularly shaped and thus have a lower density and higher drag coefficient, they accelerate faster than the spherical glass beads. No effect of particle size, loading, or phosphor coating on particle velocity was detected. Thus the assumption of no slip between the gas and particles seems justified for evaluation of the pressure drop data with coal. These data are currently being processed to determine the static and frictional components of the total pressure drop.

A diagram of the heat transfer section for which fabrication and installation are now complete is shown in Figure 3. Several heat transfer runs with gas alone have been made to test the operation of the equipment and determine the heat loss. The mixed-mean temperature of the outlet gas is calculated by assuming a gas velocity profile and then integrating the

measured temperature profile. Since the heat input is
adjusted at each gas flow rate to give approximately the
same wall temperature profile, the heat loss to the surroundings
should be constant for all runs. However, the heat loss at
Re = 10000 is about 10 percent of the total heat input, where-
as the heat loss at Re = 30000 is negligible. The same pro-
blem occurred in the glass bead experiments and has been
explained. Local Nusselt numbers are calculated from the
measured wall temperature, and the asymptotic values agree with
the equation of Sparrow.

Future Work

     The remaining experiments for the coal particle-air
system will be completed. Pressure drop and heat transfer
data will be taken simultaneously for two or three sizes of
coal. The results will be compared with the correlations
for pressure drop and heat transfer in the glass bead
suspensions.
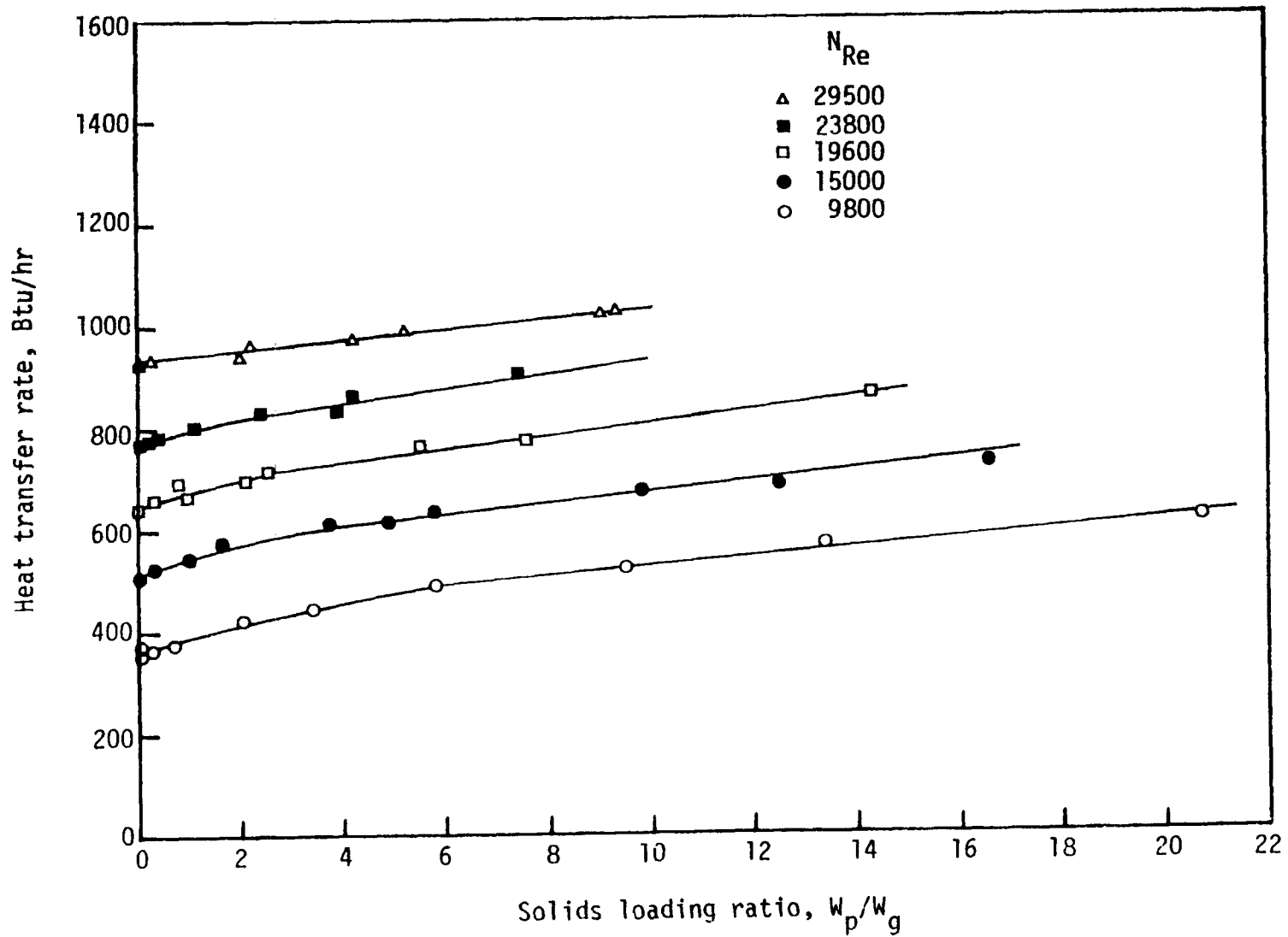
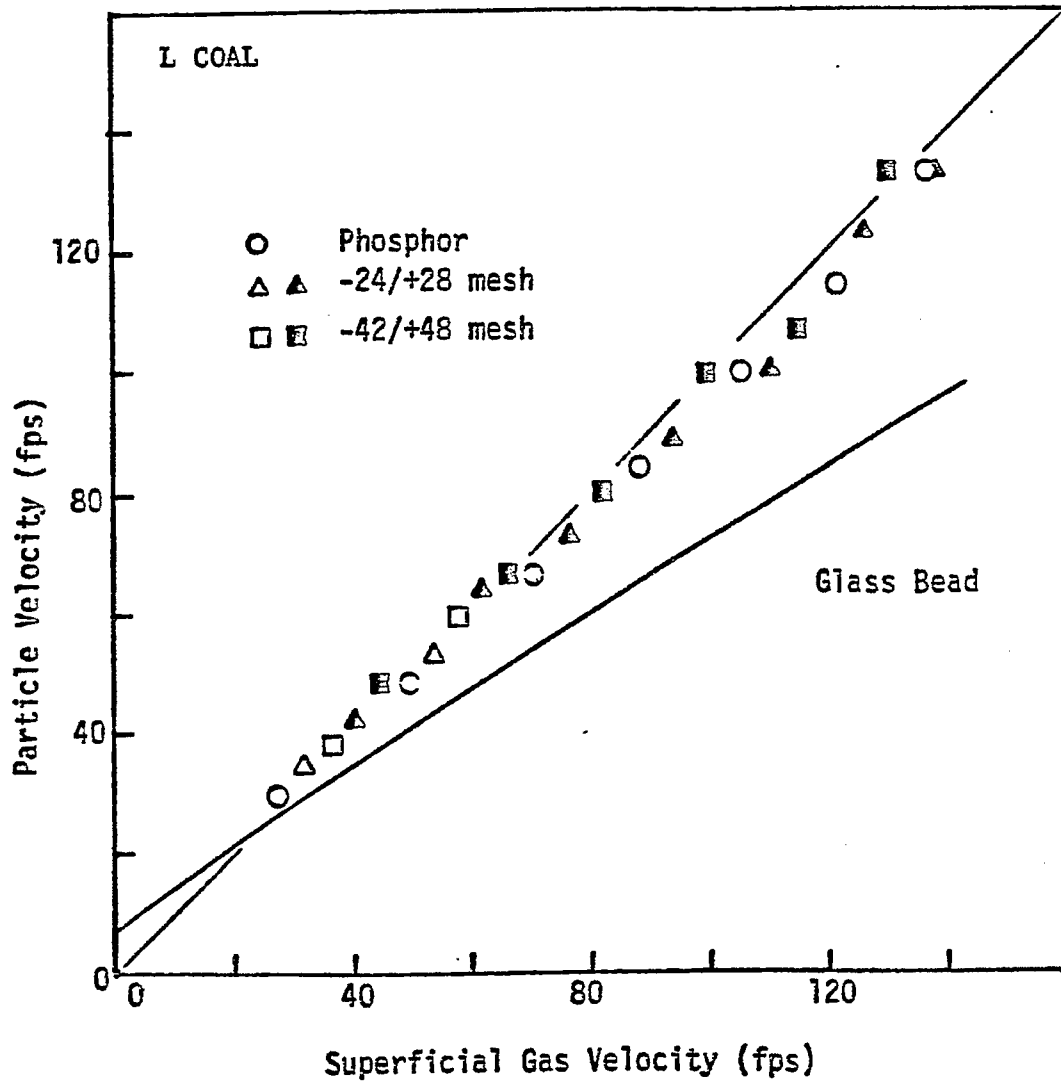Figure 1   Effect of solids loading ratio on heat transfer rate

Fig. 2. Comparison of Measured Coal Particle Velocity and
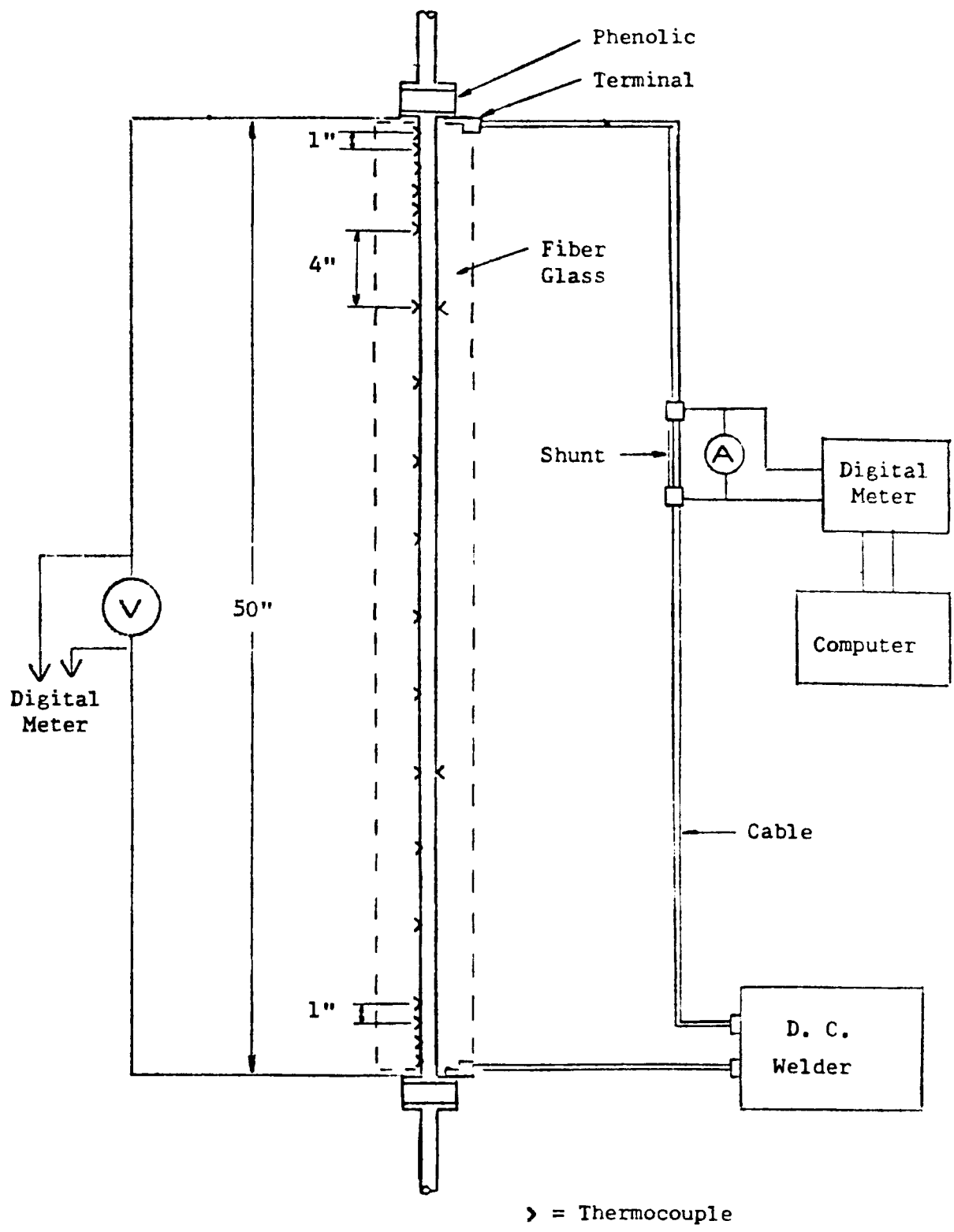Glass Bead Velocity Calculated from Holdup

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Fig. 3.   Heat Transfer Section to be Used in Coal Experiments

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Coal Particle and Catalyst Characteristics for
Hydrogenation Evaluation and Testing

Faculty Advisor: R.E. Wood
Graduate Student: J.M. Lytle

Introduction

This effort is related to the effects of coal particle
size and temperature on the rate of coal hydrogenation in
a coiled tube reactor and also a microreactor. The existing
hydrogenation equipment was used with OCR (Office of Coal
Research) Project, FE(49-18)-1200 and with ERDA-DOE Project
FE(49-18)-2006. The reaction vessel consists of a series of
coiled tubes, each approximately 20 ft long and may be
divided into two zones, preheater and reactor. The pre-
heater consists of two coils each 20 ft long and 3/16 inch
ID. The reactor consists of 1 to 4 coils, 20 ft long and
1/4 inch ID.

The residence time of coal and residual solids is
measured in the reaction vessel of the coiled tube reactor
using powdered iron as a tracer. The detection device
consists of a coil of copper wire placed coaxially with the
reactor tubing such that the ID of the copper coil is the
same as that of the tubing. For residence time detection
and measurement, one coil is placed at the beginning of the
preheat section and a second at the end of the reactor.

The microreactor is a small batch reactor which may
be heated rapidly to reaction temperature by a flame and
cooled by water quench. Reactions normally may be considered
nearly isothermal. The small size of the reactor also
makes it convenient to weigh the whole system on a 5 place
balance. This device will be used to study coal character-
istics and coal-catalyst interactions.

Project Status

This project has been completed. As the project was
brought to an end, several interesting conclusions were
obtained from the data. A previous quarterly report, con-
tained figures to show the conversion of total matter,
volatile matter and fixed carbon in the coal to liquids
and gaseous products.[1] These functions were developed for
three particle sizes and fractions of coal and for four
temperatures. The use of an "unreacted-core-shrinking
model" for the hydrogenation of coal particles in the coiled
tube reactor was discussed in the last report.[2] The
demonstration of a chemically controlled reaction regime
and an ash-diffusion controlled regime were discussed.

A variety of projections can be made from the data previously published provided that the chemical control mechanism holds for an extended range of temperature, hydrogen partial pressure and particle diameter. These projections may or may not be valid depending on the physical aspects of the system in which they are tested. That is, a reactor wherein the coal particles are essentially separated is necessary. Validity of the projections also depends on relative rates of reactions which do not contribute to the production of liquids. For instance, at high temperatures the production of gases is increased. This is especially true at temperatures greater than $600^\circ C$. The polymerization reaction may also be temperature and pressure dependent. The projections based on measured relationships represent the most rapid reaction that could be expected. This is because system reversion to a diffusion control regime will give a reduced reaction rate.

Figure 1 illustrates the very rapid increase in reaction rate with an increase in temperature. However, elevated temperatures have operational problems. Temperatures in excess of $500^\circ C$ are troublesome because of particle agglomeration. Also, hydrogen consumption is increased and product gases increase at the expense of liquid production.

Figure 2 shows the effect of pressure on the rate of reaction. An increase in pressure is effective in increasing the reaction rate. Since the chemical rate is proportional to pressure, the rate increases with pressure until depletion of hydrogen at the surface of the unreacted core exceeds the hydrogen made available by diffusion through the inert layer. At this point, the reaction rate is independent of the hydrogen pressure.

Although pressure is effective in increasing chemical reaction rate, it also increases the expense of process equipment. The largest rate may not necessarily be the most economical. The lower the pressure the more "off the shelf" equipment is available. The feeding of dry coal into and the removal of products from a high pressure environment becomes easier with a reduction in pressure.

Figure 3 shows the effect of coal particle diameter on the chemical reaction rate. The rate increases remarkably with a reduction of size. The smaller particles of coal (2.5 to 10 microns) are somewhat difficult to obtain because of grinding costs. However, recent advances in grinding technology have made the use of smaller particles possible. As expected, the power requirements for grinding increase rapidly with a decrease in the average particle size. Medium particle sizes of 19, 11, 7, 4 and 3 microns were attained with a power requirement of 13, 80, 199, 402 and 842 kilowatt hours per ton of coal, respectively. This was accomplished with samples of Montana Rosebud coal in an "attritor" grinding device. An economic analysis would be required to discover what particle size coal should be used.

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Figures 4 and 5 further illustrate the particle size effect. If coal is to be converted 75% (X_{FC} = 0.6) to liquids and gases at less than 500°C, the particle size should be less than 100 microns. This reaction may be done in 25 seconds or less as shown in Figure 6. The time requirement becomes less as the particle size is reduced. If the time requirement was 10 seconds or less, the particle size should be 32 microns or less. The pressure in these instances is 12.4 MPa H_2. If the pressure is reduced, the time requirement for 75% conversion increases (Figure 6). The projection is that 55 seconds reaction time would be required for 75% conversion for 50 micron coal particles and a pressure of 3.5 MPa.

The general conclusions from this study are as follows: A coal hydrogenation reactor has been designed which 1) facilitates the feeding of dry coal particles instead of a liquid-coal slurry into a medium pressure and medium temperature reactor, 2) reacts the coal in a short time (1-200 seconds) to produce liquids and gases, and 3) has a large space rate utilization factor (1-150 kg/m^3 sec).

The coal hydrogenation reaction may be monitored by following the change in fixed carbon in the residual char or unreacted coal with time. Fixed carbon requires hydrogen for conversion to liquids, gases or volatile matter whereas volatile matter does not require additional hydrogen for conversion to liquids or gases. This viewpoint is an approximation only.

The data from the coal hydrogenation reactor has been applied to the unreacted-core-shrinking model. The results of this application are as follows: 1) The effects of coal particle size, temperature and pressure are quantitatively explained by the unreacted-core-shrinking model; 2) The rate of coal hydrogenation may be controlled by (a) the rate of the chemical reaction on the outer surface of the unreacted core of the coal particle or (b) the rate of diffusion of hydrogen into the coal particle through its inert outer layer; 3) The reaction rate will be chemically controlled with small coal particles, low pressures and low temperatures; 4) The reaction rate is inversely proportional to the coal particle diameter with a chemically controlled and inversely proportional to the square of the particle diameter for a diffusion controlled reaction; 5) Projections based on this model show that conversions of 75% or above may be attained at 3.5 MPa (500 psig) in less than two minutes at 500°C and a particle size of 50 x 10^{-6} meters and 6) The unreacted-core-shrinking model has been applied in the study of coal combustion, but not previously applied to coal hydrogenation.

The data which lead to a chemical mechanism of coal pyrolysis-hydrogenation illustrates the following ideas:

1. The addition of molecular hydrogen without catalyst is

very slow at temperatures below 600°C.

2) The hydrogenation reaction is very rapid with $ZnCl_2$ added as a catalyst to the coal.

3) The $ZnCl_2$ hydrogen complex provides an alternate source of hydrogen to the hydroaromatic hydrogen already available in the coal.

4) Thermally produced free radicals in the coal are stabilized by the addition of hydrogen (catalytically or from the hydroaromatic) or by the recombination of two free radicals.

5) Addition of hydrogen tends to produce liquids and gases, whereas the recombination of two free radicals tends to produce solids.

A final report has been prepared and will be incorporated as part of the contract Final Report.

References

1. W.H. Wiser et al., DOE Contract No. E(9-18)-2006, Quarterly Progress Report, Salt Lake City, Utah, Oct- Dec 1978.

2. ibid., Jan-Mar 1979.
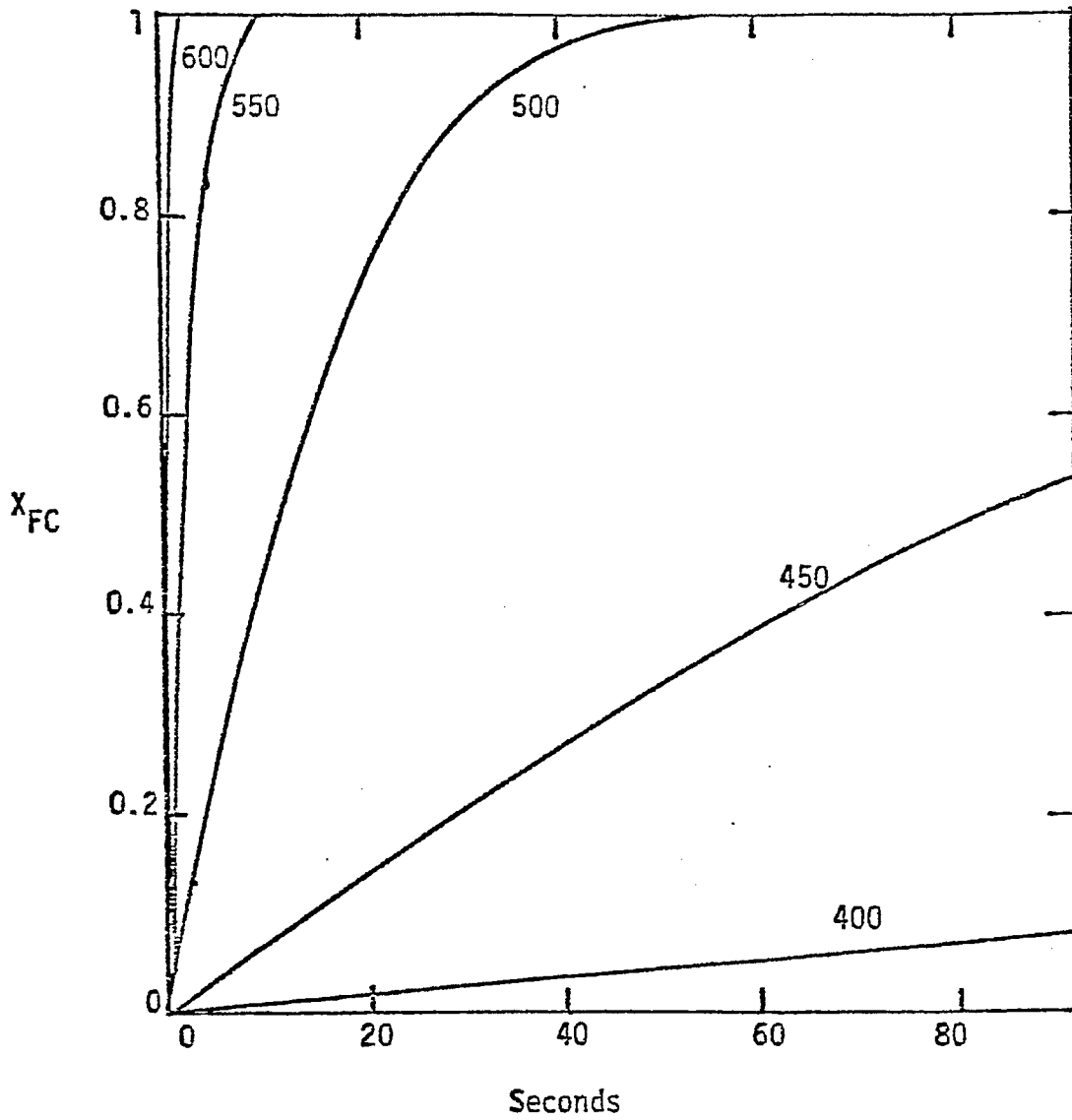
Figure 1. X_{FC} vs. Time for various temperatures (^{o}C listed on lines). Pressure is 12.4 MPa H_2 and initial particle diameter in 50 x 10^{-6} meters. Calculated numbers shown in Table C3.
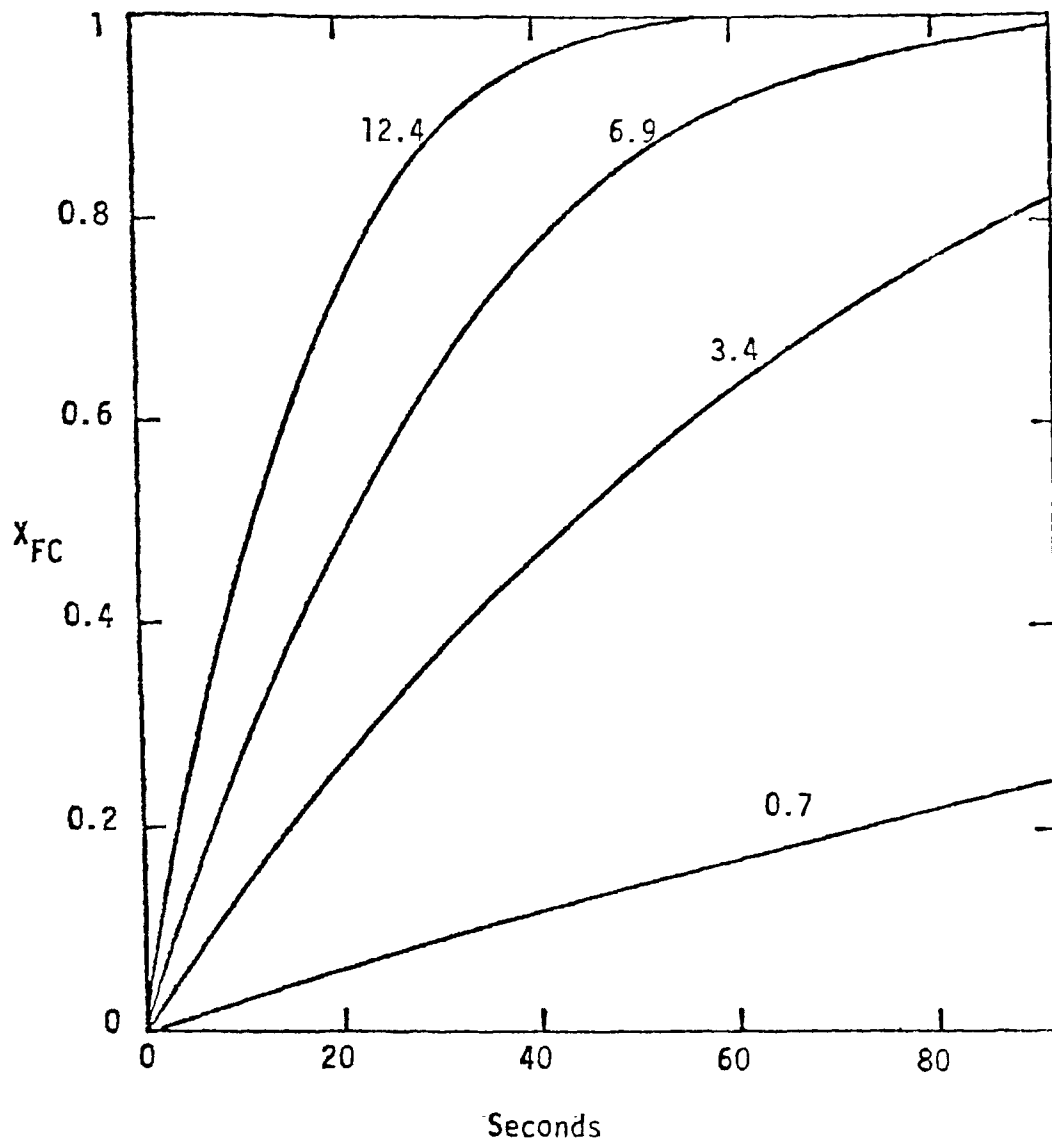
Figure 2. X_{FC} vs. time for various pressures (MPa listed on the lines). Temperature is 500°C and initial particle diameter is 50 x 10⁻⁶ meters. Calculated numbers shown in Table C4.
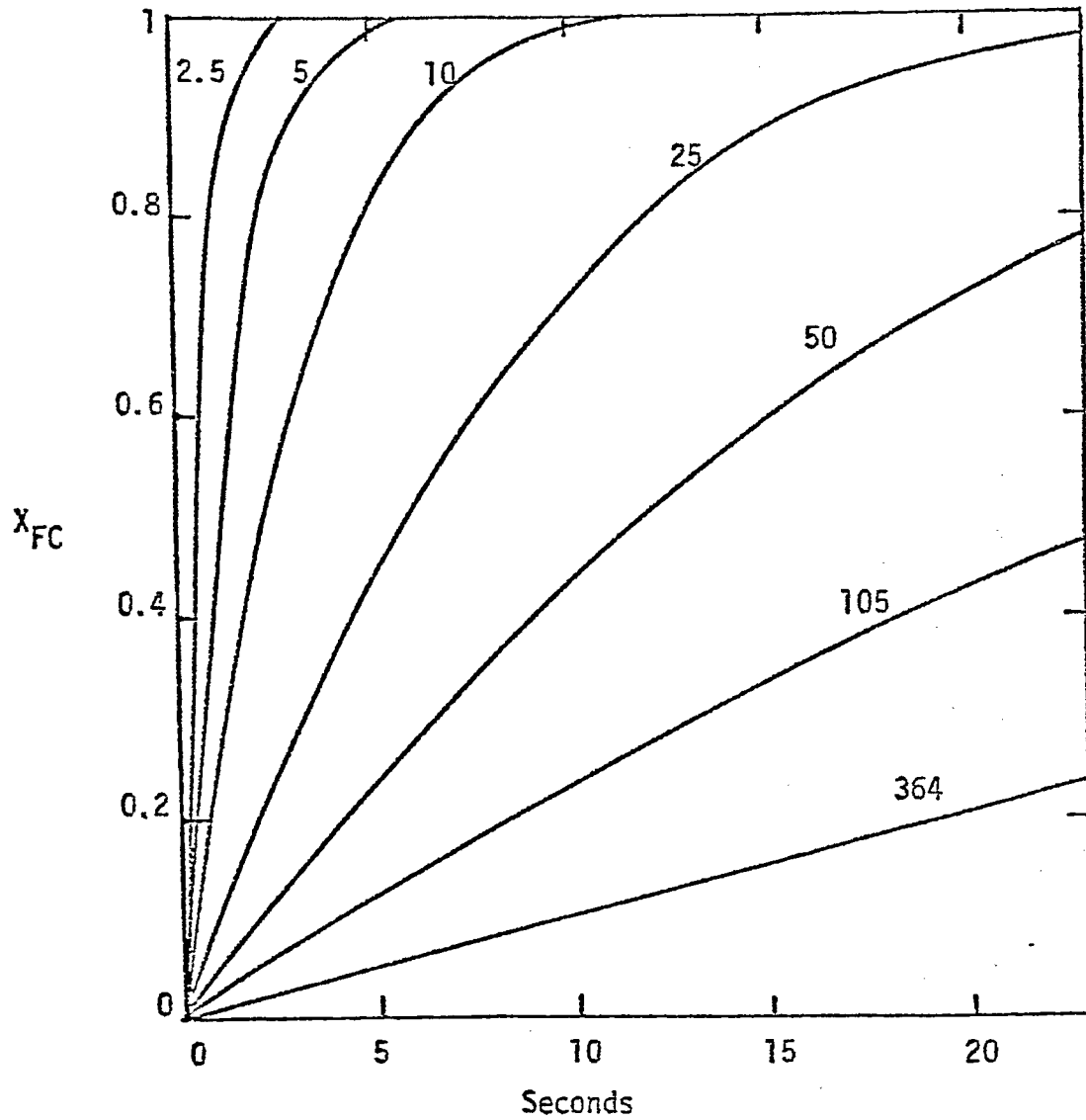
Figure   3. X_{FC} vs. time for various initial particle diameters (10^{-6} m listed on curves).' Temperature is 500°C and pressure is 12.4 MPa H_2.   Calculated numbers are listed in Table C5.
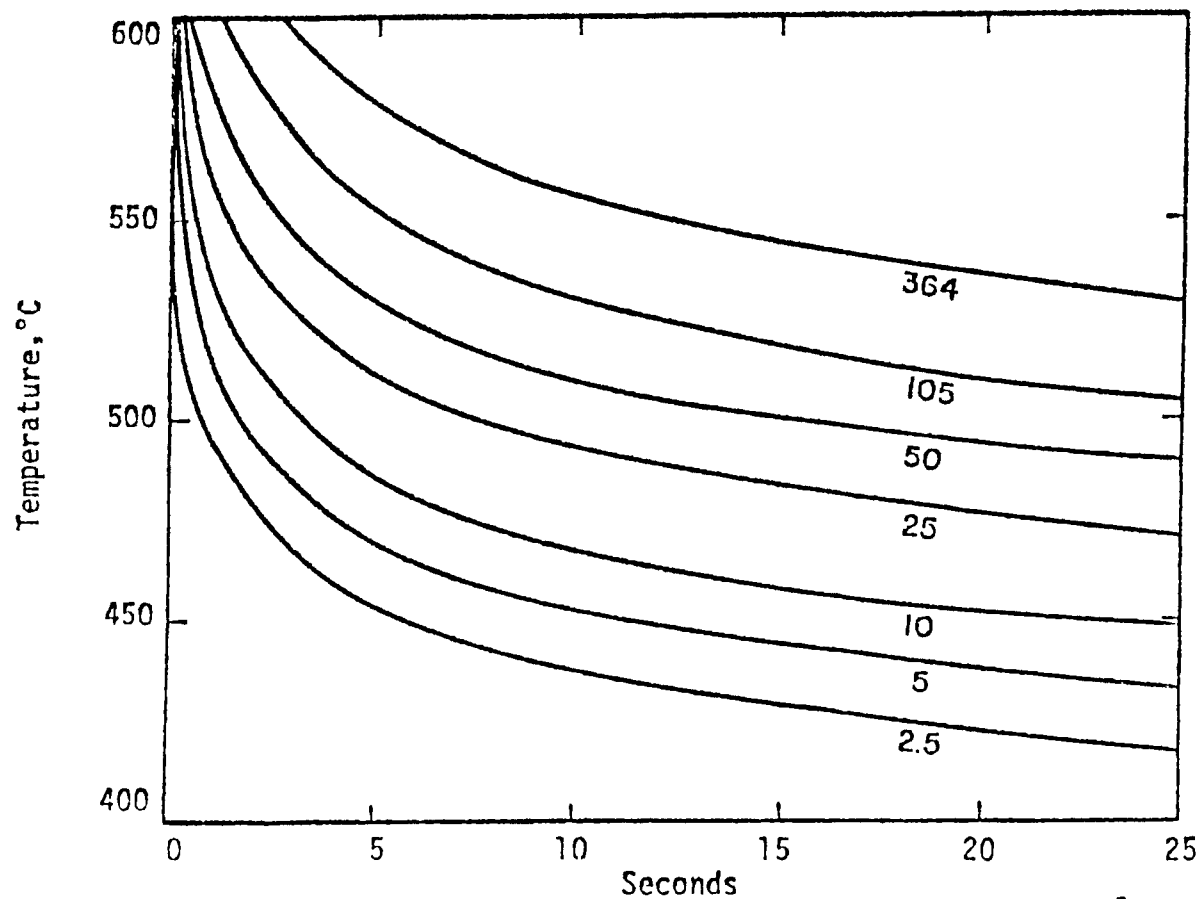
Figure 4. Time vs. temperature for various sizes of coal particles, (10^{-6} meters listed on curves) to reach $X_{FC} = 0.6$ (approximately 75% coal conversion). Pressure is 12.4 MPa H_2 and catalyst is 6.25% $ZnCl_2$ on Clear Creek, Utah coal. Calculated numbers shown in Table C6.
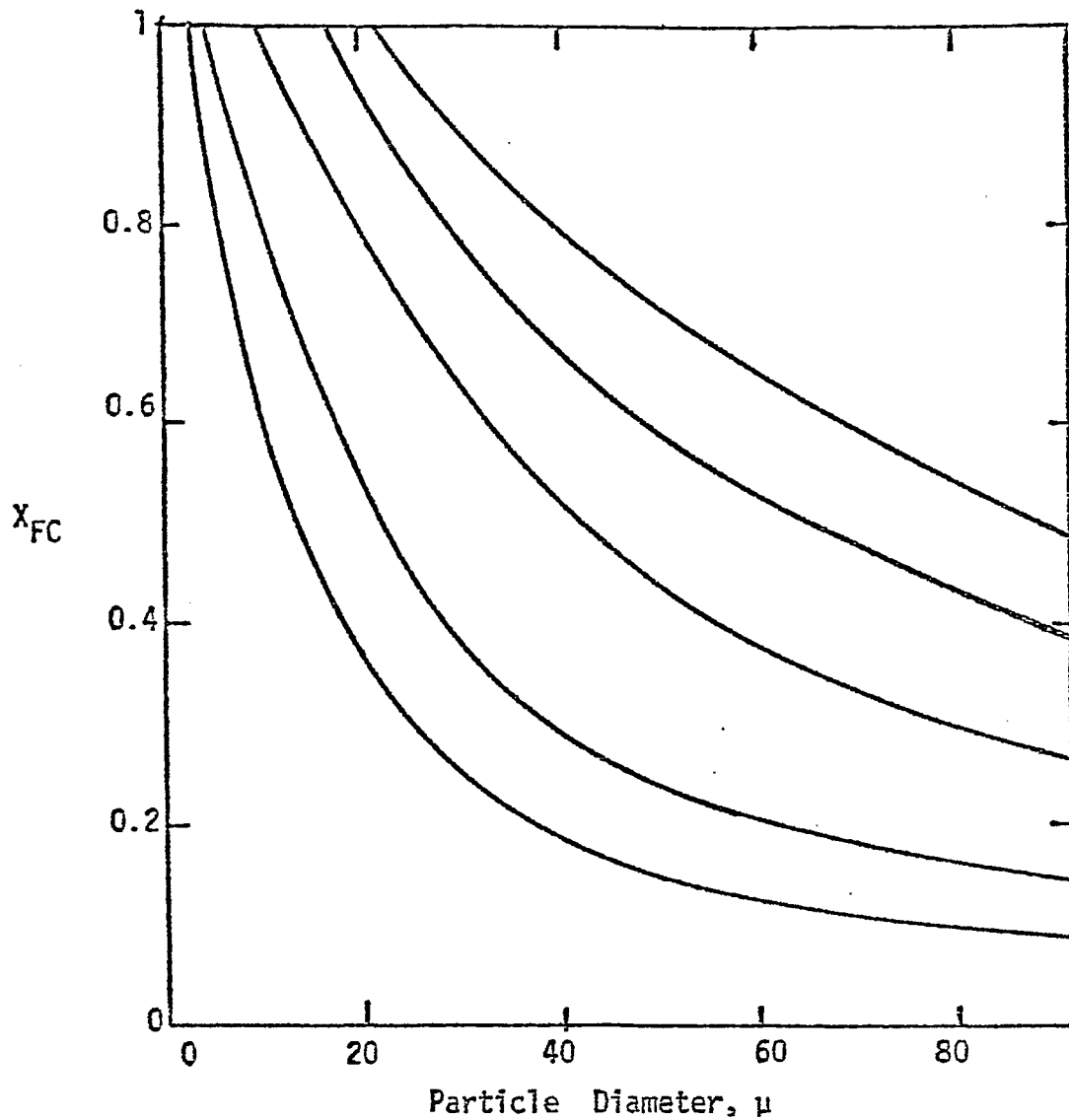
Figure 5. X_{FC} vs. particle diameter for various times (seconds listed on curves). Temperature is 500°C and pressure is 12.4 MPa H_2. Curves are formed by taking specific points from Figure 55.
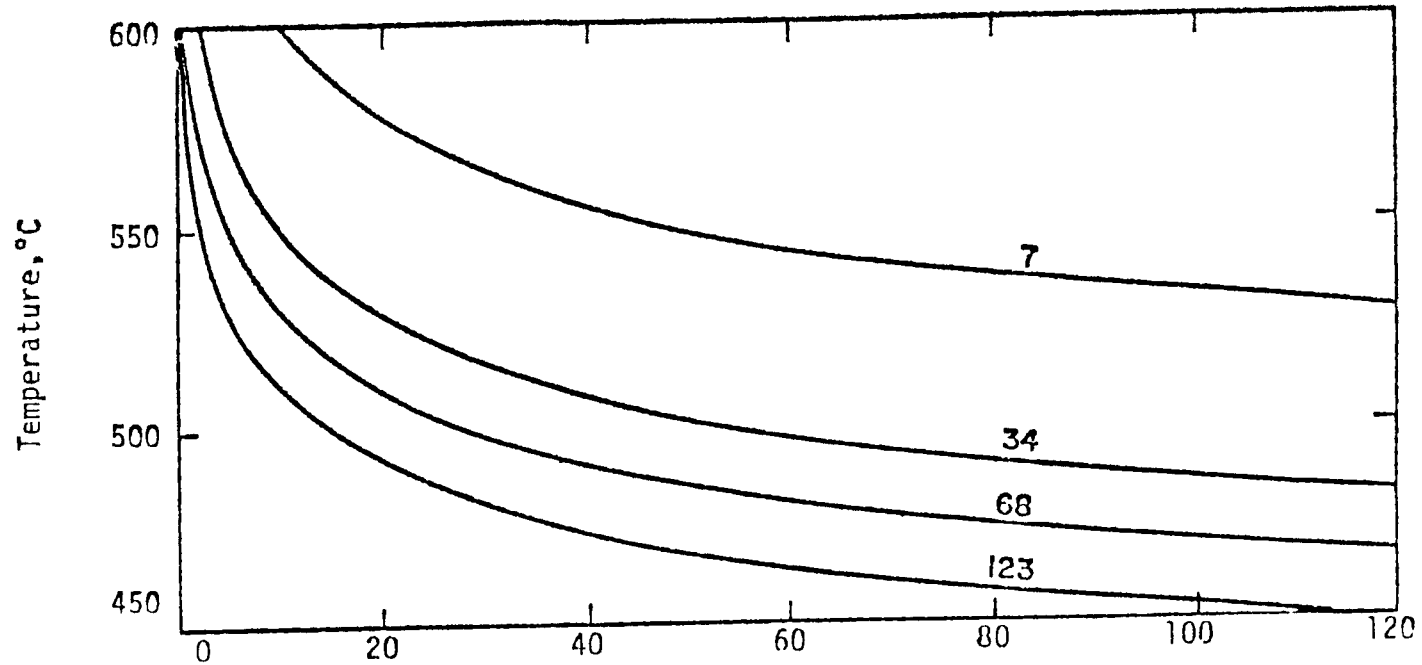
Figure 6. Time for Various Temperatures and Pressures (Atm Listed on Curves; 1 atm = 0.1013 MPa) to reach $X_{FC} = 0.6$ Which is Equivalent to about 75% Total Conversion. Catalyst is 6.25% $ZnCl_2$ on Clear Creek, Utah Coal. Particle Diameter = 50 x 10^{-6} meters. Calculated Numbers are Listed in Table C7.

Project D-1

Coal Particle and Catalyst Characteristics for Hydrogenation Evaluation and Testing

Faculty Advisor: R.E. Wood
Graduate Student: R. Jensen

Introduction

The mechanism of coal hydrogenation is being studied using $ZnCl_2$ as a catalyst and a small pressureized reactor, called a microreactor. This work will be a continuation of previous studies sited in a paper by D.P. Mobley et al.[1] The same model compounds will be stuided using the optimum conditions of the University of Utah's coal hydrogenation system. These compounds represent various connecting groups found in coal and will be subjected to different temperatures, catalyst concentration and reaction times. The reaction products will be analyzed by gas chromatography and compared to proposed products from dealkylation of the model compounds, yielding reaction mechanism information.

Previous work includes 1) the acquisition of model compounds, 2) the manufacture of reactors and 3) the testing of model compounds using various catalyst concentrations and temperature ranges.

Project Status

Preliminary results indicate that $ZnCl_2$ functions as a duel purpose catalyst. At lower temperatures, i.e., $400^{\circ}C$, $ZnCl_2$ appears to behave as a reverse Friedel Crafts acid catalyst, while at higher temperatures, i.e., $500^{\circ}C$, $ZnCl_2$ behaves as a hydrogenating catalyst.

Future Work

Five compounds have been studied. Nineteen compounds will be tested. The results from these experiments should provide a better understanding of the function of the $ZnCl_2$ catalyst.

References

1. D.P. Mobley, S. Salim, K.E. Tanner, N.D. Taylor and A.T. Bell, Preprints, Div. of Fuel Chemistry, American Chemical Society, Miami, Florida, Sept 1978, Vol. 25, No. 4.

Project D-4

A Pyrolysis-Gas Chromatography Study of Coals and Related Model Compounds
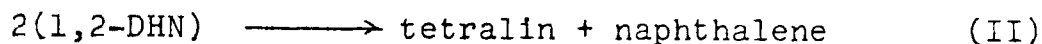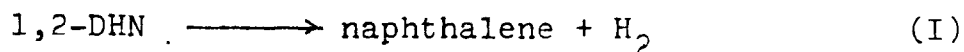
Faculty Advisor: R.R. Beishline

Introduction

This project deals with the pyrolysis and hydrogenation of coal and coal-related model compounds both in the presence and absence of catalysts.

Since coal hydrogenations are normally carried out at thermolytic temperatures, reactions other than hydrogenation likely occur concurrently, e.g., pyrolysis and reactions that can be catalytically initiated at subthermolytic temperatures and that would proceed at accelerated rates at thermolytic temperatures. A knowledge of these latter reactions is a necessary background to the understanding of the hydrogenation chemistry. To elucidate some of this background, the subthermolytic (165°C) zinc chloride-catalyzed decomposition of the model compound 1,2-dihydronaphthalene (1,2-DHN) has been studied.

The decomposition occurs by a mechanism in which hydrated zinc chloride donates a proton to the double bond of 1,2-DHN to form a carbonium ion. This carbonium ion adds to 1,2-DHN to give two dimers and abstracts hydride from 1,2-DHN to produce tetralin and naphthalene.

A study of the pyrolysis of 1,2-DHN has been initiated, and preliminary kinetic results suggest that the following scheme of simultaneous first and second order reactions is operative.

$$1,2\text{-DHN} \longrightarrow \text{naphthalene} + H_2 \qquad (I)$$

$$2(1,2\text{-DHN}) \longrightarrow \text{tetralin} + \text{naphthalene} \qquad (II)$$

The 1,2-DHN is an intermediate in the hydroliquefaction of coal when tetralin is used as the hydrogen donor solvent.[1] Reactions (I) and (II) are thus part of the overall hydrogen transfer scheme

$$\text{coal} + \text{tetralin} \longrightarrow \text{hydrogenated coal} + \text{naphthalene}$$
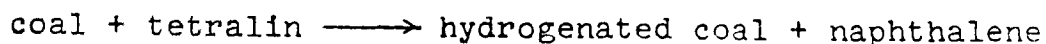
and are of considerable interest.

Since 1,2-DHN can dehydrogenate a dihydroaromatic ring into an aromatic ring, it is of interest to know whether it will dehydrogenate a tetrahydroaromatic ring to a dihydroaromatic ring. When mixtures of 1,2-DHN and tetrahydrophenanthrene (THP) were heated at 400 and 450°C, the changes in the THP were identical to those observed when pure THP was heated under the same conditions in the absence of 1,2-DHN. These limited results suggest that 1,2-DHN will not dehydrogenate a tetrahydroaromatic ring.

Project Status

Kinetic data for reactions (I) and (II) have been collected through the temperature range 380-410°C, and rate constants and activation energies have been calculated. There is a very slight but reproducible curvature in the rate plots, which may result from inappropriate application of an estimated correction for reaction during heat up of the tubes. (In a given run, tubes containing different initial concentrations of reactants are all heated for the same time, and in the past, the same estimated heat up correction was applied to each tube. However, in a given heat up period, the contents of a tube containing a greater initial concentration of starting material will undergo more reaction than those of a tube containing a smaller initial concentration, and it is therefore inappropriate to apply the same heat up correction to each tube.) A series of experiments (different temperatures and initial concentrations) for a period slightly in excess of the heat up time is now being run. Analysis of the reaction mixtures from these tubes will give exact heat up corrections, and the rate constants and activation energies will then be recalculated and reported.

The syntheses of 1,2-DHN- and 3,4-dihydrophenanthrene have been completed, and a study of the pyrolysis of these compounds has been initiated. The objective of this study is to determine whether these compounds disproportionate in a manner analogous to the disproportionation of 1,2-DHN.

Reference

L.L. Anderson, D. Kang and W.H. Wiser, DOE Contract No. (49-18)-2006, Quarterly Progress Report, Salt Lake City, Utah , July-Sept, 1977.

Hydrodesulfurization of Heavy Hydrocarbon Liquids in a Fluidized Bed Reactor with Hydrogen as the Continuous Phase

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Introduction

Several coal liquefaction processes are being developed by various government-industry groups in the USA. The initial objective is the production of low sulfur boiler fuels for power generation. However, the upgrading of these coal liquids will be necessary to make acceptable quality fuels for the home, transportation and industry. Studies have been conducted on the upgrading of coal-derived liquids, tar and anthracene oil and are reported in the literature. More recently Eisen hydrogenated syncrudes from a western Kentucky coal and a Utah coal in an attempt to prepare gas turbine engine fuel.[1] Stein et al. reported their exploratory studies on the hydro-process of solvent refined coal and H-coal.[2] These process are operated in a fixed bed mode. For these, fine catalyst particles cannot be used because of the excessive bed pressure drop; neither can fresh catalyst be added without reactor shut down. However, with a fluid bed reactor, it is possible to 1) operate at near isothermal conditions because of the radial and axial agitation induced by the bubbles, 2) maintain constant activity of the catalyst by continuous circulation of the spent or coked catalyst between the reactor and regenerator, 3) have an essentially constant yield and quality of the products from operating at a constant temperature and catalyst activity, 4) change the feed or product quality on a given feed by controlling the catalyst withdrawal rate which adjusts the equilibrium activity and 5) employ very small catalyst sizes for catalytic effectiveness.

The objective of the present study is to determine the feasibility of the vapor-phase fluidized bed hydrodesulfurization of coal liquids. The operational parameters and catalyst used have been given in the previous report.

Project Status

The determination of the minimum fluidization velocity was done at 1000 psig, 425°C and 1250 psig, 425°C according to the method recommended by Kunii and Levenspield and shown in Tables 1 and 2 and Figures 1,2,3, and 4. The bed fluidized at a pressure drop close to the theoretical value and equivalent to the bed weight. Also the $\Delta p/\Delta p_{eq}$ ratio indicated an absence of channeling and slugging in the bed.

The distillate coal liquids from the SRC II process have been hydroprocessed in the fluidized bed, continuous flow

catalytic reactors between 425-475°C and 1000-1500 psig.

Future Work

The HDS products will be analyzed to determine the effects of process variables and to quantify the kinetics of sulfur removal.

References

1. F.S. Eisen, US Navy Contract N00014-74-C-0568, Mod. P00001, Final Report, Phase 11, February 1975.

2. Roland H. Heck and Thomas R. Stein, Preprints, American Chemical Society, Div. Petrol. Chem., Chicago, Illinois, August 1977, Vol. 22, No.3, p 948.

Table 1

Bed Conditions

Temperature: $425^{\circ}C$

Pressure: 1250 psig

Particle: Sulfided Co-Mo-Al (Harshaw 0603)

Particle Size: 49 microns

Bed Weight: 63.79 grams

Pressure Drop Equivalent to Bed Weight, ΔP_{eq}: 4.97 inches of H_2O

Fixed Bed Depth/Column Diameter: 4.84

H_2 Flow Rate		H_2 Vel at R_x Cond	ΔP Across Bed, in. H_2O	$\Delta P/\Delta P_{eq}$
Rm Temp, cc/sec	Std, cc/sec	cm/sec		
5.11	3.97	0.60	1.00	0.20
9.09	7.07	1.07	2.60	0.52
15.00	11.66	1.76	4.05	0.82
20.05	15.59	2.35	4.80	0.97
29.59	23.00	3.46	5.30	1.07
35.46	27.57	4.15	5.20	1.05
42.74	33.23	5.00	5.15	1.04
54.35	42.26	6.36	4.90	0.99
68.97	53.62	8.07	4.90	0.99
84.75	65.89	9.92	5.20	1.05

Table 2

Bed Conditions

Temperature: $425^{\circ}C$

Pressure: 1000 psig

Particle: Sulfided Co-Mo-Al (Harshaw 0603)

Particle Size: 49 microns

Bed Weight: 63.79 grams

Pressure Drop Equivalent to Bed Weight, ΔP_{eq}: 4.97 inches of H_2O

Fixed Bed Depth/Column Diameter: 4.84

H_2 Flow Rate		H_2 Vel at Rx Cond.	ΔP Across Bed, in.	$\Delta P/\Delta P_{eq}$
Rm Temp, cc/sec	Std, cc/sec	cm/sec	H_2O	
4.82	3.75	0.70	1.4	0.28
9.31	7.24	1.36	2.5	0.50
16.23	12.62	2.37	4.0	0.81
21.74	16.91	3.16	4.7	0.95
25.19	19.60	3.66	5.1	1.03
32.57	25.32	4.75	5.3	1.07
43.86	34.10	6.40	5.1	1.03
46.84	36.42	6.84	5.1	1.03
57.47	44.68	8.39	5.1	1.03
70.42	54.75	10.28	5.1	1.03
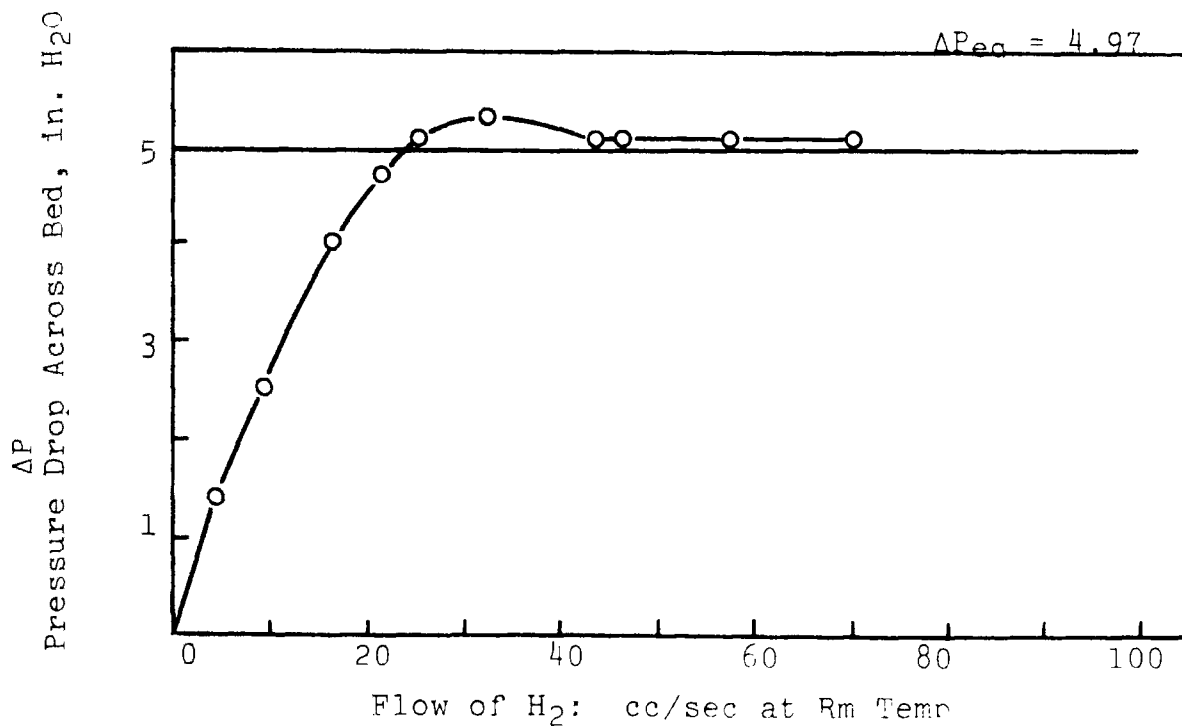
Figure 3.   Pressure Drop Vs. Gas Flow Rate.

Figure 4.   Ratio of Experimental Bed Pressure Drop
to that Equivalent to the Bed Weight Vs. Hydrogen
Velocity.
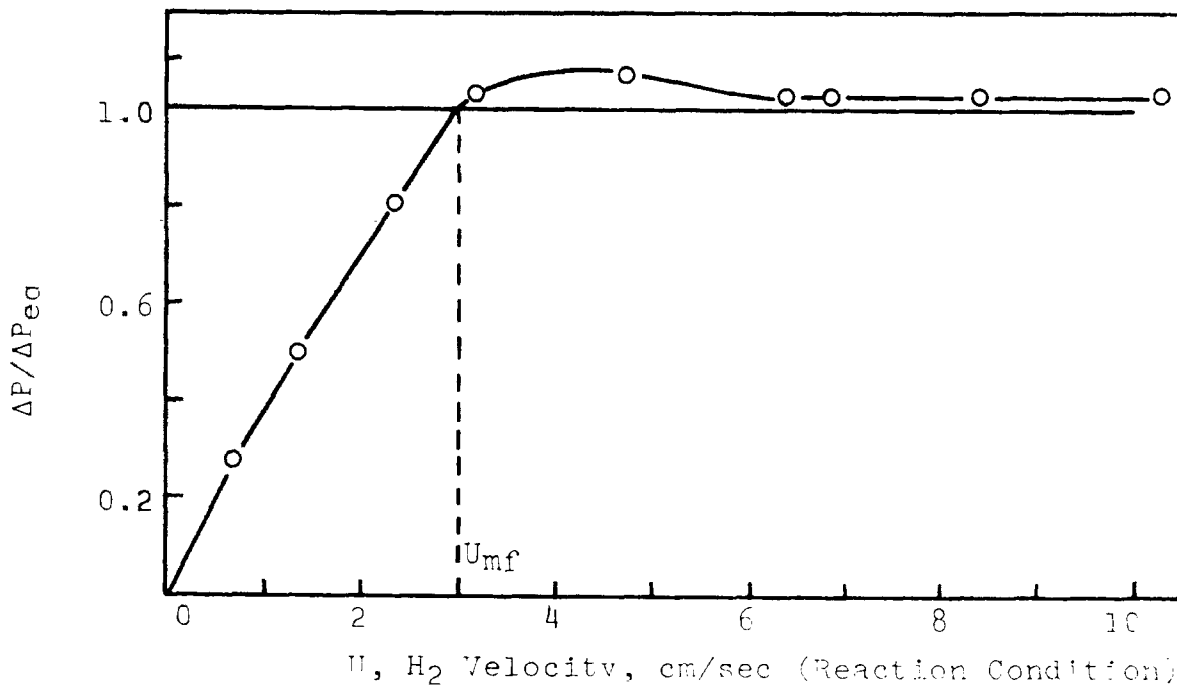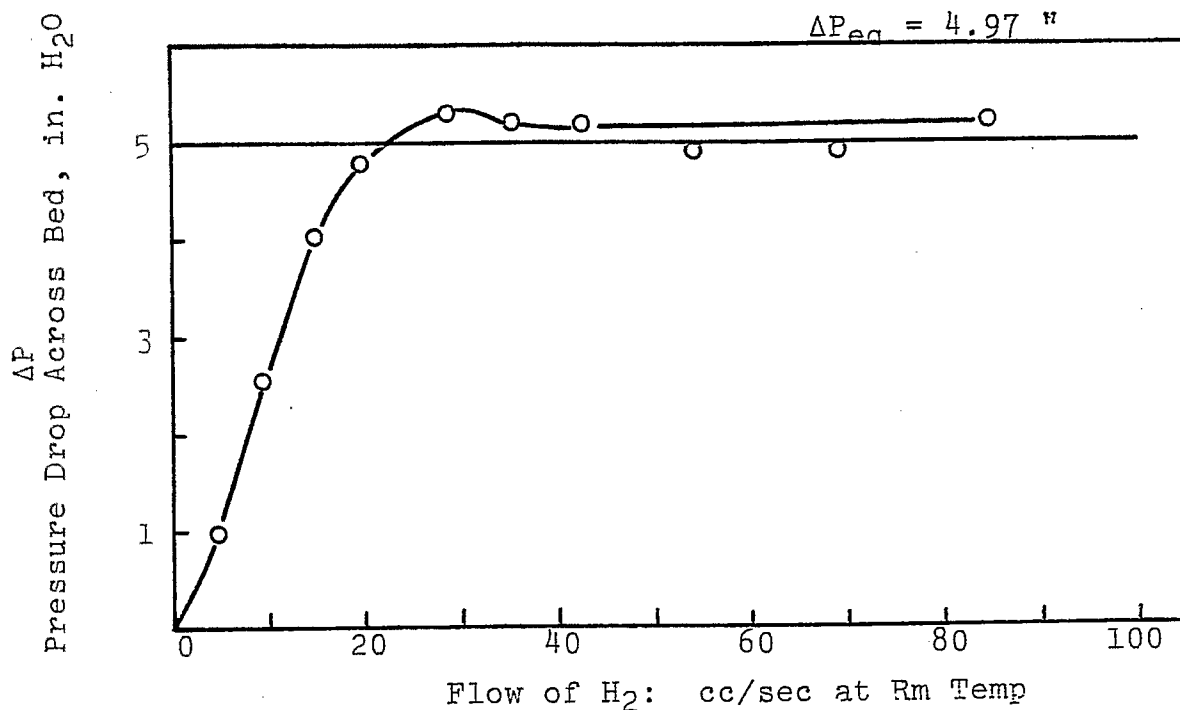
Figure 1.   Pressure Drop Vs. Gas Flow Rate.

Figure 2.   Ratio of Experimental Bed Pressure Drop to that Equivalent to the Bed Weight Vs. Hydrogen Velocity.
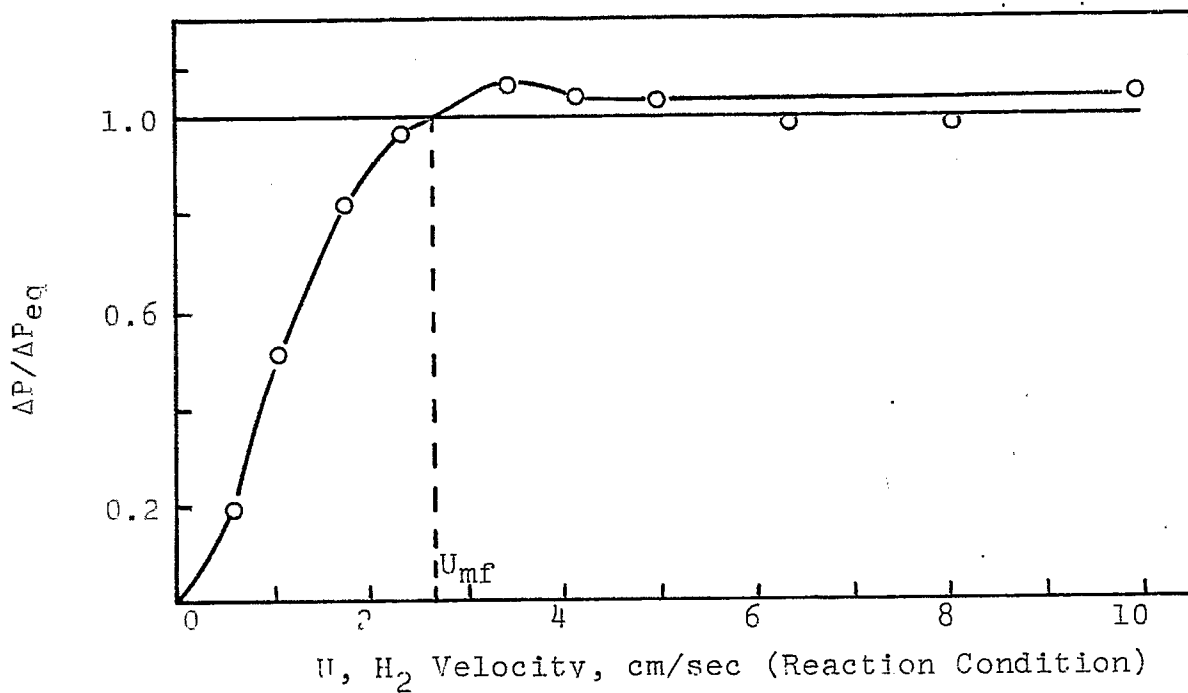
V.   Conclusion

    This completes the Quarterly Progress Report on this
contract. Some projects will be continued under a new contract.