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APPLIED RESEARCH AND EVALUATION OF PROCESS CONCEPTS FOR LIQUEFACTION AND GASIFICATION OF WESTERN COALS. QUARTERLY PROGRESS REPORT, JULY--SEPTEMBER 1978

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

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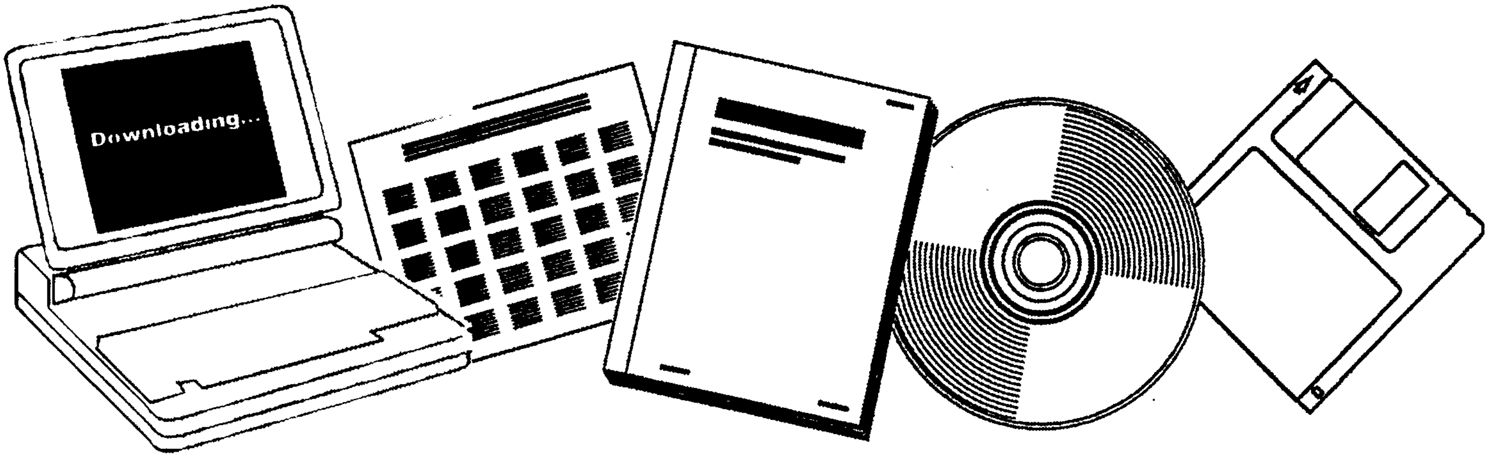

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Applied Research and Evaluation of Process Concepts for Liquefaction and Gasification of Western Coals

Quarterly Progress Report
for the Period July-Sept 1978

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CONTENTS

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.

III Summary of Progress to Date

Research Highlights

Students have completed work on projects A-1, A-2, A-7 and A-8 and are preparing theses. The Department of Energy conducted a Project Review on August 15 and 16, 1978.

Publications, Presentations and Activities

L. L. Anderson and Doohee Kang, "Kinetics and Mechanism of Solvent Extraction of Coal-Relations to Chemical Structure," Preprints Div. of Fuel Chemistry, Amer. Chem. Soc., 23 (4), 118 (1978).

J. Shabtai and A.G. Oblad, "Hydropryolysis of Coal-Derived Liquids and Other Heavy Oils and Solids," Preprints Div. of Fuel Chemistry, Amer. Chem. Soc., 23 (4), 119 (1978).

W. H. Wiser, "Some New Evidence Pertaining to the Chemistry and Mechanisms of Coal Liquefaction," Preprints Div. of Fuel Chemistry, Amer. Chem. Soc., 23 (4), 116 (1978).

Ronald J. Pugmire, Kurt W. Zilm, David M. Grant, Wendell H. Wiser and Ralph E. Wood, "Carbon-13 Nuclear Magnetic Resonance: A Powerful Tool in the Assessment of the Structure of Solid Coals," Preprints Div. of Fuel Chemistry, Amer. Chem. Soc., 23 (4), 117 (1978).

L.L. Anderson, Program Chairman, Fuel Chemistry Division, American Chemical Society.

W.H. Wiser, H.H. Storch Award, Fuel Chemistry Division, American Chemical Society.

Project A-2

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 commercial 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 and (5) a new procedure for molecular weight determination by vapor phase osmometry. Currently a new characterization scheme for CDL is being developed.

Project Status

Additional analytical data on the fractions from the new characterization scheme were obtained, such as elemental composition, oxygen content by a direct determination and proton NMR spectra. From these raw data, structural parameters and functional group contents were estimated. These chemical characteristics of the fractions were used to evaluate the usefulness of the new scheme.

The NMR spectra of three representative fractions are shown in Figure 1. Most spectral assignments have been discussed in the literature except two. The behavior of the phenolic hydroxyl group (ϕ-OH) has been described in an earlier report.[1] The protons at δ 2-2.3 ppm have been seldom mentioned and were included in H_α, protons at δ 2-4 ppm. According to extensive studies on model compounds and petroleum products,[2] the protons at δ 2-2.3 ppm are from $(-CH_3)_\alpha$, methyl protons α to an aromatic ring. Recently, Whitehurst et al.[3] observed these protons with model compounds and light fractions of a CDL. The distinctive appearance of $(-CH_3)_\alpha$ deserves special attention.

From the three spectra, peaks for $(-CH_3)_\alpha$ and ϕ-OH are the largest in the spectrum of "light", while they are the smallest in that of "resid". The position of H_A, protons on aromatic rings, changes with the fractions. H_A in "light" appear between δ 6-8 ppm with a symmetrical distribution around its center at δ 6.9 ppm. H_A in "resid" spread themselves from

δ 6-9.3 ppm showing an unsymmetrical distribution. The center or highest point of the distribution is at 7.3 ppm with its left side having convex shape and its right side concave side concave shape. These spectral differences reveal qualitatively different chemical characteristics among the fractions and will be discussed later in detail.

The NMR spectra were examined quantitatively with the other data as summarized in Table 1. Molecular weights and yields are from the previous report.[4] Structural parameters on an average molecule of each fraction were obtained from the following formulae:[9-11]

Number of aromatic carbons

$$C_A = C - \frac{1}{2}(H_{2\alpha} + H_\beta) - \frac{1}{3}(H_{3\alpha} + H_\gamma) \tag{1}$$

Total number of rings

$$R = \frac{2C - H + 2}{2} - \frac{1}{2} C_A \tag{2}$$

Number of carbons on rings

$$C_R \approx 2 + 4R \tag{3}$$

Fraction of aromatic carbons (aromaticity)

$$f_A = \frac{C_A}{C} \tag{4}$$

Number of aromatic rings

$$R_A \approx \frac{C_A - 2}{4} \tag{5}$$

Number of naphthenic rings

$$R_N = R - R_A \tag{6}$$

Ratio of the peripheral aromatic carbons to aromatic carbons

$$r_{AP} = \frac{C_{AP}}{C_A} = \frac{H_A + \frac{1}{2} H_{2\alpha} + \frac{1}{3} H_{3\alpha}}{C_A} \tag{7}$$

Accuracies of these parameters depend upon NMR spectral assignments and the correctness of the formulae used.[4] The employment of this type of structural analysis is based on the excellent internal consistency among the parameters as shown in Table 1. Further verification will be sought as more experimental data are available.

The functional group contents are semi-quantitative or tentative. The ϕ-OH contents for all fractions have been determined by the NMR method.[1] To check the values, a silylation-NMR method[5] has been tried on the "light" fraction, but it produced precipitation and distorted the NMR spectrum yielding a much lower ϕ-OH value. The estimations of $(-CH_3)_\alpha$ and $(-CH_3)_\gamma$ were made from $H_{3\alpha}$ and H_γ in the NMR spectra, but they have not been checked by other means.

The data in Table 1 reveal much information on the nature of CDL. The distribution of molecular size as well as those of other structural parameters is remarkable. Even though the average molecular weight of a whole liquid, CDL-P, is 258, the major fractions of CDL-P have molecular weights significantly smaller or larger than that of CDL-P. Furthermore, the fractions of smaller molecular weight, "light" and "middle" fractions, account for nearly one-half of CDL-P in terms of number of molecules. This large number of small molecules needs to be taken into consideration in investigating the nature of CDL as well as coal structure.

The structural parameters in Table 1 give detailed information on the constituents of CDL-P. The number of aromatic rings per molecule, R_A, reveals that there are one to five aromatic ring compounds, with the major fractions having one to two or larger than four rings. There are also significant amounts of naphthenic rings as indicated by the parameter, R_N. More than 60% of the average molecules in "light" and "middle" have a naphthenic ring and every molecule in "heavy" and "resid" had more than one naphthenic ring. This aromatic-naphthenic structure gives three types of carbons: on the average 60% of the carbons are aromatic, 20% are naphthenic and 20% are acyclic aliphatic. The carbon-type distribution, e.g., f_A, remains relatively unchanged while other parameters, R, R_A and R_N, change markedly from one fraction to another.

The ratio, r_{AP} in Eq (8), can be used to determine whether aromatic rings in a molecule form one cluster or more. An aromatic cluster is defined as one or more aromatic rings fused together, but not linked by any saturated bond. There is a good correlation[6] between r_{AP} and C_A to estimate the number of aromatic clusters per average molecule. The three fractions (except "resid") consist of components having one aromatic cluster. Most components in "resid" have one aromatic cluster, but about 30% of them have two. This structural feature is of fundamental importance in assessing the structure of coal and its derivatives, which will be discussed later.

The functional group analyses show that an average molecule of each of the four fractions has a similar number of ϕ-OH. However, $(-CH_3)_\alpha$ contents show that "resid" has the smallest value among the four fractions. The $(-CH_3)_\gamma$ content varies from the highest value for "heavy" to the lowest for "light." Although the content of the three functional groups changes from one fraction to another, the changes are not drastic and the functional group content is mostly less than one. Significance of this functional group distribution will be discussed in conjunction with the linkages in coal structure.

The above information on the nature of CDL-P is not complete. The results obtained so far give valuable information on the molecular size, structural characteristics and functional group distribution of the coal-derived liquid. This information can be utilized in further processing of CDL-P or in elucidation of coal structure and the phenomena involved in liquefaction of coal.

One of the most important structural features of CDL-P is that almost all components in each of the four fractions have one aromatic cluster. This indicates that CDL-P is a completely depolymerized product from the University of Utah coal liquefaction process since coal is considered as a cross-linked polymer with numerous aromatic clusters connected by weak bonds.[7] The completely depolymerized product, CDL-P or its four fractions would not be further depolymerized under usual coal liquefaction conditions. This point is also supported by non-convertability of one fraction to another in CDL-P. For example, although the molecular weight of "resid" is twice that of the "light" fraction, comparison of structural parameters, R, R_A and R_N, for the two fractions suggests that converting one "resid" molecule to two "light" molecules is unlikely.

The above mentioned differences and non-convertability among the four fractions in CDL-P suggest that the four were derived from four different building blocks or structural units within the coal. Also the distribution of the four structural units should be similar to that of the four fractions. If this is true, the nature of CDL-P has much to do with coal structure.

The characteristics of CDL-P indicate that two distinctive component groups can be differentiated. One group consists of two fractions, "light" and "middle," called Group A. The other includes "heavy" and "resid," called Group B.

Group A contains smaller molecule weight components which are fluid at room temperature, while Group B contains larger molecular weight components, being solid at room temperature.

Structural units A and B are therefore envisaged in coal as precursors for Groups A and B, respectively. This recogni= tion of two kinds of structural units in coal is of practical importance in coal liquefaction. The quantization of two structural units may indicate the yields of the two groups even before liquefaction. Also any intermediate, i.e., partially depolymerized product, can be recognized in terms of the structural units. The NMR spectral difference in the aromatic region, δ 6-9.5 ppm, between Group A (includes mostly "light") and Group B (includes mostly "resid") gives results that may be used to elucidate the two types of structural units present in coal. So far in the literature, a simple structural unit has been mentioned.[12,13]

The functional group contents of the two component groups give valuable information on weak bonds connecting the structural units in coal. The weak bonds are proposed to be etheric and alkyl linkages. The functional groups observed in the component groups are considered to be remnants of the weak bonds in coal. The kinds, amounts and distributions of the functional groups have much to do with those of the weak bonds. The data from functional group analysis suggest that no one type of weak bond prevails, but that two or three types exist in significant amounts in coal. These bonds seem to distribute themselves similarly in smaller structural units as well as in larger ones.

Etheric linkages may become hydroxyl groups (-OH) upon depolymerization. Many etheric linkages probably exist as aryl ethers since all of -OH appear as ϕ-OH in CDL-P. There has been no follow-up explanation on the breaking of $-(CH_2)_n-$ linkages, although such linkages have been considered important.[8] A large amount of $-(CH_3)_\alpha$ in CDL-P has been observed. This functional group is most likely the result of thermal breakages of $-(CH_2)_n-$attached to aromatic rings.

To clarify these implications on coal structure, coal or partially depolymerized coal is being examined. There are many difficulities in examining coal directly, but partially successful proton NMR spectra on a treated coal showed qualitatively that the suggested relationships exist between CDL and coal.

Future Work

Work on the direct examination of coal or partially treated coal will be continued to obtain a clearer structural relationship between coal and CDL. Also refinement on the characterization scheme will be continued.

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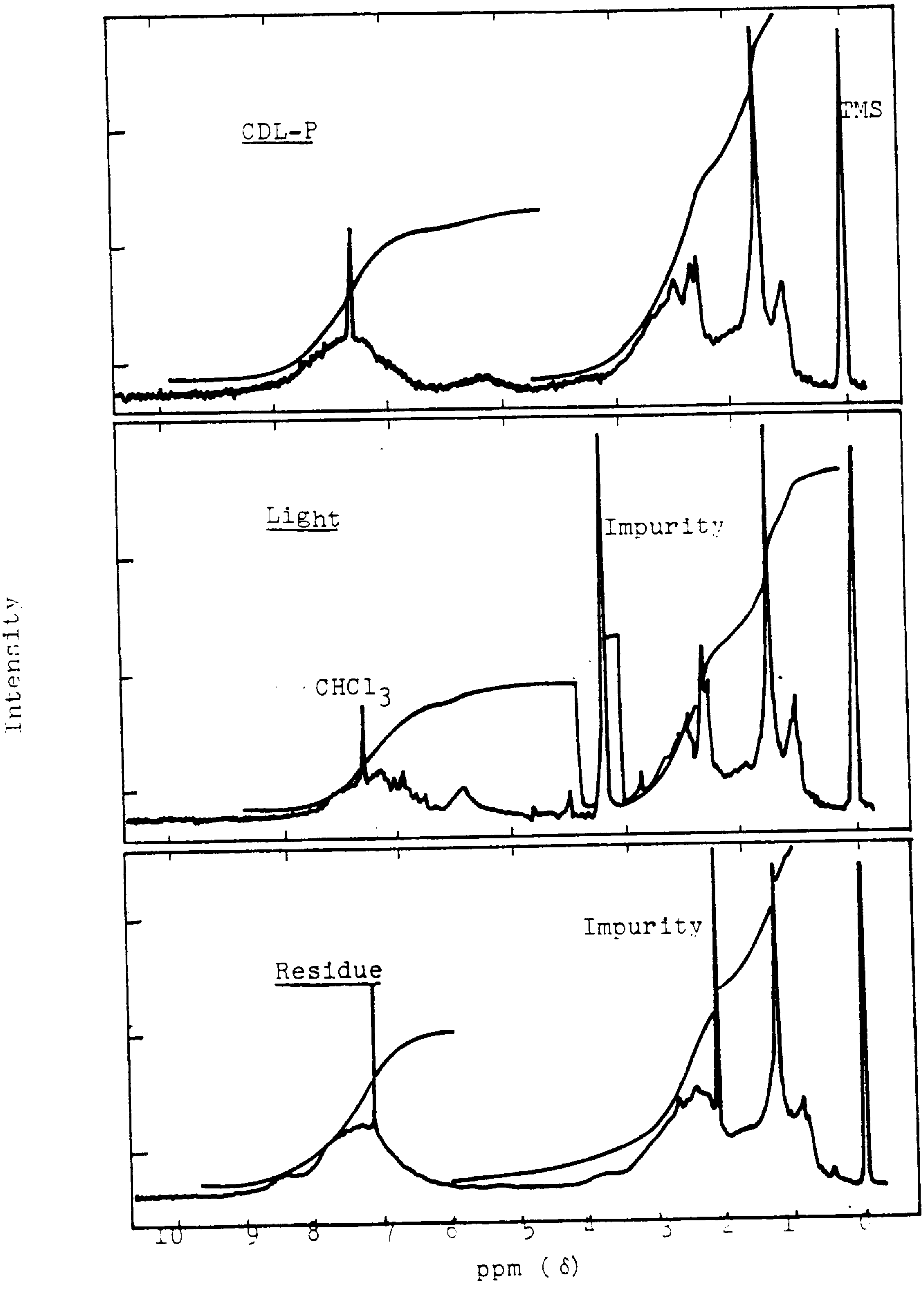

Figure 1. Proton NMR spectra of CDL-P and its two fractions in $CHCl_3$.

Table 1. Analytical Data on CDL-P and Its Fractions

	CDL-P	Light	Middle	Heavy	Resid
Weight, %	100[*1]	19.2	15.7	17.6	40.0
Mole, %	100	27.1	19.3	16.7	26.1
Mol. Wt.	258 (268)[*2]	183	210	272	396
f_A	0.63 (0.62)	0.55	0.58	0.59	0.68
R	3.2 (3.0)	1.8	2.3	3.7	5.6
R_A	2.4 (2.2)	1.2	1.6	2.4	4.4
R_N	0.8 (0.8)	0.6	0.7	1.3	1.2
# Cluster		1.0	1.1	1.1	1.3
ϕ - OH[*3]	0.71 (0.65)	0.61	0.98	0.68	0.70
$(-CH_3)_\alpha$[*3]	0.74 (0.50)	0.70	0.54	0.64	0.38
$(-CH_3)_\gamma$[*3]	0.62 (0.72)	0.58	0.62	1.24	0.89

[*1] Includes loss

[*2] Values in parentheses are calculated from those of the four fractions.

[*3] Numer of each functional group per average molecule.

CDL-P = coal-derived liquid with paraffinic material removed.[4]

Cluster = number of aromatic cluster per average molecule

Project A-2

A Systematic Study of Coal Structure by Extractive Liquefaction Under Mild Reaction Conditions

Faculty Advisor: J. Shabtai
Graduate Student: H.B. Oblad

Introduction

This study is concerned with extractive coal liquefaction under mild experimental conditions, using a variety of solvents and homogeneous catalysts. Coal slurries will be processed in a small integral flow reactor which will be operated at temperatures of 100-300°C, hydrogen pressures of 100-1000 psig and very short residence times. The mild conditions will be adjusted to obtain very low coal conversions, e.g., 2-5 percent to avoid secondary reactions. The slurry will be quenched, the liquids will be removed and analyzed, and the washed solids will be reloaded into the reactor with fresh solvent and catalyst. Repetition of this procedure coupled with the application of selective catalysts should yield relatively simple primary products. The information gathered should reveal the types of original structural components and interconnecting functional groups present in coal.

Present Status

Glassware and equipment have been collected for the preliminary low temperature studies. A sample of Hiawatha coal has been repeatedly extracted at room temperature with cyclohexane (five times) and with hexane (one time) to remove the resin. The coal to solvent ratio in each extraction was approximately 50 grams of coal to 500 ml of solvent. Each time the coal-solvent mixture was agitated with a magnetic stirrer for about 6 hours and then allowed to stand overnight. The first and last extracts were evaporated and the solvent-free residue was subjected to infrared absorption analysis. The spectra were taken from resin smears on KBr crystals. Examination of the absorption maxima shows that the resin from the last extraction contained a higher concentration of aromatic rings (1595 cm^{-1}). Also the last extract contained a higher concentration of phenyl-conjugated ester groups (1735 cm^{-1}, 1702 cm^{-1}) as compared with the first extract.

Two samples of the deresinated coal were then extracted with decane and dodecane at 130°C and 172°C, respectively. The 10 g coal/100ml solvent mixtures were heated to gentle reflux, stirred constantly for five hours and then allowed to stand overnight. These extracts are now being prepared for IR analysis.

The techniques for low temperature extraction are being tested for reproducibility and accuracy. Further, infrared analysis is being adapted for quantitative determination of different functional groups present in the extracts.

Future Work

The Hiawatha coal samples will be progressively extracted with a series of solvents with increasing solvent polarity. The extracts will be analyzed by infrared and proton and ^{13}C NMR spectrometry. Kentucky coal will also undergo the same series of extractions and analyses. Later homogeneous catalysts will be added and any products of reaction will be scrutinized. These low temperature extraction and catalytic coal-liquefaction experiments are expected to provide information on the original components present in the coal structure.

Project A-4

Steam Reforming of Aromatic Compounds

Faculty Advisor: A.G. Oblad
Graduate Student: Shri Goyal

Introduction

The objective of this research is (1) to study the thermodynamics and kinetics of steam reforming and (2) to develop an appropriate catalyst for the steam reforming of aromatic compounds. The general reforming process and details of the equipment have been previously reported.

Project Status

For reforming of hydrocarbons various catalysts have been studied, i.e., Pt, Pd, Ir, Rh, Ru, Os, Ni, Co. Platinum, Pd, Ir, Rh, Ru, Os, are precious metals and the cost per unit activity of these catalysts is very high.[1] Nickel is the most effective metal and is being used in all the commerical catalysts. Cobalt can be used but it is less effective and more expensive.[1] There have been a few investigations using precious metals as steam reforming catalysts.[2-7] The most comprehensive study was done by Rostrup-Nielsen.[3] He worked on steam reforming of ethane using different noble metals and found Rhodium to be the most active. Recent studies made by Grenoble [2] have supported the previous results that the activity sequence for the noble metals catalyzed steam reforming reaction is

$$Rh > Ru > Pt > Pd > Ir$$

Nickel metal is the most effective catalyst for the steam reforming process and has been studied extensively.[3,8-20] Most of the research has been carried out for methane and naphtha reforming.

The catalysts used in these studies were prepared by impregnation of $Ni(NO_3)_2$ on α-Al_2O_3 [16-18], γ-Al_2O_3 [14,20] and other refractory materials mostly containing CaO and MgO [1,3]. These components have an influence over physical properties of the catalyst, such as strength and density. The commercial catalysts have a total specific surface of 40 to 50 m^2/g which decreases during the course of reaction, and the nickel metal area is less than 1 m^2/g of catalyst.

The steam hydrocarbon reaction is activated by nickel metal and particularly by the nickel surface exposed for the reaction. The nickel metal, especially in the form of very small crystals and at temperatures above one-half of its melting point (mp 1453°C), will sinter very fast.[1] To keep the nickel particles apart, nickel is impregnated on refractories which act as "spacers" and stop the metal sintering. These refractories have been called "stabilizers" or catalyst support or carrier. The various functions and properties of different carriers are given elsewhere.[21] For the steam reforming reaction, the carrier should be able to hold high surface area at high temperatures and in the atmosphere of steam and hydrogen.

Sintering of various refractory materials have been studied by Rostrup-Nielsen[3] at different temperatures. The γ-alumina may hold up to 17 m^2/g in the H_2O/H_2 atmosphere at 780°C even after 170 hours. Alumina mixed with magnesia did not hold the surface area of even 1 m^2/g under the same conditions because of hydration effects on magnesia. Silica being volatile at high temperatures and under high pressure steam forms orthosilicic acid $Si(OH)_4$.[22-24] Zirconia (ZrO_2) is also a high refractory material and has not been considered extensively as a catalyst support because zirconia loses its surface area at low temperatures.[25] However, a sample of ZrO_2 powder was heated at 700°C for one hour and the specific surface area was 1.5 m^2/g by the BET method with N_2 adsorption. The commercial catalyst G56B (25% Ni) supplied by Chemitron Company was heated at 850°C for different periods of time and the results are given in Table 1. The G56B catalyst stabilized to approximately 10 m^2/g when heated in the atmosphere of steam.

A similar study of γ-alumina supplied by Alpha Products was carried out and the results are shown in Table 2. This γ-alumina decreased its surface area to 7.0 m^2/g at 900°C after 50 hours.

Further F-1 γ-alumina and H-151 Alumina Gel supplied by ALCOA were sintered at 900°C and the surface areas were measured (Table 3 and plotted in Figure 1).

H-151 alumina was tentatively selected to study the effect of steam on its sintering. The steam was passed on the H-151-900-96 (already sintered at 900°C for 96 hr) at 800°C with the water flow of 2 cc/min. The samples were taken out after cooling the system at different times. The results of surface area measurements are shown in Table 4. Since the surface area of H-151-900-96 stayed almost constant, it was chosen as the catalyst support for this experimental work.

The amount of Ni salt solution absorbed on 200 g support was 100 cc and 98 cc in the first and second dip, respectively. The amount of nickel metal impregnated was calculated to be 23.065% on weight basis. This catalyst prepared will be designated as Ni-3.

Catalyst Ni-3 was reduced at 700°C for 2 hr in H_2 (1000 cc/min) and a sample was taken out. The reduced catalyst was treated in steam (water flow 2 cc/min) for 2, 5, 10, 20 hr and reduced in hydrogen. The surface areas of these samples show (Table 5) that there is not an appreciable decrease in surface area of the support. Nickel metal is often deposited as small particles (crystallites) on the support. X-Ray diffraction permitted determination of particle sizes[26] through X-ray line broadening, and the results of X-ray examination are shown in Table 5. Nickel surface area was calculated assuming that the nickel is present as cubes and that one side is in contact with the alumina.[27] The nickel particles probably do not become buried in the alumina since the decrease in total surface area (Table 5) is not significant.

Specific surface area of nickel as m^2/g of catalyst is plotted vs. time of steaming in Figure 2. X-Ray investigations show that steaming after five hr has no appreciable effect on total surface area and nickel particle size, i.e., specific surface area of nickel remains constant.

Further X-ray diffraction patterns of H-151 had very broad peaks of γ-Al_2O_3 indicating that H-151 is a gel and not a crystalline material. For H-151-900-96 support, γ-Al_2O_3 peaks were slightly higher showing the presence of poorly crystalline γ-Al_2O_3. Reduced catalyst Ni-3 after steam treatment contained almost the same amount of γ-Al_2O_3 as in H-151-900-96 and no α-Al_2O_3.

Future Work

The Ni-3 catalyst will be impregnated with different amounts of sodium to obtain an optimum. The kinetic study of the steam reforming of benzene will begin.

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Table 1

Sintering of G56B catalyst at 850°C

Time/hours	0	20	49	88
Surface Area m^2/gm	68.69	26.17	21.44	21.27

Table 2

Sintering of γ-Al_2O_3 (Alpha Products) at 800 C

Time/hours	0	2	4	8	21	30	52	94
Surface Area m^2/gm	143.88	108.48	100.78	90.24	79.16	73.72	64.02	56.64

Table 3

Sintering of F-1 and H-151 (ALCOA) at 900°C

Time/hours		0	6	18	28	45	69	96
Surface Area m^2/gm	F-1	253.17	94.97	83.10	65.37	45.70	42.80	36.33
	H-151	348.16	212.42	200.05	181.57	168.37	164.49	156.53

Table 4

Steaming of H-151-900-96 at 800°C

Time/hours	0	1	5	10	20
Surface Area m^2/gm	156.53	154.06	152.06	150.00	149.50

Table 5

Steaming of Reduced Ni-3 at 700°C

Time Hours	Total Surface Area m^2/gm (BET)	X-ray Examination					
		Particle Size Å		Ni area/gm.Ni		Specific Surface Area Ni area/gm.Cat.	
		111	200	111	200	111	200
0	122.6	187	233	30.0	24.0	7.17	5.74
2	124.2	252	286	22.2	19.6	5.31	4.69
5	117.3	232	317	24.2	17.7	5.79	4.23
10	108.6	312	286	18.0	19.6	4.29	4.69
20	107.9	278	325	20.2	17.3	4.82	4.12

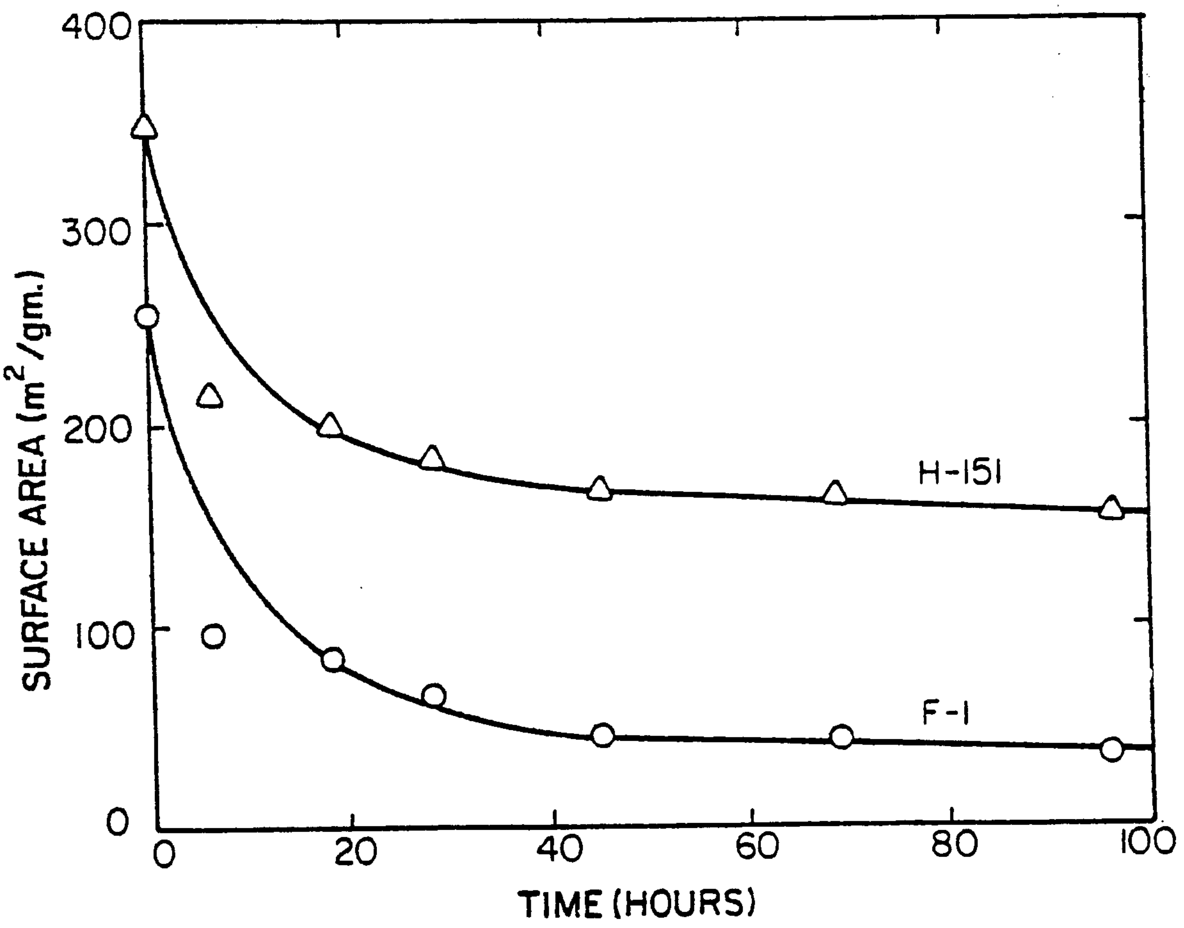

Figure 1. Sintering of F-1 and H-151 (ALCOA) at 900°C.

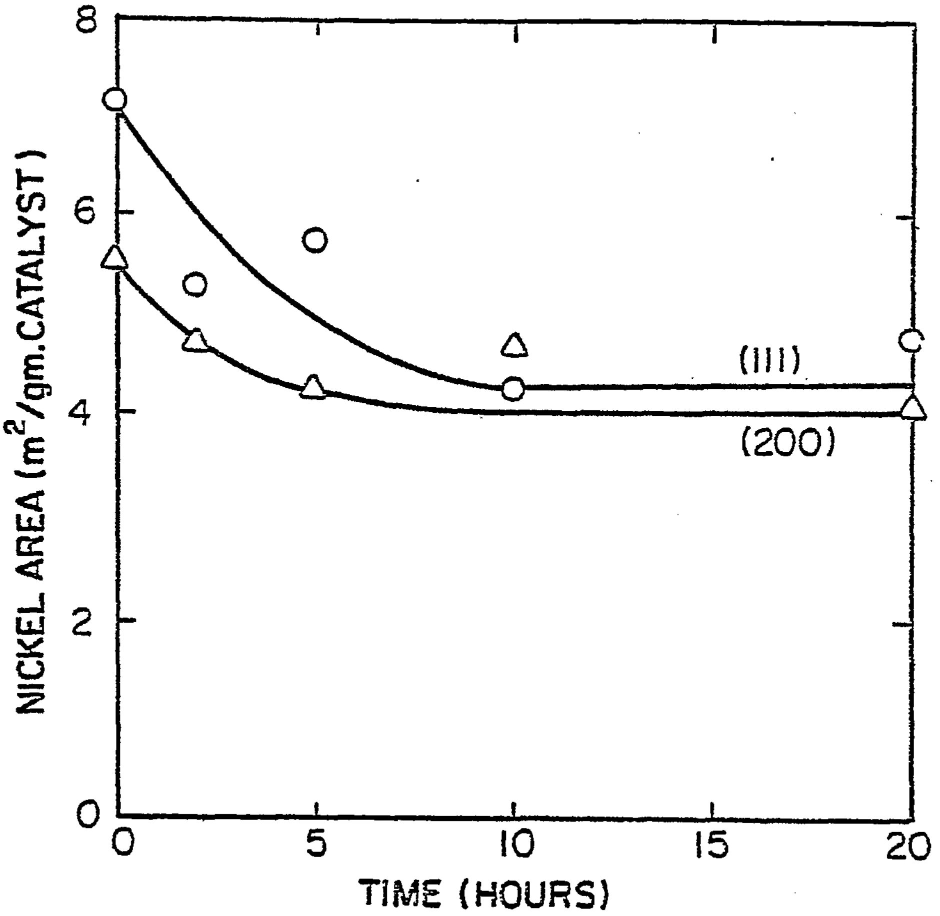

Figure 2. Effect of steam on reduced Ni-3 at 700°C.

Project A-7

Catalytic Cracking of Hydrogenated Coal Liquids and Related Polycyclic Naphthenes

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

Introduction

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

The present project is concerned with the following interrelated subjects:

(1) Systematic catalytic cracking studies of model polycyclic naphthenes found in hydrogenated coal liquids, e.g., decalin, perhydrophenanthrene and perhydroanthracene, as a function of catalyst type and operating conditions.

(2) Systematic catalytic cracking studies of hydrogenated coal-derived liquids (hydro-CDL) as a function of the same variables.

Catalysts applied in the study include both conventional zeolite-containing systems, e.g., Mobil Durabead, as well as newly developed large pore molecular sieves. The latter are prepared by cross-linking of layer silicates and are designated as CLS catalysts.[2,3] Strongly acidic H-forms of CLS are being tested as cracking catalysts. Such H-CDL systems have an important advantage over conventional zeolites in possessing sufficiently large pore sizes, e.g., 10-20 Å, for admission of polycyclic naphthenes in the catalyst intracrystalline channel system.

The equipment used and the methods of identification of products have been previously reported.

Project Status

Results obtained with conventional cracking catalysts, e.g., Mobil Durabead, show that polycyclic naphthenes or hydrogenated coal liquids are excellent feedstocks for catalytic cracking, yielding primarily light liquid products. Types of products obtained by cracking decalin were reported last quarter. Similar studies on perhydrophenanthrene were completed this quarter.

In the mild temperature range of 350-400°C, perhydrophenanthrene yielded 70-80% by weight of light liquids, 20-25% of gaseous products and about 2% of coke. The gaseous product consisted mostly of saturated C_3-C_4 components. The liquid products were analyzed at the molecular level by combination of high efficiency gas chromatography and mass spectrometry. The products contained significant amounts of C_5-C_8 paraffins (mostly branched), C_6-C_8 cyclopentanes, C_6-C_8 cyclohexanes and C_7-C_8 alkylbenzenes. In addition the products contained decalin, hexahydroindan, C_{11}-C_{14} decalins and small amounts of tricyclic components. Part of the monocyclic and bicyclic products were olefinic. The depth of catalytic cracking was easily controllable by variation in operating conditions.

The change in product composition as a function of temperature shows that the cleavage of the tricyclic system is a stepwise process. Splitting of an end ring produces C_{11}-C_{14} alkyl decalin derivatives which on further cracking yield monocyclic compounds and open-chain products. Cleavage of the middle ring yields two single-ring compounds on further cracking. Dehydrogenation by hydrogen transfer leads to the formation of aromatics.

Future Work

The systematic catalytic cracking of polycyclic naphthenes and hydrogenated coal liquids and their variations with operating variables will be continued.

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Project A-7

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

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

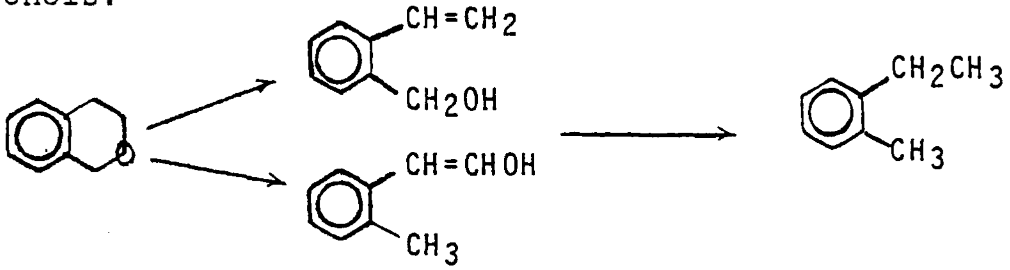
Introduction

Coal-derived liquids contain a high proportion of oxygen-containing compounds. Therefore, a systematic catalytic hydrodeoxygenation study of coal-derived liquids and related model compounds is being carried out. The study provides also information concerning the role of oxygen-containing compounds in coal liquefaction.

Project Status

Some systematic hydrodeoxygenation experiments with a model compound, i.e., isochroman () were carried out.

Under mild operating conditions (150-200°C, hydrogen pressure 1000-1500 psig) the above compound undergoes noneliminating hydrogenolysis to yield selectively unsaturated alcohols.



An increase in temperature and/or contact time results in gradual hydrodeoxygenation of these alcohols to 1-methyl-2-ethylbenzene.

Experiments are presently being carried out with other ethers and ketones as feedstocks for identifying the intermediate products of noneliminating hydrogenolysis as well as the final products resulting from hydrodeoxygenation.

Future Work

The systematic hydrodeoxygenation studies of coal liquids and related oxygen-containing compounds will be continued.

Project A-7

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 investigation is to extend this work to coal-derived liquids.

Project Status

The fabrication and assembly of the experimental apparatus is nearly complete. Temperature and pressure testing of the apparatus and calibration of the flowmeters and the temperature controllers are being carried out at the present time.

Future Work

The initial experiments will be conducted with a typical heavy virgin gas oil feedstock to shake down the equipment. Additional experiments will be made with a variety of catalytic cracking feedstocks (derived from paraffinic and naphthenic crudes) of different boiling ranges to provide a benchmark for the study of the catalytic cracking of coal-derived liquids.

The reference set of experiments will be conducted at temperatures from 723-873°K, at catalyst-to-oil ratios of 2-5 wt/wt and at atmospheric pressure. Feedstocks for the subsequent experiments will consist of coal-derived liquids (5-25%) blended with typical catalytic cracking feedstocks. The coal-derived liquids will be obtained from a subbituminous coal, a high volatile bituminous coal and a medium volatile bituminous coal. Commercially available amorphous (high pore volume, high and low alumina silica-aluminas) and crystalline (zeolites) alumino-silicate catalysts will be utilized for this work.

Project A-8

Synthesis of Light Hydrocarbons ~~From~~ CO and H_2
(Continued)

Catalyst Characterization Studies

Faculty Advisor: F.E. Massoth
Graduate Student: Brent Bailey

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, evidence for alloy formation, phase structures and catalyst stability. Also, variables in catalyst preparation and pretreatment are examined to establish 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.

Work thus far has concentrated on the $CoCu/Al_2O_3$ catalyst which has shown some potential for producing low molecular weight hydrocarbons from the CO and H_2. Hydrogen pretreatment of the oven-dried catalyst was necessary to achieve large metal areas. Furthermore, a low temperature hold in H_2 during pretreatment gave even better metal dispersions. Copper and cobalt seem to have a synergistic relationship; cobalt helps to disperse the copper while copper aids in reduction of cobalt to the active state. Several catalysts which had been tested in the pressure reactor were characterized. Analysis of these data indicated that catalytic activity for CO conversion was related to effective metal area as measured by O_2 adsorption.

Studies revealed that the nonreducible cobalt in the Co/Al_2O_3 catalyst is most likely combined with the alumina as a $CoAl_2O_4$ spinel phase. The presence of Cu in the catalyst apparently hinders the formation of this phase during catalyst prereduction.

Project Status

Work during this quarter has concentrated on infrared (IR) and temperature programmed desorption (TPD) studies of CO adsorption on the mixed CoCu/Al_2O_3 catalysts. The apparatus and techniques have been previously described.[1,2] All samples were prereduced in H_2 at 500°C. Infrared spectra were rather poor because of the opaque nature of the reduced samples (black). Some catalysts exhibited broad desorption peaks, making interpretation difficult. Figure 1 shows some typical TPD results.

A summary of the results obtained in these studies is given in Table 1, together with reduction and catalyst selectivity properties reported previously. The catalysts are arranged in order of increasing copper content based on the reduced catalyst composition. These values were obtained from catalyst reduction measurements, assuming complete reduction of the copper and incomplete reduction of the cobalt. As the nominal copper composition increased, the extent of cobalt reduction increased. An exception was catalyst 18, which showed an extremely low degree cobalt reducibility for some unknown reason. The unreduced cobalt is combined with the alumina, probably as a cobalt aluminate phase,[2] and has no bearing on the metallic phases present on the catalyst.

The IR results showed only two important absorption peaks, one at 2100 cm^{-1} assigned to CO adsorption on a Cu phase and one at 2030-2050 cm^{-1} assigned to CO on an alloy phase. A Co phase (2010 cm^{-1}) was not detected in any of the samples. These assignments were determined from separate cobalt and copper catalyst samples and agree with the values in the literature, except for the alloy which has not been reported.

Assignments of phases present are more uncertain for the TPD data due to broadened peaks and some overlap. However, some significant differences between samples were observed as seen in Figure 1. The 100° peak is associated with a Cu phase, whereas the 210° and 160° peaks most likely indicate an alloy phase. Peaks and tailing of peaks above 250° are due to a cobalt oxide-alumina phase.

Although the results indicate a Cu-like phase in these catalysts, this is most likely a Cu surface rich alloy in view of the low methanol produced by these catalysts (last column of Fig 1) compared to the high yield of methanol obtained with the Cu/Al_2O_3 catalyst (86%). Apparently, a small amount of Co in this phase is sufficient to moderate the catalytic activity away from methanol production. The catalyst richest in Cu (18) did exhibit increased methanol yield, and this may be attributed to a small amount of a separate Cu phase.

The catalysts having highest C_2-C_4 selectivity (37 and 42) showed positive indication of an alloy phase, in addition to the Cu surface rich alloy. Strangely, this did not show up as a separate, low temperature desorption peak, indicating similar desorption energetics of the two phases. Nevertheless, the tentative conclusion is that this alloy is the one primarily responsible for C_2-C_4 catalyst selectivity, since the Cu rich phase was present in all catalysts.

Future Work

Work on the CoCu/Al_2O_3 catalyst has been completed and a final report will be written. Work has been initiated on iron based catalysts. Techniques similar to those developed for the CoCu/Al_2O_3 catalysts will be used to characterize the iron catalysts.

References

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2. W.H. Wiser *et al.*, DOE Contract No. E(49-18) - 2006, Quarterly Progress Report, Salt Lake City, Utah, Oct-Dec 1977.

Table 1. Data for mixed CuCo/Al_2O_3 catalysts.

Cat. No.	Cu %	Co %	Red. Co %	$\left(\frac{Cu}{Cu+Co}\right)_{Red.}$	IR Peaks cm^{-1}	TPD Peaks °C	Metal Phases Deduced	H.C. Sel., % C_2-C_4	CH_3OH
19	1.3	7.4	36	0.31	--	100, 210	Cu + A_1	33	0
17	4.9	7.5	61	0.50	2090	160	Cu(?)+A_2(?)	37	3
37	8.1	9.8	62	0.55	2100, 2030	--	Cu + A_3	48	4
42	15.5	5.5	59	0.81	2100, 2050	110, 270	Cu + A_3	50	2
18	16.1	8.1	17	0.92	--	110, 270	Cu	38	21

A - represents possible alloy phase.

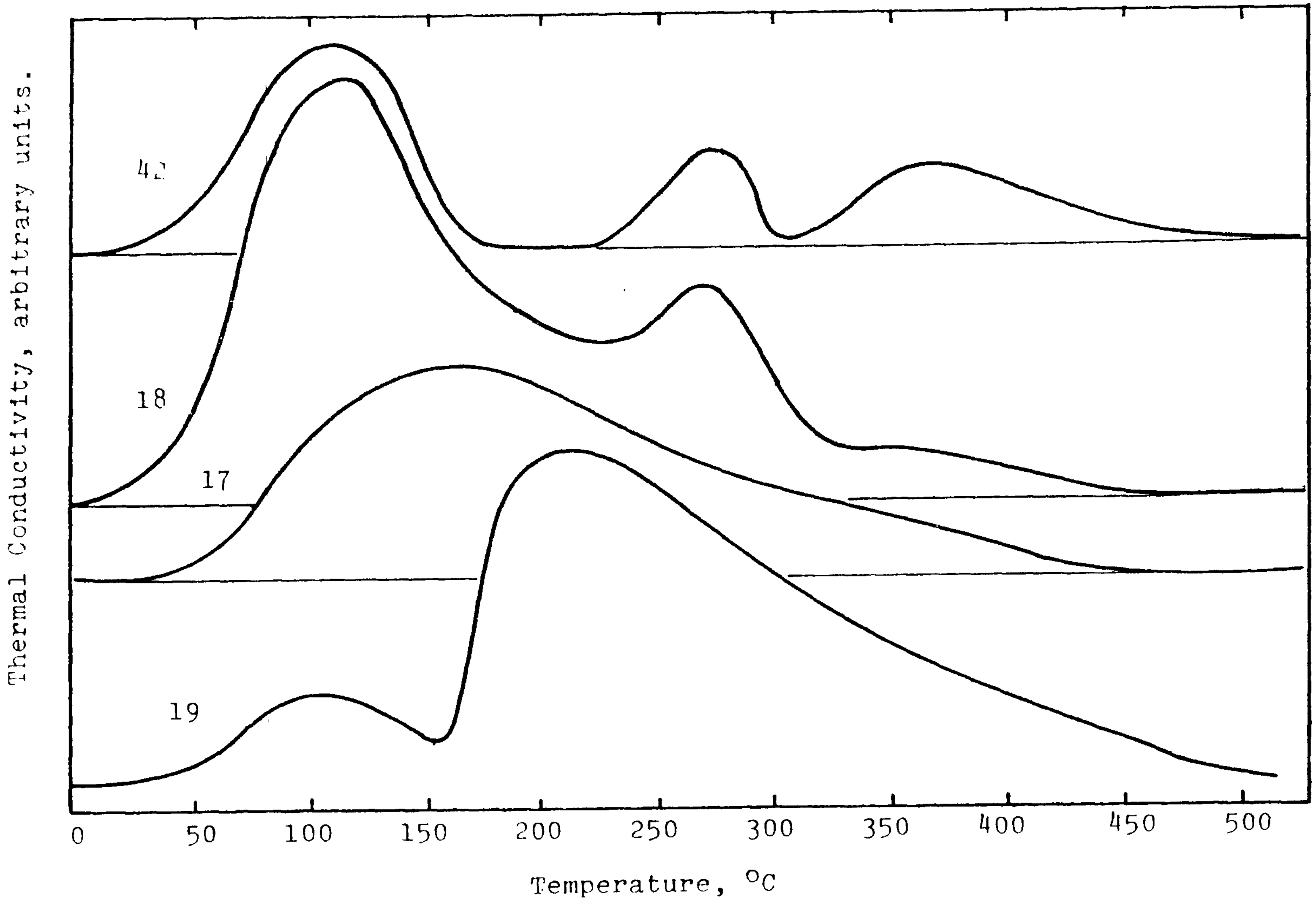


Figure 1. TPD of CO adsorbed on various CuCo/Al_2O_3 catalysts.

Project A-8

Synthesis of Light Hydrocarbons from CO and H_2

Carbon Monoxide Hydrogenation in a Slurry Reactor

Faculty Advisor: F.V. Hanson
Graduate Student: Y.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 accelerates 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, it is imperative that the heat of reaction be dissipated to prevent these undesirable side reactions. The objective of this investigation is to explore the potential of the slurry reactor for the dissipation of the heat of reaction, thereby maintaining the catalyst activity and selectivity.

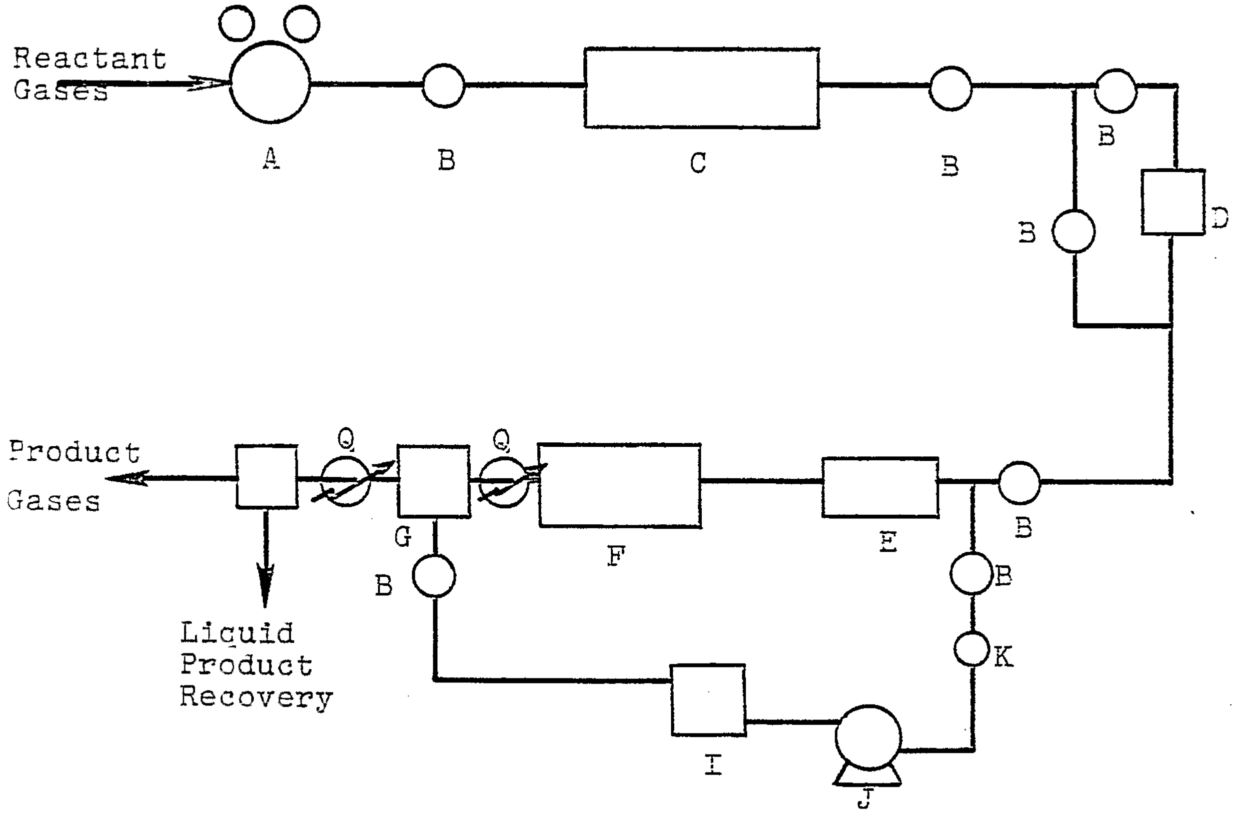
Project Status

The slurry reactor apparatus is in the design stage. Two distinct reactor types, a fixed-bed reactor and a "Carberry" or rotating basket reactor, are under active consideration for use in this project. The feed introduction system has been designed to achieve the mixing of the reactant gases (H_2 and CO) and the heat transfer medium (a high molecular weight normal paraffin or a nonreactive, temperature stable synthetic oil) external to the reactor preheater. The gas-liquid mixture will be brought to the reaction temperature in the preheater (an internal spiral in the fixed-bed reactor and an external heat exchanger for the rotating basket reactor) and contacted with the active catalyst under isothermal conditions. Gaseous reaction products will be separated from the heat transfer liquid and withdrawn from the system in a high pressure separator. The heat transfer liquid will be recycled to the heat exchanger/reactor inlet by means of a high pressure liquid circulation pump. A schematic of the apparatus is presented in Figure 1.

Future Work

The slurry reactor apparatus will be fabricated, and preliminary equipment testing and evaluation will be conducted. The fixed-bed reactor will be fabricated and tested while the rotating basket reactor is under construction. 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 - Autoclave valves
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 - Heat transfer liquid reservoir
J - Heat transfer liquid circulating pump
K - Metering valve
Q - Condenser/heat exchanger

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, multiringed 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 of model aromatic compounds is carried out using a stirred batch reactor. The preferential uptake of the aromatic from the aliphatic solvent is measured using a UV spectrometer. Adsorption isotherms are determined to supplement the diffusion studies.

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

Project Status

Work on this project has been reinitiated with a new student. Prior findings were reviewed to determine the best course of continued research on this project. Two areas have been singled out for detailed study and are discussed below.

The previous finding that measured diffusivities exceeded predicted pore diffusivities led to the conclusion that appreciable surface diffusion was occurring in these systems.[1] However, the predicted pore diffusivity depends on a value for bulk diffusivity. Since experimental values of the latter are not available, an empirical correlation is being used.[2] This correlation is based on data for small molecules and extrapolation to the larger molecules used in this study is tenuous. Therefore, it was deemed prudent to experimentally determine bulk diffusivities for the systems under study.

An apparatus for measuring bulk diffusivities has been set up similar to one described by Ouano.[3] A schematic diagram is presented in Figure 1. The main features are (1) a solvent pump, (2) an injection port for introducing a pulse of solute-solvent solution, (3) a diffusion tube and (4) a UV flow cell. The diffusion tube consists of a coiled length of 650 ft of stainless steel tubing having a 0.020 inch ID, which was specially fabricated to give a smooth inner bore. The basis of the method involves measurement of the peak spreading of a pulse of solute-solvent due to axial diffusion in the diffusion tube. The peak, obtained on the UV recorder, is sensitive to the solute (aromatic) and not the solvent (aliphatic). Analysis of the peak allows calculation of the diffusivity of the solute-solvent combination used. Preliminary tests showed good response, and measurement of several known mixtures agreed with the literature values.

The second area of investigation concerns restrictive diffusion of large molecules in small catalyst pores. Due to the apparently large surface diffusion rates obtained in the prior studies, assessment of restrictive pore diffusion is difficult. The contribution of surface diffusion depended on adsorption in the following way:[1]

$$D_e = D_p K_r + K D_s \qquad (1)$$

where D_e is the overall measured diffusivity, D_p is the predicted pore diffusivity, D_s is the surface diffusivity, K_r is the restrictive drag coefficient and K is the equilibrium adsorption constant. According to theory, the drag coefficient, K_r, is a measure of the reduction in diffusivity arising from increased frictional drag on the solute close to the pore walls and is only important for relatively large molecules in small pores.[4] In prior work, using naphthalene as the solute,

K_r is essentially unity since naphthalene is relatively small compared to the pore dimensions of the catalysts used. By altering the catalyst equilibrium adsorption (heating at different temperatures), the relationship of Eq (1) with $K_r = 1$ applied.

In some limited experiments using mesotetraphenylporphine as solute and the smallest pore size catalyst, the measured diffusivity was appreciably smaller than expected according to Eq (1) with $K_r = 1$. Since this system represents the largest solute molecular size (∿20Å) and the smallest catalyst average pore size (∿50Å), the low diffusion rate obtained may be due to a drag coefficient considerably less than unity. As the main object of this project is to assess the effect of molecular size vs. pore size on restrictive flow, a more detailed study of this system is warranted. Therefore the naphthalene study will be repeated using the porphine compound in an attempt to extract meaningful values of K_r by systematically decreasing the equilibrium adsorption constant of the catalyst.

Future Work

Measurements of bulk diffusivities of solute-solvent combinations employed in current and past studies will be made to obtain more reliable values than currently available. Diffusion studies using porphine will be initiated.

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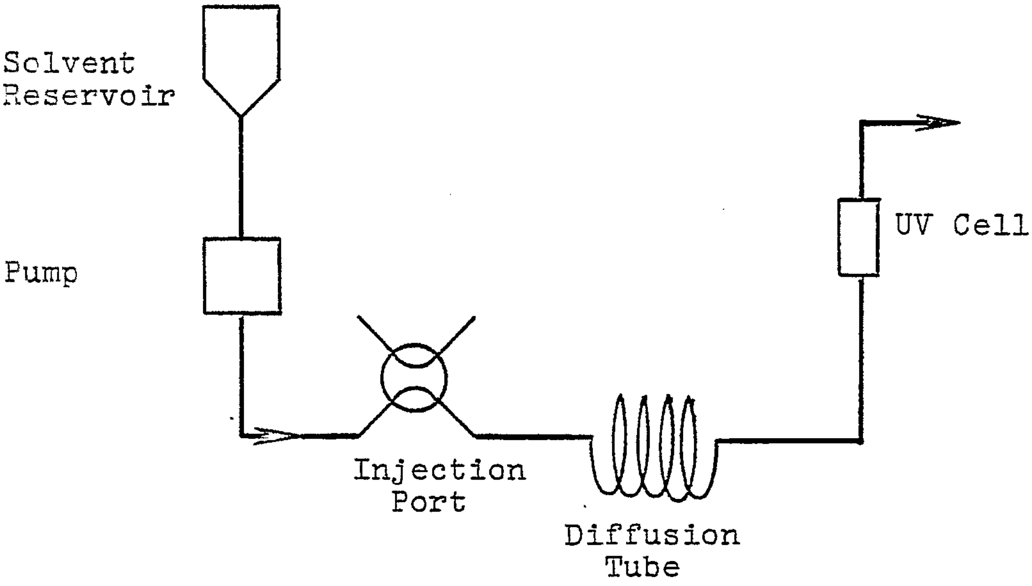
Figure 1. Schematic diagram of bulk diffusitity apparatus.



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 hydrotreating and hydrodesulfurization of petroleum feed stocks is well known. These catalysts are also being studied for hydrodesulfurization and liquefaction of coal slurries and coal-derived liquids. However, these complex feed stocks result in rapid deactivation of the catalysts. To gain an insight into the deactivation mechanism, detailed kinetics of the hydrodesulfurization of the model compound benzothiophene are compared before and after addition of various poisons and coke presursors. 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 found to be irreversible poisons. 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. Studies on benzothiophene coking tendencies showed little coking (mostly reversible) in H_2 but massive, irreversible coking in N_2. The catalyst alumina carrier by itself gave appreciable coke in H_2, showing that the active components of the catalyst serve to inhibit coking tendencies of the carrier.

Project Status

While awaiting fabrication of the new metal reactor for kinetic studies, temperature programmed desorption (TPD) studies were continued. These involved measurement of desorption profiles for thiophene adsorbed on freshly sulfided and subsequently poisoned catalysts. The apparatus and procedure has been described earlier.[1]

In the initial runs, the thiophene was adsorbed at room temperature. Desorption resulted in a large broad peak around 100°C and a much smaller one at about 150°C, which often merged with the larger peak. The activation energy of the larger peak corresponded to 5 kcal/mole for all catalysts tested. Since this value seemed low for chemisorption and the same value was obtained for pure alumina and silica, it was concluded that this adsorption was predominately physical. Therefore, to avoid overlap of this larger physical adsorption with the smaller chemisorption peak, the experiments were repeated using a starting thiophene adsorption temperature of 100°C. Now, only the second peak, attributable to chemisorption, was obtained and its peak temperature could be accurately determined. Following tests on the freshly sulfided catalysts, quinoline was added to poison active sites and the TPD sequence repeated to ascertain the effect of the poison on the catalyst chemisorptive properties.

To determine if the desorption peak being measured was associated with the active catalyst sites and not the alumina phase of the catalyst, pure MoS_2 was run. The peak observed occurred at the same position as that for the sulfided Mo/Al_2O_3 catalyst, confirming that the chemisorption was on the MoS_2 phase of the catalyst.

Table 1 presents the results obtained on the Mo/Al_2O_3 and $CoMo/Al_2O_3$ catalysts before and after poisoning. The Mo/Al_2O_3 catalyst chemisorbed considerably less thiophene indicating less adsorption sites than the $CoMo/Al_2O_3$ catalyst. After poisoning, about one-half of these sites were still active for chemisorption. All desorption peaks were rather sharp indicating a uniformity in the adsorption sites. The activation energy for desorption was about the same for both fresh catalysts showing that the strength of the adsorption sites were essentially identical in the two catalysts. The activation energy was only slightly higher for the poisoned $CoMo/Al_2O_3$ catalyst, whereas a large increase was obtained for the Mo/Al_2O_3 catalyst. In either case, the poisoned catalyst showed only one well-defined peak, precluding the possibility that some of the thiophene may have adsorbed on the quinoline. These results for the Mo/Al_2O_3 catalyst imply that adsorbed quinoline not only blocks active sites, but it significantly alters the adsorption characteristics of the remaining sites, i.e., it increases their adsorptive strengths. The presence of cobalt somehow moderates this effect.

Previous studies of pyridine poisoning on reaction of benzothiophene[2] showed that this technique could be used to assess the number of active sites on the catalyst. The basis of this method involved simultaneous measurement of the weight of pyridine added and benzothiophene conversion under reaction conditions using the flow microbalance reactor. A possible source of error could arise if some of the pyridine adsorbed on inactive sites, e.g., the alumina, giving rise to a high estimate in the number of active sites. To check this possibility, adsorption of pyridine on the γ-Al_2O_3 support alone was measured under reaction conditions. Adsorption on Al_2O_3 was small, in the order of 5-10% of that obtained on the catalyst. Thus, the pyridine adsorption takes place predominantly on the active catalyst component, and the technique appears to be valid.

Future Work

Temperature programmed desorption tests will be carried out on coked catalysts to ascertain what effect coke has on catalyst adsorption properties. When the new metal reactor is available, trial runs of reactor performance will be conducted prior to kinetic runs on benzothiophene hydrodesulfurization.

References

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

2. *ibid.*, July-Sept 1976.

Table 1. TPD Results on Catalysts.

Catalyst	Relative Amount Desorbed	Activation Energy Kcal/mole
$CoMo/Al_2O_3$	1.0	11.8
+ Poison	0.5	14.8
Mo/Al_2O_3	0.6	12.7
+ Poison	0.25	25.2

Project B-4

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 as a function of temperature, pressure and catalyst using Infrared Spectroscopy. Other parameters for possible consideration are atmosphere, residence time and type of coal.

Friedel et al. have associated various coal structures with peaks in its IR spectrum.[1] These peaks have been investigated at the University of Utah as a function of reaction temperature, catalyst and atmosphere. Results of this study have been published.[2] Further experiments will include reactions under pressure.

Project Status

Work this quarter has been to establish procedures which will give reliable quantitative results. The coal char samples will be prepared in a micro reactor in Project D-1. Two variables have been identified this quarter affecting the reproducability of the IR spectrum. The first is particle size which will affect both the apparent absorbtivity of the sample and the amount of radiation scattering. Extensive grinding of the sample controls the particle size but introduces contamination peaks into the spectrum. The second variable is the amount of contamination introduced in sample preparation.

Equipment being used include a Perkin-Elmer Auto Balance Model AD-2, a Wig-L-Bug with a stainless steel vial and pestle, a hydraulic press and dye for pellet preparation and a Perkin-Elmer Infrared Spectrometer Model 283.

Future Work

Several alternatives are being evaluated in the sample preparation procedure. Among those tried so far are heating the sample to remove moisture contamination peaks, and grinding in a solvent to avoid moisture reactions with the potsssium bromide. Work will begin on the next phase of the project once the procedure has been perfected.

References

1. Friedel et al., U.S. Dept of the Interior, U.S. Bureau of Mines, Bulletin 640, Government Printing Office, Washington, D.C., 1969.

2. Jun Moung Lee, Preprints, Division of Fuels Chemistry, American Chemical Society, 23, 275 (1978).

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 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

Clear Creek, Utah coal (0.83% H_2O, 6.50% ash, 45.42% VM and 47.25% FC) was hydrogenated in a short-residence, coiled-tube reactor. Zinc chloride, $Co\text{-}Mo/Al_2O_3$, red-mud plus sulfer and presulfided red-mud were used as catalysts. The particle size was -100, +200 mesh and the catalyst ranged from 6.4% for $ZnCl_2$ to 10.7% for the others. Coal was also hydrogenated without catalyst. The temperature ranged from 400°C to 500°C and the hydrogen pressure was 1800 psi. Residence time (8 - 372 sec) was varied by choice of the tube length (40 - 120 ft).

Products were separated by stepwise extraction using hexane, toluene and pyridine. The extraction scheme is shown in Figure 1. Part of the results are shown in Table 1. Results of hydrogenation at 920°F for 8∿12 sec in the presence of different catalysts and without catalyst are compared in Figure 2. The conversions are all about 20%. The catalytic effect on conversion and product distribution is not apparent. This indicates that at least up to 20% of Clear Creek, Utah coal converts noncatalytically into liquid and gas. This is similar to the results on Japanese coals.[1,2]

In Figure 3 the effect of temperature and time at 920°F on conversion and product distribution using $ZnCl_2$ catalyst are shown. The effect of temperature during short residence times of 8 to 13 sec is observed, however, it is not large. Conversions increase from ca. 6 to ca. 18% with the increase of temperature from 750 to 920°F. However, the effect of time at 920°F is great, for example, conversions increase from ca. 18 to ca. 35% during the period from 8 to 21 sec.

These results indicate that in this reactor the reaction up to 920°F and 12 sec proceeds noncatalytically. About 20%

of the coal takes part in the reaction. After 920°F and 12 sec, the reaction proceeds catalytically and is greatly affected by residence time.

Future Work

Toluene-insolubles will be separated from the products with pyridine and liquid products extracted with hexanes. Structural analysis of the various products will be performed.

References

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2. R. Yoshida, Y. Maekawa, G. Takeya, J. Fuel Soc. (Japan), 51, 1225 (1972).

Table 1. Yield of products from hydrogenation

Catalyst	Temp. (°F)	Tube length (ft.)	Time (sec.)	Product distribution(%,d.a.f.)						Conversion (%,d.a.f.)
				liquid			gas	residue		
				aqueous phase	liquid	total		toluene-solubles	toluene-insolubles	
$ZnCl_2$	750	120	13	1.7	1.9	3.6	2.0	0.6	93.8	6.2
	840	120	13	4.0	5.7	9.7	3.2	2.5	84.6	15.4
	920	40	8	4.2	7.8	12.0	2.0	3.7	82.3	17.7
		60	21	4.9	19.1	24.0	3.5	8.0	64.5	35.5
		80	8	3.9	9.6	13.5	2.9	2.3	81.3	18.7
		120	372	7.4	38.8	46.2	11.0	17.0	25.8	74.2
Co-Mo	920	120	12	3.3	10.4	13.7	2.6	2.9	80.8	19.2
Presulfided red-mud	920	120	12	4.5	11.8	16.3	4.1	2.5	77.1	22.9
Red-mud plus sulfur	920	120	12	4.3	12.0	16.3	3.3	2.5	77.9	22.1
No	920	120	10	2.9	10.7	13.6	3.4	3.0	80.0	20.0

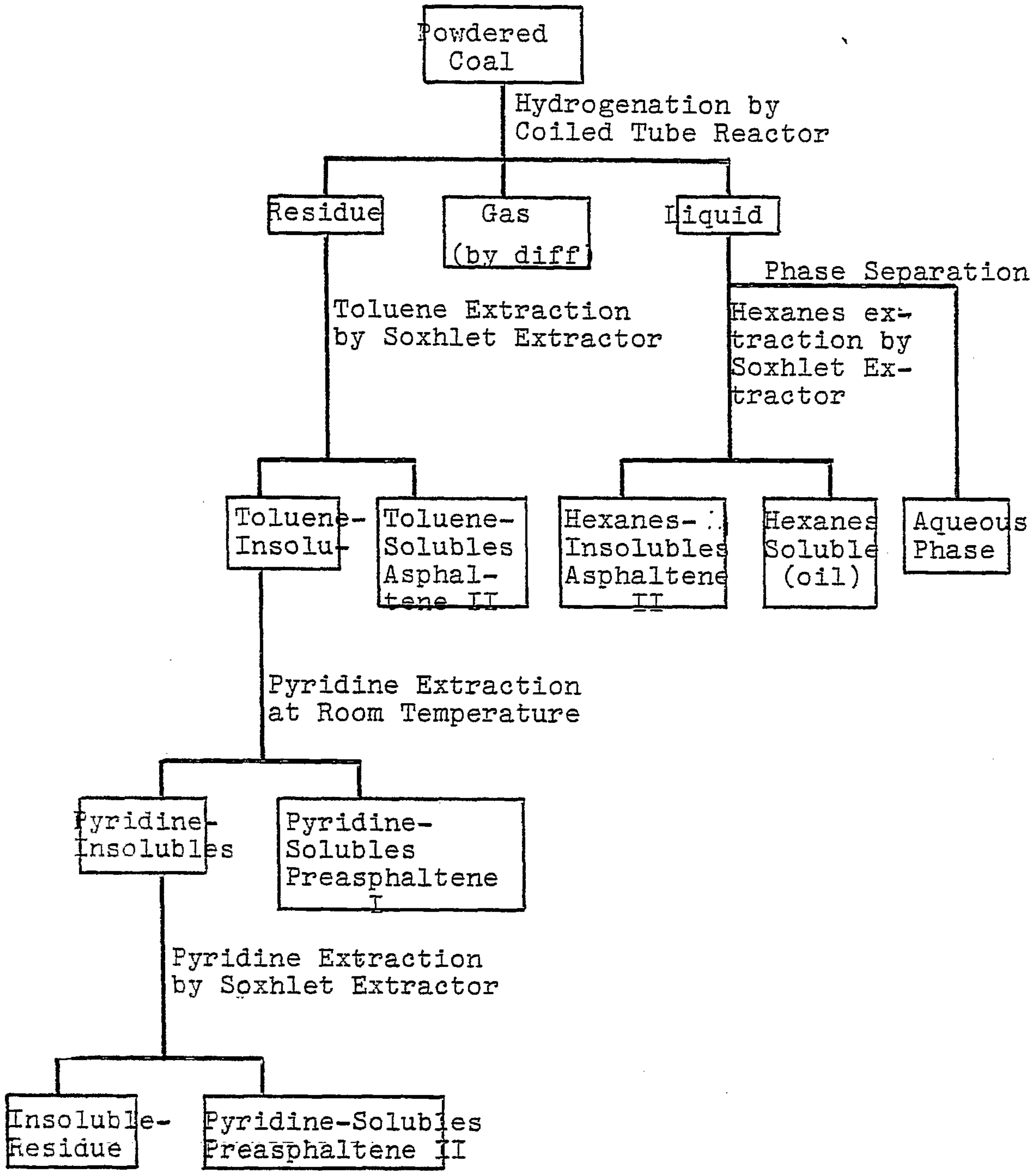


Figure 1. Flow diagram for the processing of products from the hydrogenation by coiled tube reactor.

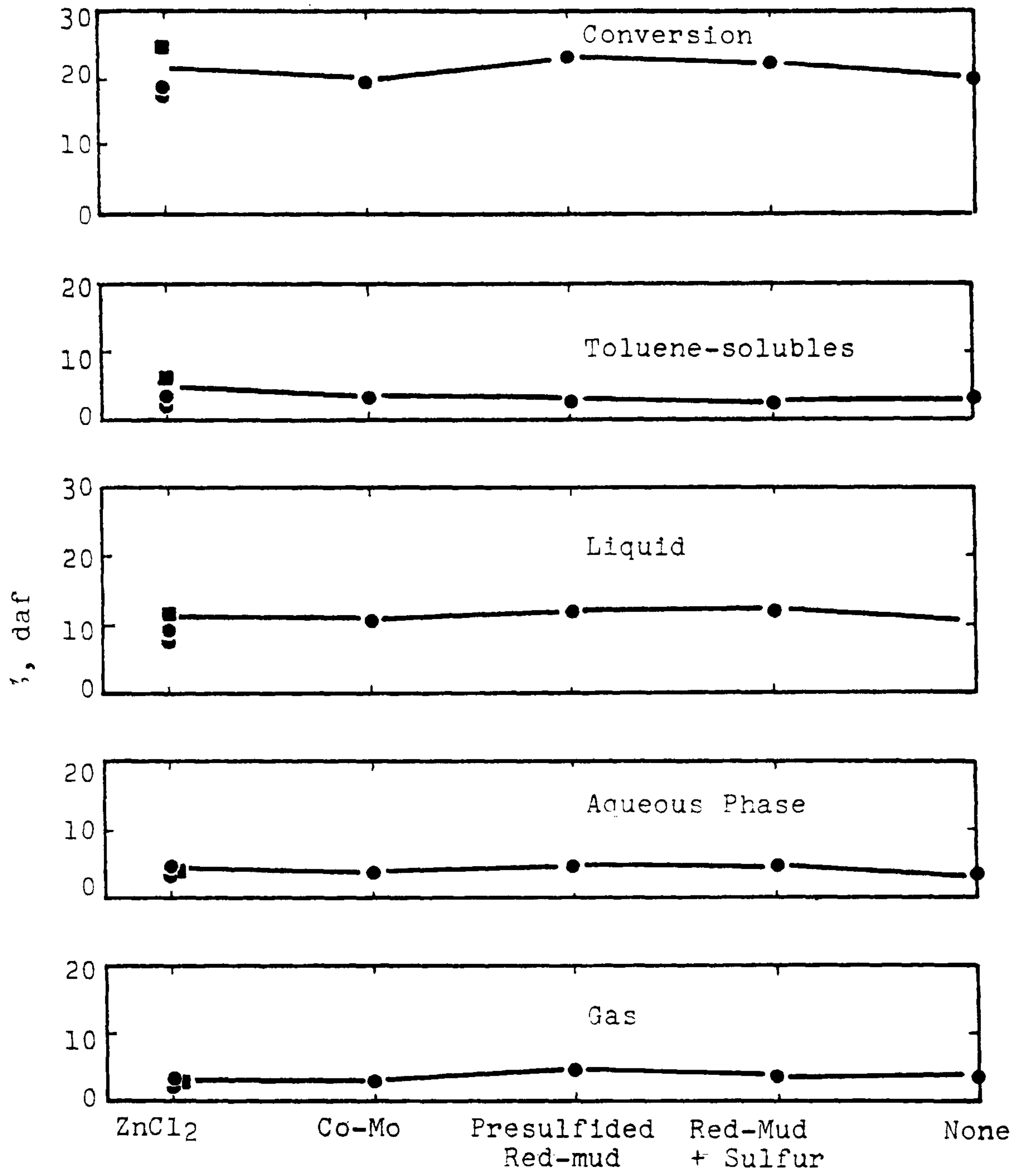


Figure 2. Product distribution in the presence of catalysts. Temp = 920°F, Time = 8∿12 sec, x = correspond to 12 sec.

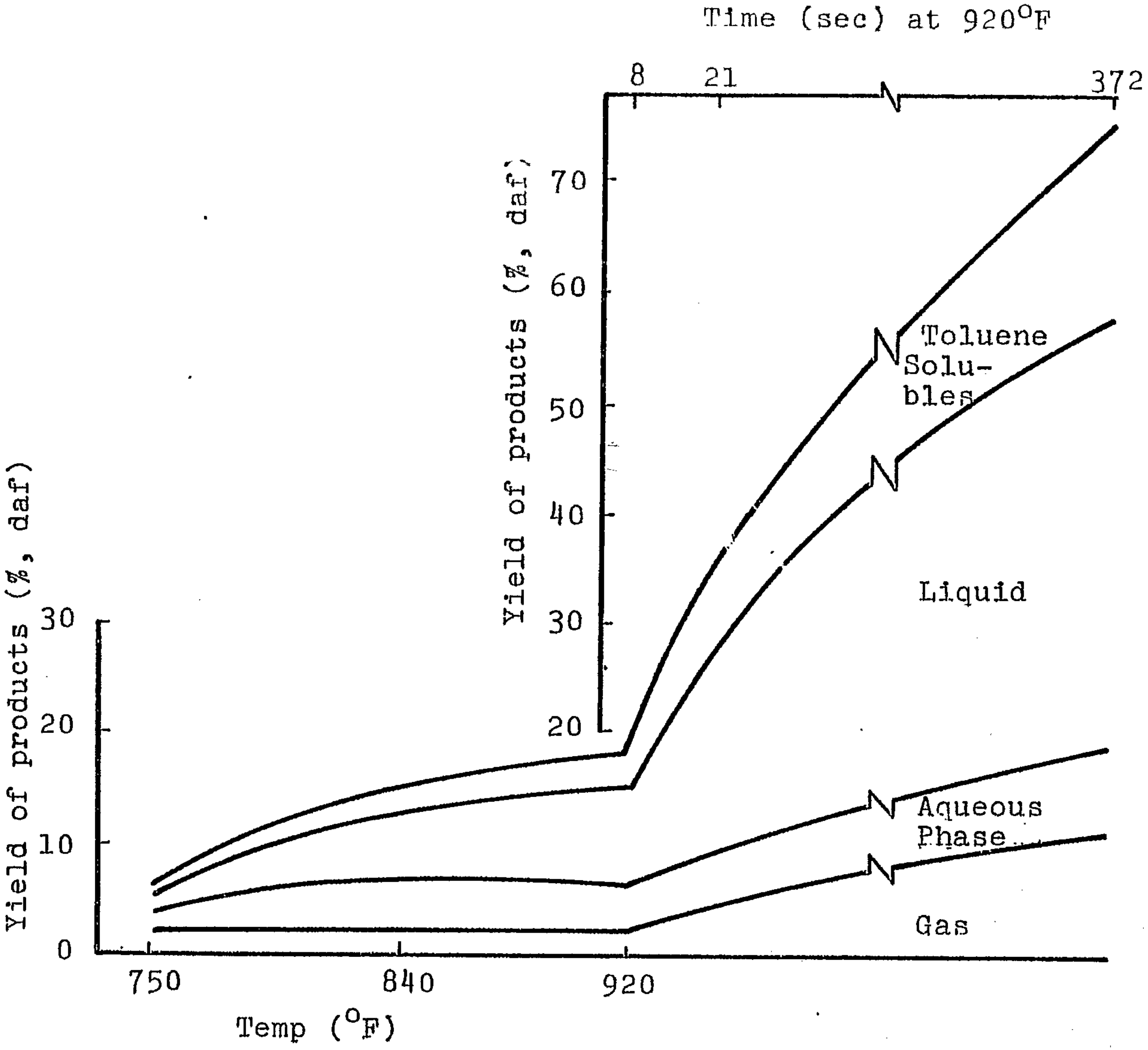


Figure 3. Effects of temperature and time on hydrogenation with $ZnCl_2$ catalyst.

Project C-1

The Mechanism of Pyrolysis of Bituminous Coal

Faculty Advisor: W.H. Wiser
Graduate Student: R. Muthiah

Introduction

Under conditions of coal liquefaction by either solvent extraction or catalytic hydrogenation techniques the pyrolytic reactions would also be in progress and may possibly play an important role relative to product yields. The mechanism of the pyrolytic reactions is therefore of considerable importance and interest. If one would maximize coal liquefaction processes one would do well to understand the kinetics and mechanisms of the processes.

Pyrolytic studies of coal using a linear temperature increase have usually reported the kinetics to be first order with respect to unreacted but potentially reacting coal. Isothermal pyrolytic studies at the University of Utah and in other laboratories have consistently reported second order kinetics with respect to unreacted but potentially reacting coal. Lahiri and co-workers in India observed that hydroaromatic structures in coal are essential in the production of tar during coal pyrolysis. Present studies at the University of Utah are designed to gain information concerning the role of the hydroaromatic structures in tar production during coal pyrolysis and to discern, if possible, the mechanism leading to first order or second order kinetics in coal pyrolysis.

Project Status

Five sets of pyrolysis runs were conducted and repeated at 380, 400, 425, 450 and 470°C (±2°C) in a fluidized sand bath. During each set, a reaction tube was withdrawn every 3-5 min and quenched with liquid N_2. All samples were analyzed by GC, 12 ft 1/8 inch stainless steel column packed with SP-2250 on Chromosorb 100/120. The GC-MS analyses confirmed the presence of benzene, toluene, bibenzyl, 1,2,3,4-tetrahydrocarbazole, carbazole, 9-benzyl, 1,2,3,4-tetrahydrocarbazole and 9-benzyl carbazole and a very small amount of methyl indole.

The data points obtained from the runs at 380 and 470°C were scattered. The data reduction for the runs at other temperatures are being done. The reasons for the scatter may be due to the loss of benzene and toluene vapors when the reaction tubes were opened and/or the degradation of the column performance.

Pyrolysis of 1,2,3,4-tetrahydrocarbazole (THC) was done at 380 and 470°C for 10, 20 and 40 min durations. Duplication of the runs showed close agreement with the original experiments. These results indicate that the predominate reactions do not involve thermal dehydrogenation or splitting of THC (indole derivatives). This confirms that once THC is formed from the pyrolysis of 9-benzyl, 1,2,3,4-tetrahydrocarbazole, further dehydrogenation (to carbazole) of the THC is negligible. The presence of carbazole was not evident in the IR spectra of pyrolyzed THC further confirming this conclusion.

Future Work

The data will be studied in detail to explain the scatter of the data points. Some runs will be repeated.

Project C-2

Heat Transfer to Gas-Solid Suspensions in Vertical Cocurrent Downflow

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

Introduction

Experiments are being conducted both with glass beads and with coal particles to investigate the momentum and heat transfer mechanisms in a two-phase, gas-solids mixture flowing downward through a vertical tube. An understanding of the fundamental mechanisms will lead to design correlations that will have general applicability in the field of two-phase, gas-solids transport, particularly for the continuous coal hydrogenation reactor wherein coal particles and hydrogen gas flow together downward through a vertical, heated tube. The glass bead experiments are nearing completion and the experiments with actual coal particles are in progress.

Project Status

Particle velocity and pressure drop measurements for coal particles (-28/+48 mesh) flowing downward through a vertical tube (ID 0.497") were obtained using the equipment described in a previous report. The total pressure drop, as measured at the lowest pressure tap interval (L/D=483), was fairly independent of solids loading ratio, R, for the range of investigation shown in Figure 1. The data are comparable to the pressure drop obtained with the glass beads (329 micron) at a gas Reynolds number, Re, of 10000. Data for Re greater than 10000 have not been taken because of fluctuations and instabilities in the system, which are present at the higher gas flow rates. As described in a previous progress report, the total pressure drop consists of acceleration, hydrostatic, and frictional components. If the acceleration pressure drop is negligible, then the total pressure drop, ΔP_m, is given for vertical downflow by

$$\Delta P_m = \Delta P_f - [\rho_p E_p + \rho_g (1-E_p)]gL \qquad (1)$$

where ΔP_f is the frictional pressure drop, E_p is the in situ fractional volume occupied by solids, ρ_p and ρ_g are the solid and gas densities, respectively, and L is the distance between pressure taps. Thus the insensitivity of total pressure drop to loading ratio can be explained as follows: The magnitudes of both the frictional and hydrostatic components increase with loading ratio, but their effects on the total pressure drop partially cancel because they are of opposite sign.

Direct particle velocity measurements, made by the tagged-sample injection technique described previously, indicate no slip between the gas and the coal particles at the location of measurement. Particles injected into a flowing mixture with a solids loading ratio of 17 had the same average velocity (equal to the gas velocity) as particles injected into gas alone (R=0). Glass beads (329 micron) were previously found to have a particle velocity (calculated indirectly from holdup data) equal to approximately 70 percent of the gas velocity when R was greater than one. For R less than one, the calculated particle velocity exceeded the gas velocity. It is not yet known whether the coal particles or glass beads are fully accelerated or why the particle velocity of the glass beads shows a dependence on loading whereas the coal particles do not. The calculated frictional pressure drop for the coal-air suspension based on no slip is also shown in Figure 1.

The air and coal inlet section was modified to reduce the pressure fluctuations which occur at higher gas flow rates. Due to a pressure tap problem, it is not yet known whether the modification was successful. The cause of the apparent feeder instability is also not yet known.

After initial checking of the system operation with gas alone, heat transfer experiments for the air-glass bead suspension flow have been conducted this past quarter. The experimental range covers the gas Reynolds number of 10000 to 30000 with solids loading ratios up to 20.

In the previous report, the continuity and momentum equations of a suspension flow were formulated by assuming each phase as a continuum. In the same manner, the suspension energy equation can be obtained as follows.
Gas Phase Energy Equation:

$$
\begin{aligned}
\frac{\partial}{\partial t}\left[\rho_g(1-E_p)\left(\hat{U}_g+\frac{1}{2}|U_g|^2\right)\right] = & -\frac{\partial}{\partial x}\left[\rho_g(1-E_p)U_g\left(\hat{U}_g+\frac{1}{2}|U_g|^2\right)\right] \\
& -\frac{1}{\gamma}\frac{\partial}{\partial \gamma}\left[(1-E_p)\gamma q_{g,\gamma}\right]-q_{g-p} \\
& -\frac{\partial}{\partial x}\left[(1-E_p)PU_g\right] \\
& -\frac{1}{\gamma}\frac{\partial}{\partial \gamma}\left[\gamma(1-E_p)\tau_{\gamma x,g}U_g\right] \\
& +(1-E_p)\rho_g U_g g \qquad (2)
\end{aligned}
$$

Particle Phase Energy Equation:

$$\frac{\partial}{\partial t}[\rho_p E_p(\hat{U}_p+\tfrac{1}{2}|U_p|^2)]=-\frac{\partial}{\partial x}[\rho_p E_p U_p(\hat{U}_p+\tfrac{1}{2}|U_p|^2)]$$

$$-\frac{1}{\gamma}\frac{\partial}{\partial \gamma}[E_p \gamma q_{p,\gamma}]+q_{g-p}$$

$$-\frac{\partial}{\partial x}[E_p P U_p]$$

$$-\frac{1}{\gamma}\frac{\partial}{\partial \gamma}[\gamma E_p \tau_{\gamma x,p} U_p]$$

$$+E_p \rho_p g U_p + F_D U_p \qquad (3)$$

From the total energy Equations (2) and (3), thermal energy equations can be obtained by neglecting viscous dissipation terms and using specific heat of the gas and particle at constant pressure in place of internal energy.

Gas Phase Thermal Energy Equation:

$$\rho_g(1-E_p)C_{p,g}\left(\frac{\partial T_g}{\partial t}+U_g\frac{\partial T_g}{\partial x}\right)=\frac{1}{\gamma}\frac{\partial}{\partial \gamma}\left[(1-E_p)\gamma k_g\frac{\partial T_g}{\partial \gamma}\right]-\left(\frac{6h_pE_p}{d_p}\right)(T_g-T_p) \qquad (4)$$

Particle Phase Thermal Energy Equation:

$$\rho_p E_p C_{p,p}\left(\frac{\partial T_p}{\partial t}+U_p\frac{\partial T_p}{\partial x}\right)=\left(\frac{6h_pE_p}{d_p}\right)(T_g-T_p) \qquad (5)$$

Based on the established solution technique[1,2] of the single phase analog of Equation (4), Tien[3] and Depew[4] proposed analytical solutions of the above equations for the constant wall temperature and constant heat flux boundary conditions, respectively. They defined the suspension Nusselt number based on a suspension mixed mean temperature as

$$Nu_{sm}=\frac{h_1 D}{k_g}=\frac{q_1 D}{(T_w-T_{sm})k_g} \qquad (6)$$

Both analyses predict an increase in the entrance length due to the solids, which agrees with the experimental results. However, Nusselt numbers calculated from their model do not agree with experimental data due to the assumptions that were required to make the problem mathematically tractable.

Typical curves of the Nusselt number ratio along the axial distance are shown in Figure 2, which clearly shows a trend of increasing thermal entry length with solids loading ratio. For loading ratios greater than about 3 to 4, however, the profiles become almost invariant. This phenomena might be due to the compensating nature of the following two effects:

(1) The length scale of the thermal entrance region is increased due to the increased thermal capacity of the gas by the addition of the solids.

(2) Although the particles may increase the thermal capacity of the gas, they may also increase the radial turbulent transfer of heat, which will act to reduce the entrance length.

Figure 3 shows the effect of solids loading ratio on asymptotic Nusselt numbers as defined by Equation (6). A gradual decrease in the Nusselt number occurs according to the increase in the loading ratio. For the lower air flow rate, the curves stop decreasing at a loading ratio of about 3, and the Nusselt number begins to increase.

In spite of the decreasing Nusselt numbers with the solids loading ratio, the heat flux required to keep the same wall temperature was always larger with solids than without solids. From this observation, the decreasing trend of Nusselt numbers may be more or less exaggerated due to the very definition of the Nusselt number based on the suspension mixed mean temperature which assumes that the gas and particle temperatures are the same. If direct radiation from the wall to the particle is negligible when compared to the convective heat transfer from the gas, the actual gas temperature will be higher than the particle temperature. Nusselt numbers based on the gas mean temperature using Eq (7) will therefore be higher than those indicated in Figure 2.

$$Nu_{gm} = \frac{q_i D}{(T_w - T_{gm}) k_g} \tag{7}$$

The temperature difference between the two phases can be estimated by solving the macroscopic energy balances equivalent to Equations (3) and (4).

$$\bar{U}_g \frac{dT_{gm}}{dx} = \frac{4\ q_i}{\rho_g (1-E_p) C_{p,g} D} - \frac{6 h_p E_p}{\rho_g (1-E_p) C_{p,g} d_p} (T_{gm} - T_{pm}) \tag{8}$$

$$\bar{U}_p \frac{dT_{pm}}{dx} = \frac{6 h_p}{\rho_p C_{p,p} d_p} (T_{gm} - T_{pm}) \tag{9}$$

Equations (8) and (9) were solved using the relations obtained from the fluid mechanical study and the particle Nusselt number relation

$$Nu_p = 2 + 0.6\, N_{Re,p}^{0.5}\, N_{pr}^{0.3} \quad (10)$$

In Figure 4 the temperature variation along the length of the heated tube for a single particle at a gas Reynolds number of 30000 are shown. Although the temperature difference decreases with the solids loading ratio, it is generally of the same order of magnitude as shown in this figure. For 329 micron glass beads which are used in this research, a substantial temperature difference exists between the gas and particle temperatures. From this result, the Nusselt number based on the gas-phase mean temperature represents a more realistic choice for the air-coarse particle system considered in this research. Calculations are now being made to recalculate Nusselt numbers based on the gas-phase mean temperature.

Future Work

Analysis of the air-glass bead heat transfer data will be continued. This will involve comparison of these data with the upflow results reported in the literature. A better understanding of the basic problems in defining the two-phase flow friction factors and Nusselt numbers will be sought.

For the air-coal particle studies, plans for the next quarter include solving the problems of instability and fluctuation and then obtaining data at the higher gas flow rates. This data will be compared to that obtained with glass beads. Particular attention will be given to the apparent discrepancy between particle velocity for the coal and glass beads and the dependence of this velocity on loading ratio.

References

1. C.A. Sleicher and M. Tribus, Trans.of the ASME, 79, 789 (1959).

2. E.M. Sparrow *et al.*, Appl. Sci. Res. 7, Sec A, 37 (1957).

3. C.L. Tien, Trans. ASME, J Heat Transfer, 83, 183 (1961).

4. C.A. Depew, Ph.D. Thesis, University of California, Berkeley, California, 1960.

Nomenclature

A_p	Surface area of a particle, ft^2
C_p	Specific heat, BTU/lbm ^{o}F
E_p	Holdup
g	Gravitational constant, 32.2 ft/sec^2
h_i	Wall heat transfer coefficient, BTU/ft^2 hr ^{o}F
h_p	Particle heat transfer coefficient, BTU/ft^2 hr ^{o}F
n	Number of particles per unit volume
P	Pressure, lbf/ft^2
q_i	Wall heat flux, BTU/ft^2 hr
γ	Radial distance
t	Time, sec
T	Temperature, ^{o}F
$\hat{U}$	Internal energy, BTU/lbm
U	Actual velocity, ft/sec
$\bar{U}$	Average actual velocity, ft/sec
x	Axial distance, ft
ρ	Density, lbm/ft^3
τ	Shear stress, lbf/ft^2

Subscripts

g	Gas phase
p	Particle phase
s	Suspension
m	Mixed mean

Figure 1. Total pressure drop at lower pressure tap interval.

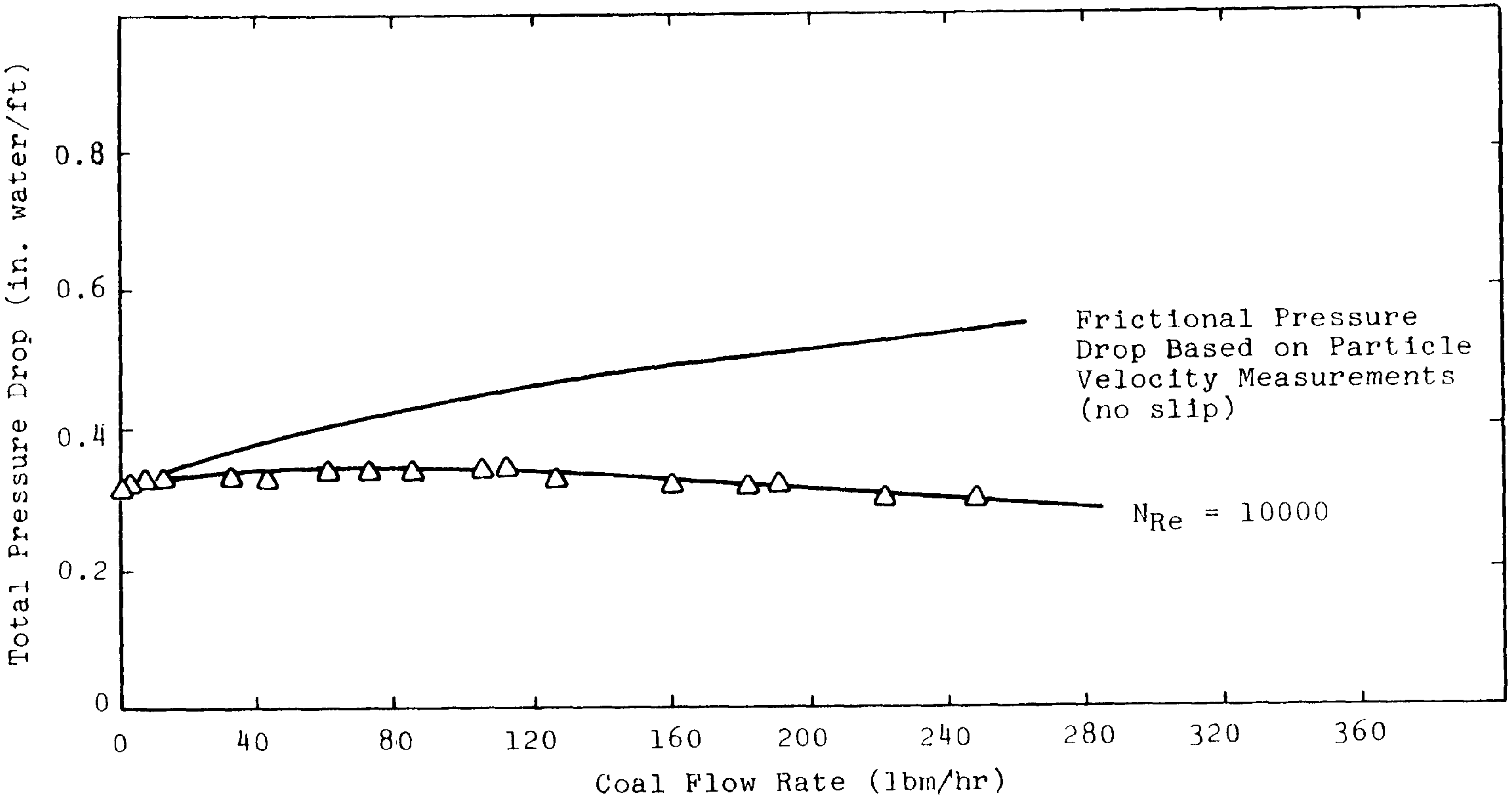


Figure 2. Effect of solids loading ratio on thermal-entry length.

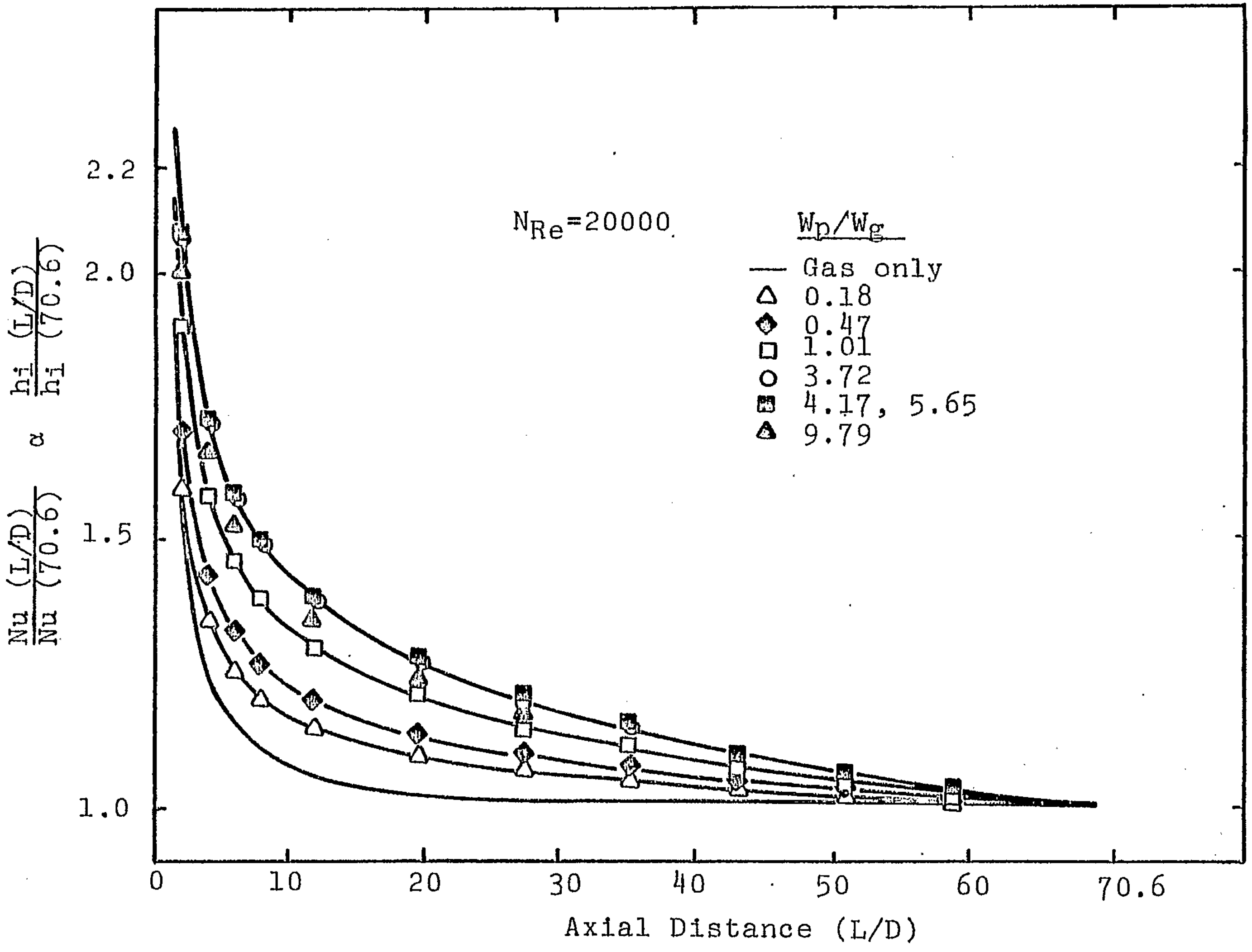
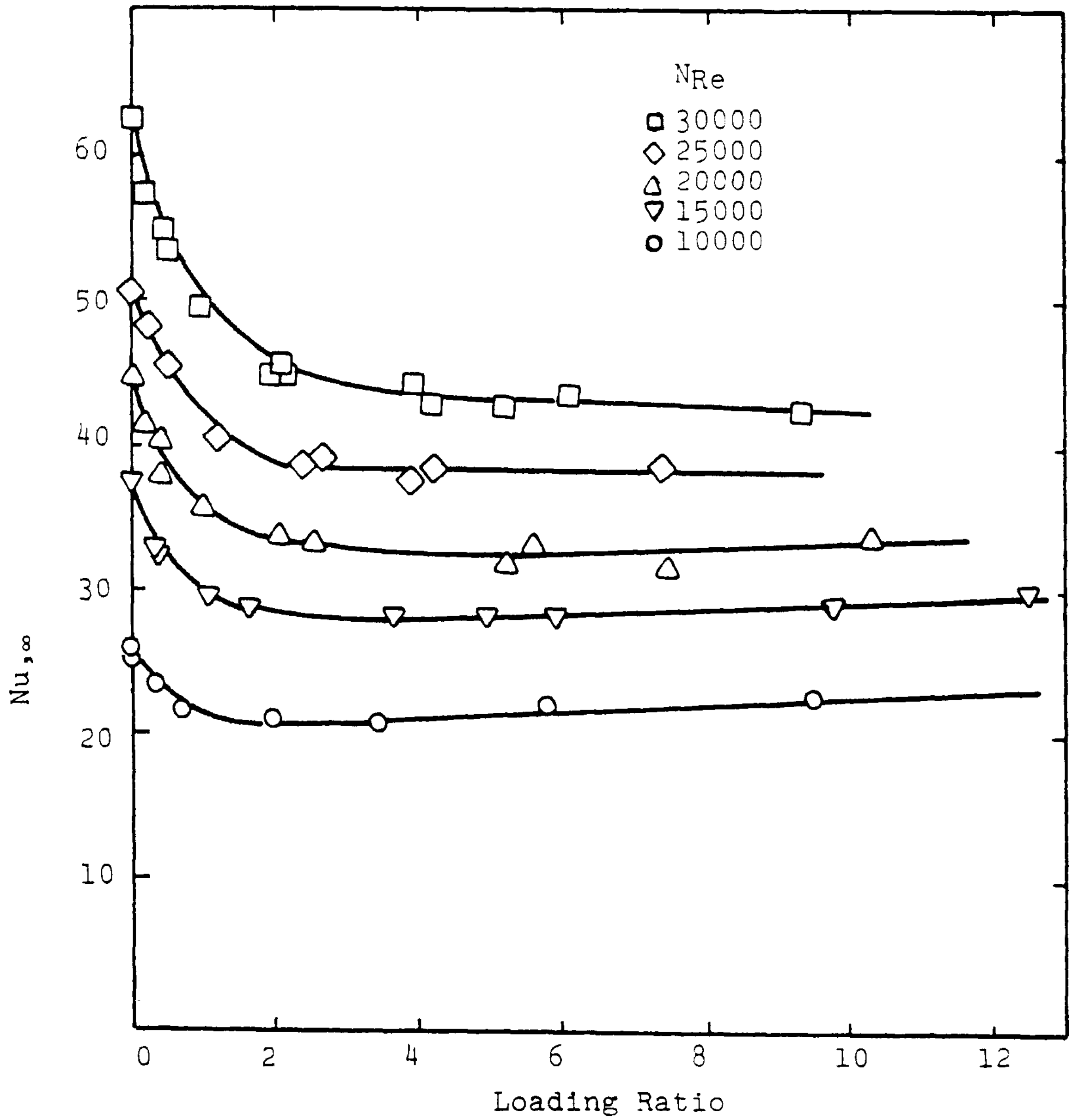


Figure 3. Effect of solids loading ratio on the asymptotic Nusselt number.



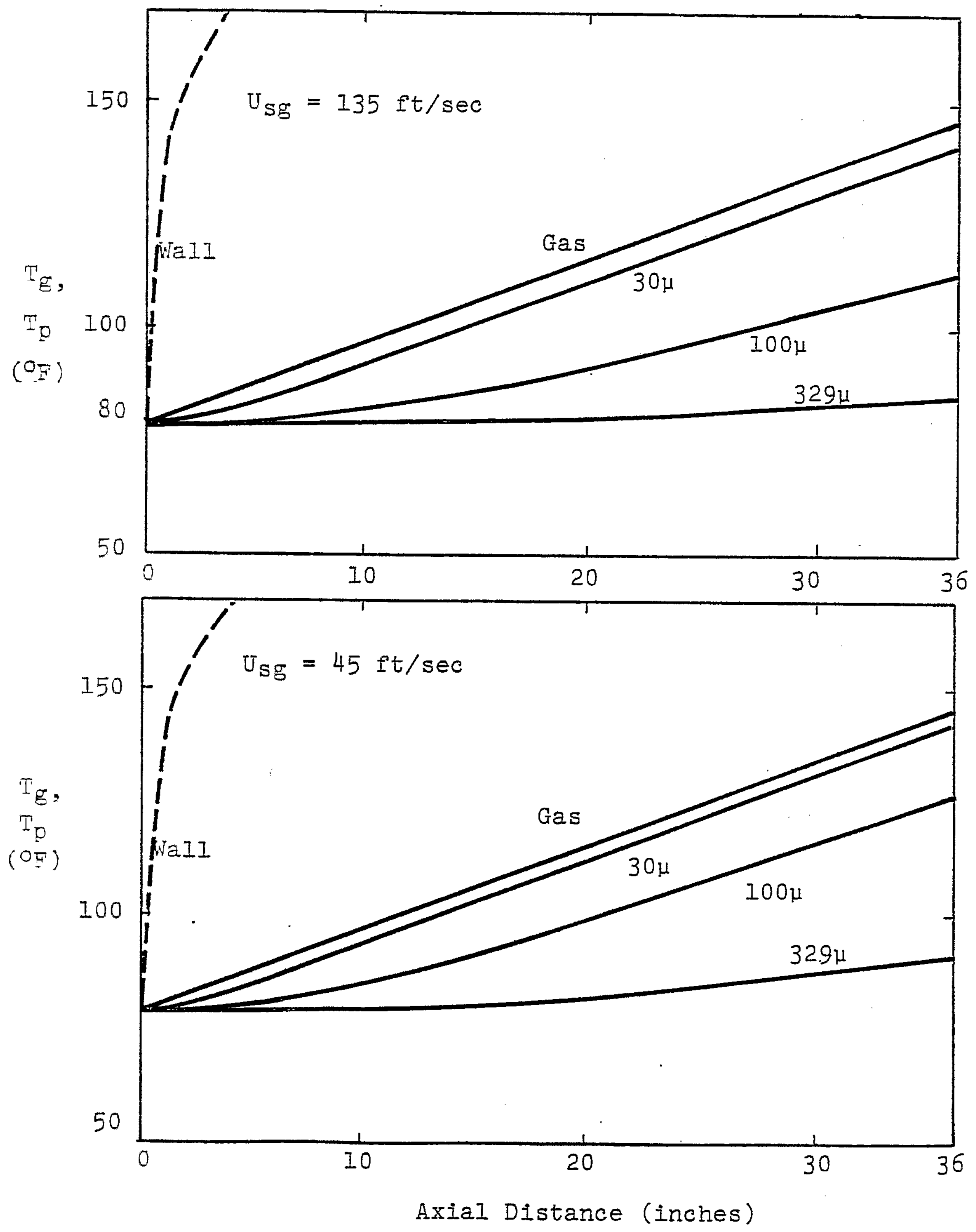


Figure 4. Axial Temperature Variations.

Project D-1

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 preheater 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.[1-3] 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 section.

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 characteristics and coal-catalyst interactions.

Project Status

Measurements with Clear Creek, Utah coal with widely different residence times in the coiled tube reactor and consquently different conversion levels have led to the data of Figure 1. As shown the volatile matter is initially reduced at a more rapid rate than is fixed carbon. As conversion becomes greater the rate of consumption of fixed carbon increases and that of volatile matter decreases. This indicates a mechanism which includes a reaction whereby fixed carbon is transformed to volatile matter and hence to liquids and gases. A similar effect has been observed with a variety of coals.[4] Other workers have observed that the volatile of coal is directly proportional to the hydroaromatic hydrogen content of the coal.[5] As the hydroaromatic content of a given coal is increased by reduction so also is the volatile matter of that coal. The mechanism of this change will be investigated further.

The details of the microreactor are shown in Figure 2. Together the reactor and filter weigh about 125 g. They, therefore, may be weighed along with reactants on a 5 place balance. Those items normally obtained with this reactor with 4 place accuracy are H_2 consumed, and H_2O, light liquids, oil, asphaltene, asphaltols and residue produced. Temperature, pressure, type of gas, residence time, catalyst type, catalyst precent, coal type, particle size and sample size are easily monitored.

The total volume of the reactor system is 1.26 cm^3. This has been determined by weighing a gas added to the reactor to a given pressure and calculating the volume by use of the ideal gas law. The pressure reported is the pressure of the reactor while at a specific reaction temperature. This value has been determined experimentally. The reactor is weighed while containing air at atmospheric pressure. The reactor is then heated with the valve open to a given temperature and then closed. It is reweighed after cooling and the difference is the air displaced on heating. Air is readmitted to the reactor so that it is again in equilibrium with the atmosphere as a check. By use of the ideal gas law, the fraction of air remaining after heating to a specific temperature can be determined. The inverse of that fraction is the pressure factor. Figure 3 shows experimentally determined pressure factors (F) as a function of reactor temperature. If P_1 is the initial pressure at room temperature, then $P_2 = FP_1$ and is the pressure reported for a reaction at a specific temperature. Figure 4 shows P_1 vs. P_2 for various pressure factors.

Considerable care must be taken to obtain accuracy to the 4th decimal place on each weigh. The first problem encountered was the hygroscopic nature of plastic parts and filter paper. The plastic parts were eliminated and the filter paper size was restricted and covered with a brass cap. Parts are stored in a dessicator.

Weights of heated parts may differ by more than 0.00200 g. Even when parts are permitted to cool according to touch to room temperature, inaccuracies of as much as 0.00075 g are observed. Therefore, a 0-5 millivolt meter has been installed in each dessicator. The meter is considered a room temperature junction. A thermocouple is inserted into the valve opening of the cooling reactor. The meter then indicates by a millivolt reading the reactors approach to equilibrium with room temp. Room temp is attained only after very long cooling periods.

Therefore, parts are weighed before actually reaching room temp and a correction is made based or the millivolt reading at the time. To reference approximate temperature, a millivolt reading of about 4 is indicated if the part is 100°C. Figure 5 shows the basis for the weight correction. After making this correction the 4th decimal place could be as much as 3 off.

Weight measurements are further complicated by a solvent extraction procedure. Cyclohexane, benzene and pyridine are used to determine oil, asphaltene and asphaltols, respectively. These solvents may not be completely vaporized from the residual without destroying part of the products. Therefore, the extraction procedure has been standardized and a correction is made for the remaining solvent. The correction is small for cyclohexane and benzene but large for pyridine. The correction for pyridine may be made smaller by a subsequent cyclohexane rinse. The correction for cyclohexane is so small that it is assumed to be zero, for benzene it is 0.00003 g per mg char and for pyridine 0.00010g per mg char. If the pyridine correction is reduced by a cyclohexane rinse, the correction becomes 0.00006 g per mg char.

The material balance includes H_2, H_2O, light liquids and gases. The H_2 consumed is measured by considering the weight of H_2 added to the reactor and the volume of H_2 remaining after the reaction. The volume of H_2 after the reaction is determined by venting reactor gases through a liquid N_2 trap. The volume of the gases passing the liquid N_2 trap is measured by water displacement. A correction based on gas chromatography is made for H_2O and CH_4 in the gas. The remaining gas is H_2. The amount of H_2 retained in the liquid N_2 trap due to its greater density is added to the volume reading. The weight of hydrogen remaining is calculated from the volume and subtracted from the original H_2 for a figure representing weight of H_2 consumed.

The gases condensed by the liquid N_2 are introduced to silica gel and 5Å molecular sieve traps in series. The weight change in these traps indicates H_2O and light liquids, respectively. That material which is not collected by the silica gel or 5Å molecular sieve is defined as gases. For a closed material balance, the material collected in the liquid N_2 trap may also be weighed. The gases are then this weight minus the H_2O and light liquids. Gas chromatographic analysis is also performed on each of these gaseous components.

Future Work

Work will continue on the microreactor. A series of 24 Utah coals will be run on a comparative basis to determine the effect on conversion of various physical and chemical analyses.

References

1. W.H. Wiser *et al.*, DOE Contract No. E (49-18) - 2006, Quarterly Progress Report, Salt Lake City, Utah , Apr-June 1976, pp 106-112.

2. *ibid.*, July-Sept 1976, pp 92-96.

3. *ibid.*, Oct-Dec 1976, pp 72-76.

4. Gregory T. Garr, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1978.

5. A.C. Bhattacharyya, B.K. Mazumdar and A. Lahiri, *Fuel*, 43 (1964).

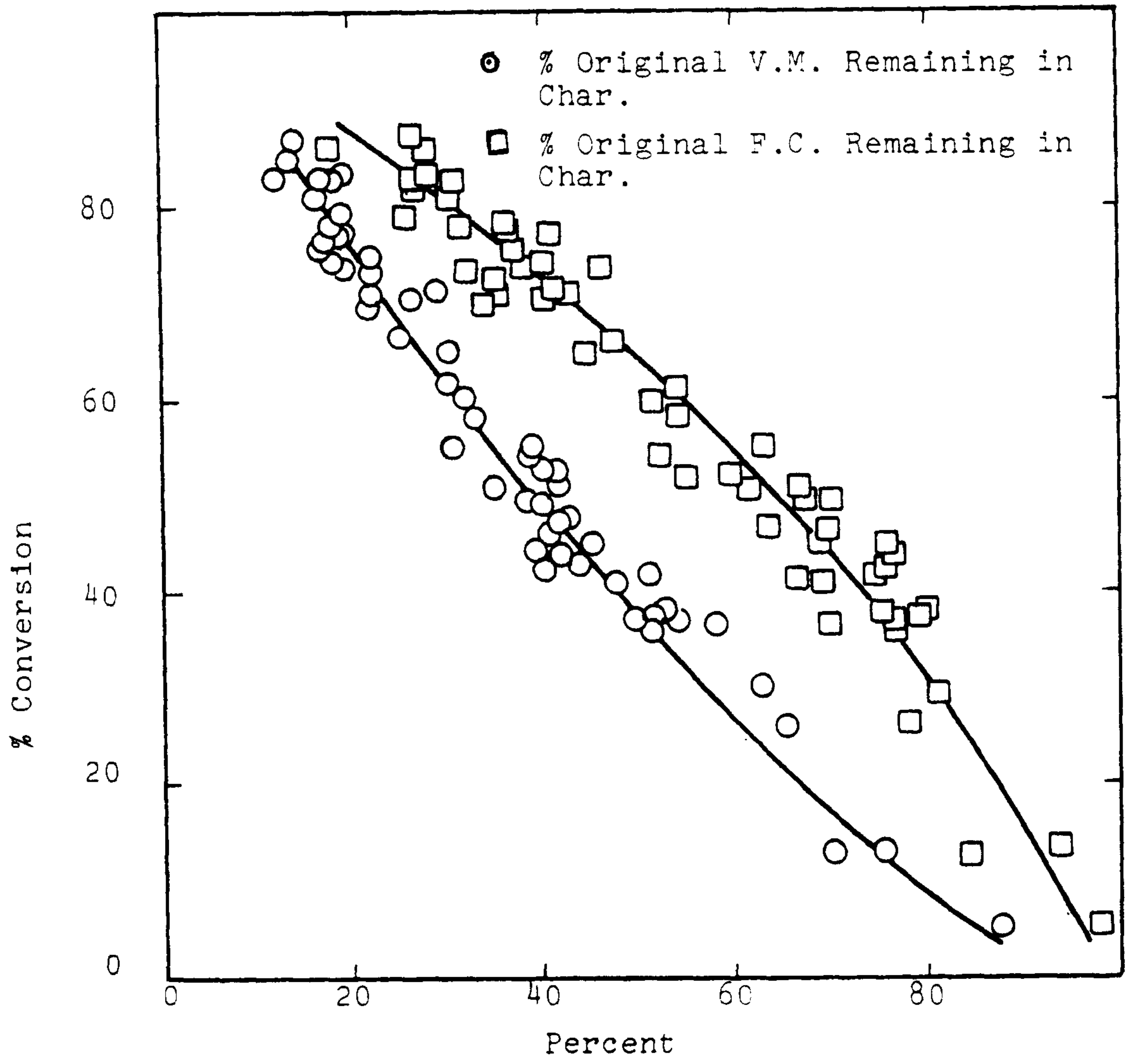


Figure 1. Volatile matter and fixed carbon remaining in char after liquefaction treatment. Clear Creek, Utah coal, pressure 1800 psig, temperature 470-510°C, reaction times 10-400 sec.

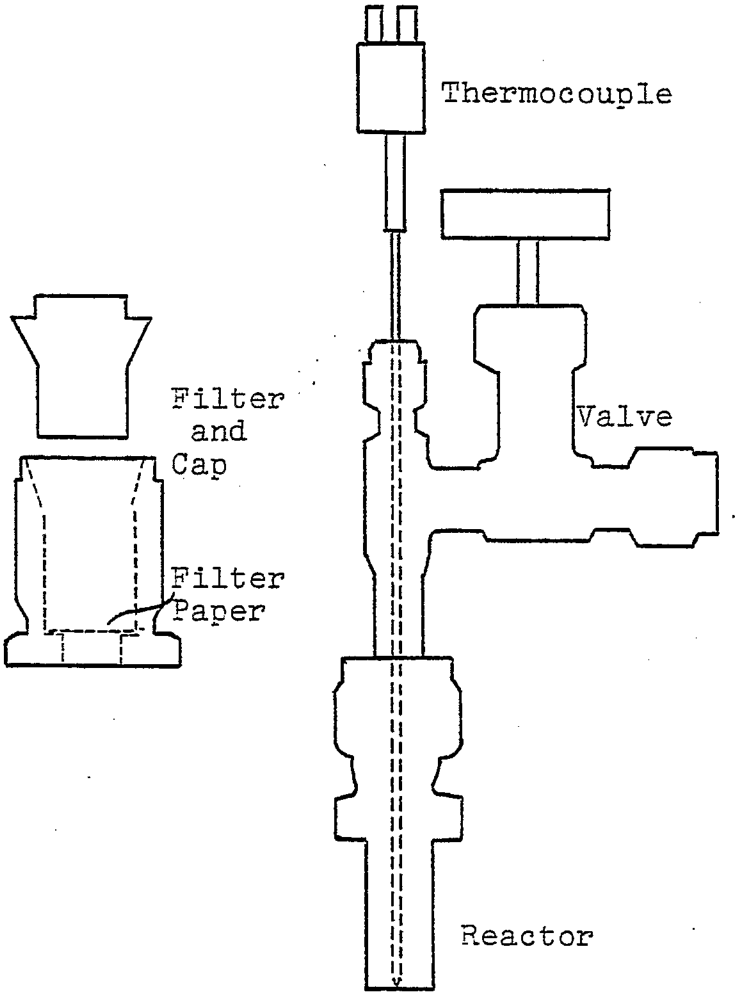
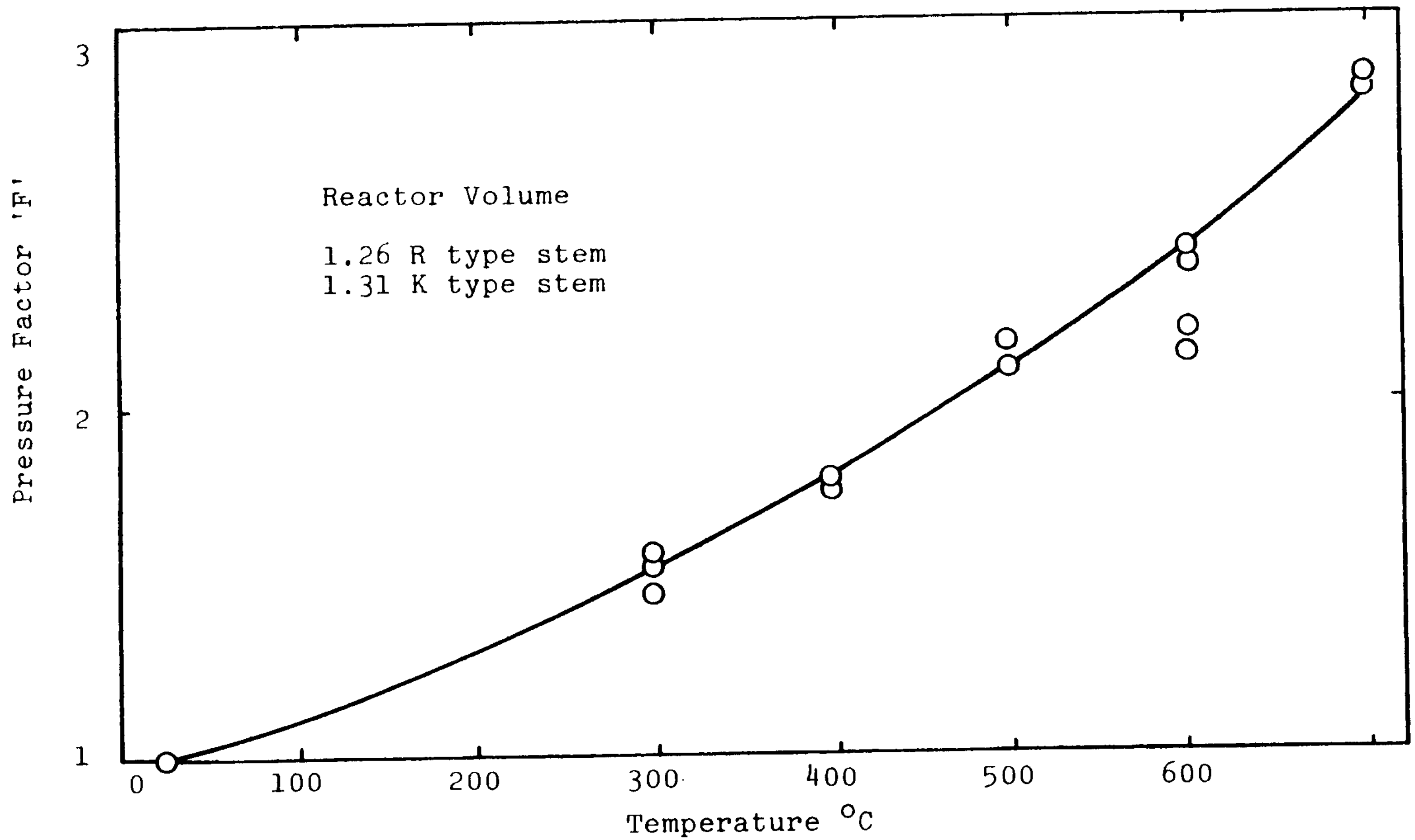


Figure 2. Microreactor and filter made from Swagelok fittings.

Figure 3. Pressure factor vs. microreactor temperature.



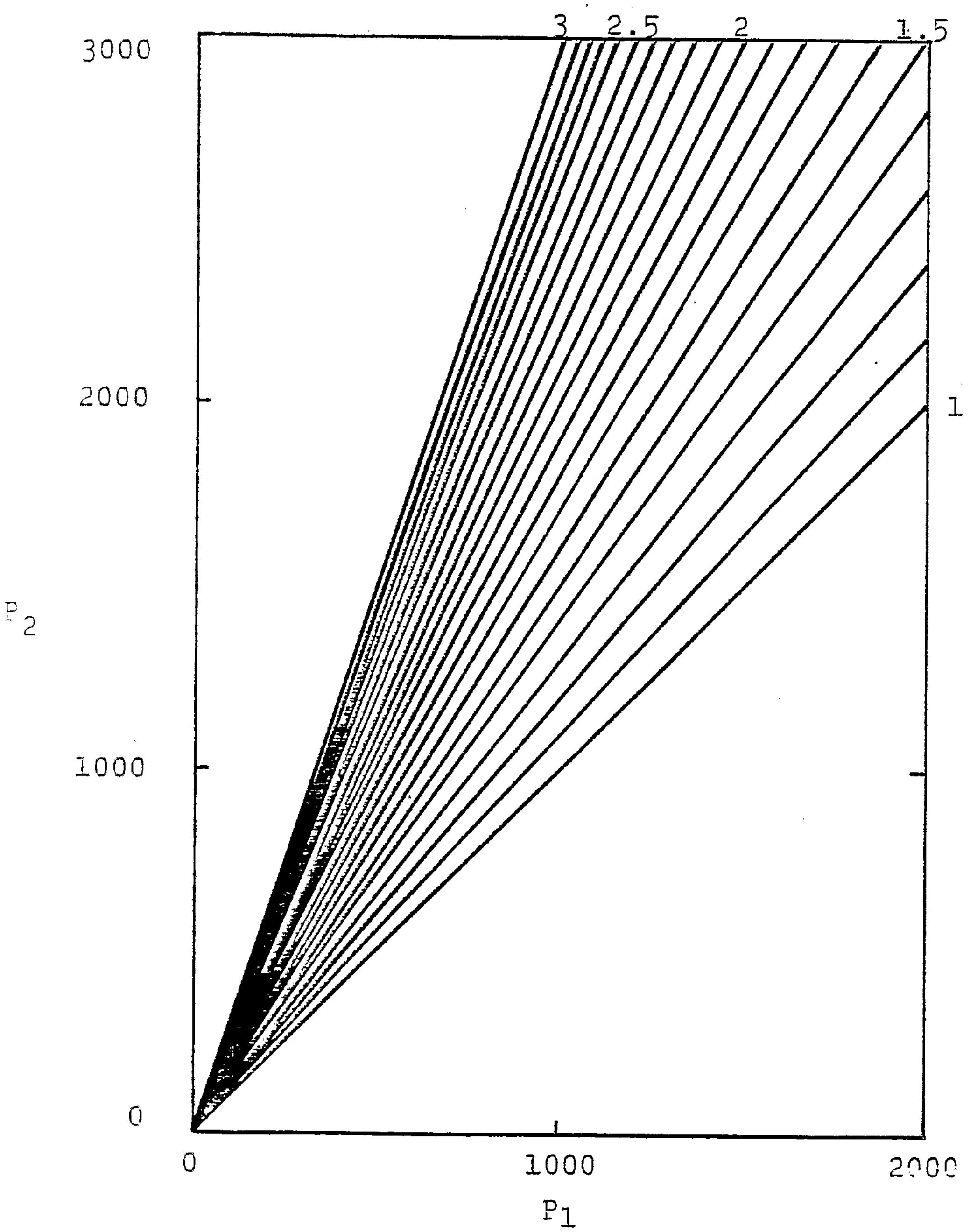


Figure 4. Initial pressure, P_1, vs. reaction pressure, P_2, for various pressure factors.

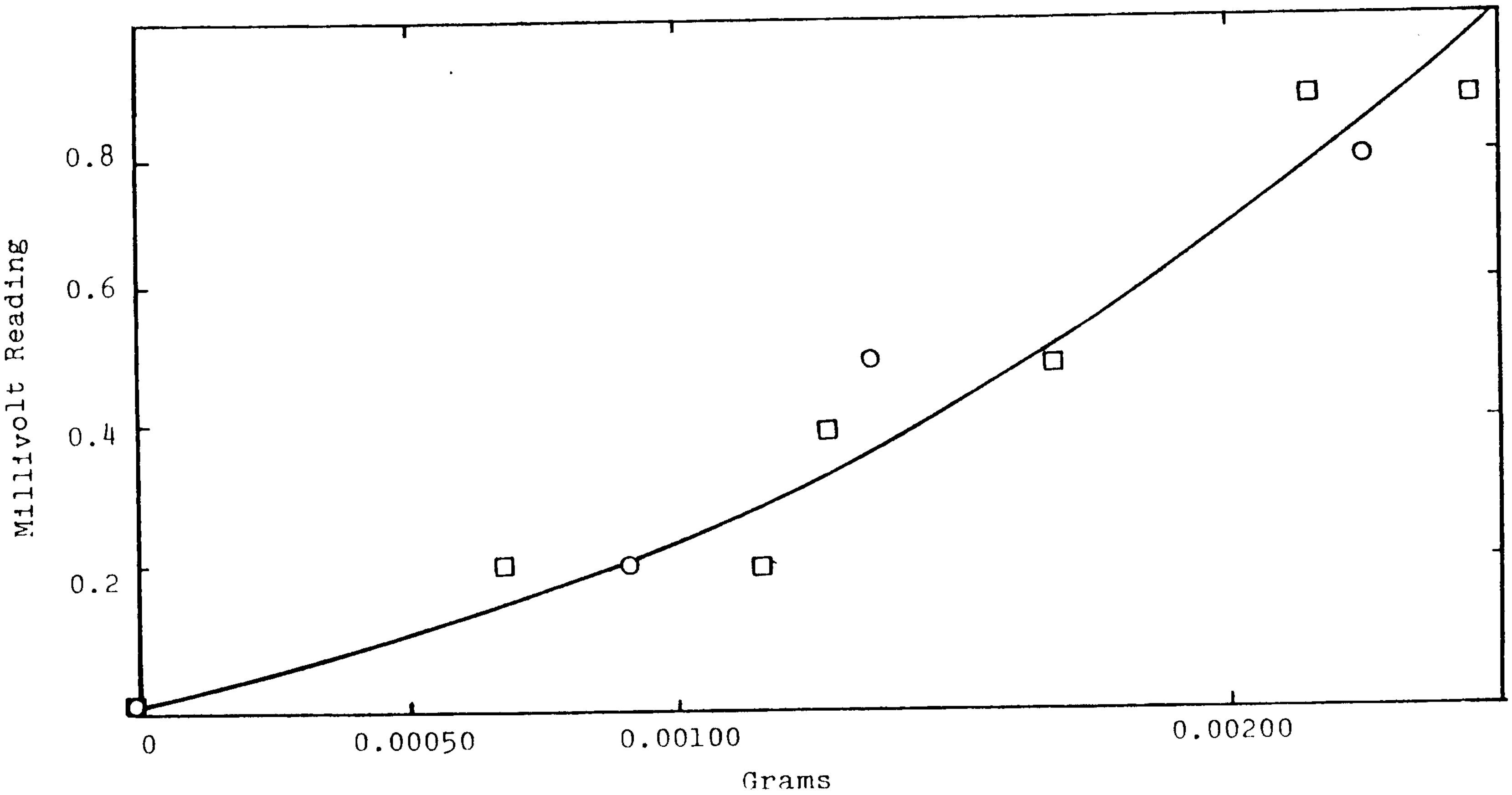


Figure 5. The weight added to a part as a function of a millivolt reading.

Project D-2

The Effect of Structure on Coal Reactivity

Structure of Coal Asphaltenes

Faculty Advisor: D.M. Bodily
Graduate Student: D. Roylance

Introduction

Asphaltenes have been thought by many investigators to be intermediates in the stepwise hydrogenation of coal to produce hexane-soluble oils. Recent reports have shown that coal can be liquified at very short reaction times and that asphaltenes and oils are produced by parallel reactions that can be interconverted by bond cleavage and polymerization reactions. Work in this laboratory (Project B-4) has shown that asphaltenes and oils from catalytic hydrogenation of coal are similar in structure, the major difference being size. Hexane-soluble oils appear to be composed of structural units comprised of condensed aromatic ring systems with alkyl groups and hydroaromatic rings attached. Asphaltenes appear to be polymers of these basic structural units. The nature of the bonds which hold these units together is of interest in this research.

The asphaltenes will be separated from the heavy oil fraction obtained by coal hydrogenation and reacted in various ways to break specific bond rupture to determine the types of bonding between structural units.

Project Status

An asphaltene sample (7.5 g) was dissolved in benzene, and hydrogen chloride gas (HCl_g) was bubbled through the solution for 5 hours. A soluable (acidic/neutral) portion and a precipitate (basic) were formed. The acidic/neutral portion recovered was 63.3% of the original sample and the base recovered was 35.8% with about 1% losses. The base was washed with 0.3 N NaOH to remove the HCl adduct and dried. Approximately 1.276 g of the base was recovered. Products from the HCl reaction were separated using GPC. Elution curves for these samples and for dehydrogenated asphaltene are shown in Figures 1-4.

A CHN analysis was performed on the asphaltene portion and the GPC fractions from the dehydrogenation reaction. A regression analysis was performed on the C/H ratios from the ultimate analysis (Figure 5). The majority of molecular hydrogen evolved from the higher molecular weight fractions (low elution volume).

Future Work

Samples from selected reactions will be characterized as to types of hydrogen (aromatic, aliphatic, etc.) by HNMR, molecular weight by vapor pressure osmometry, carbon to hydrogen ratios by untimate analysis and the presence of certain functional groups by infrared analysis.

Reference

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

Figure 1. Elution Curve for Basic Fraction.

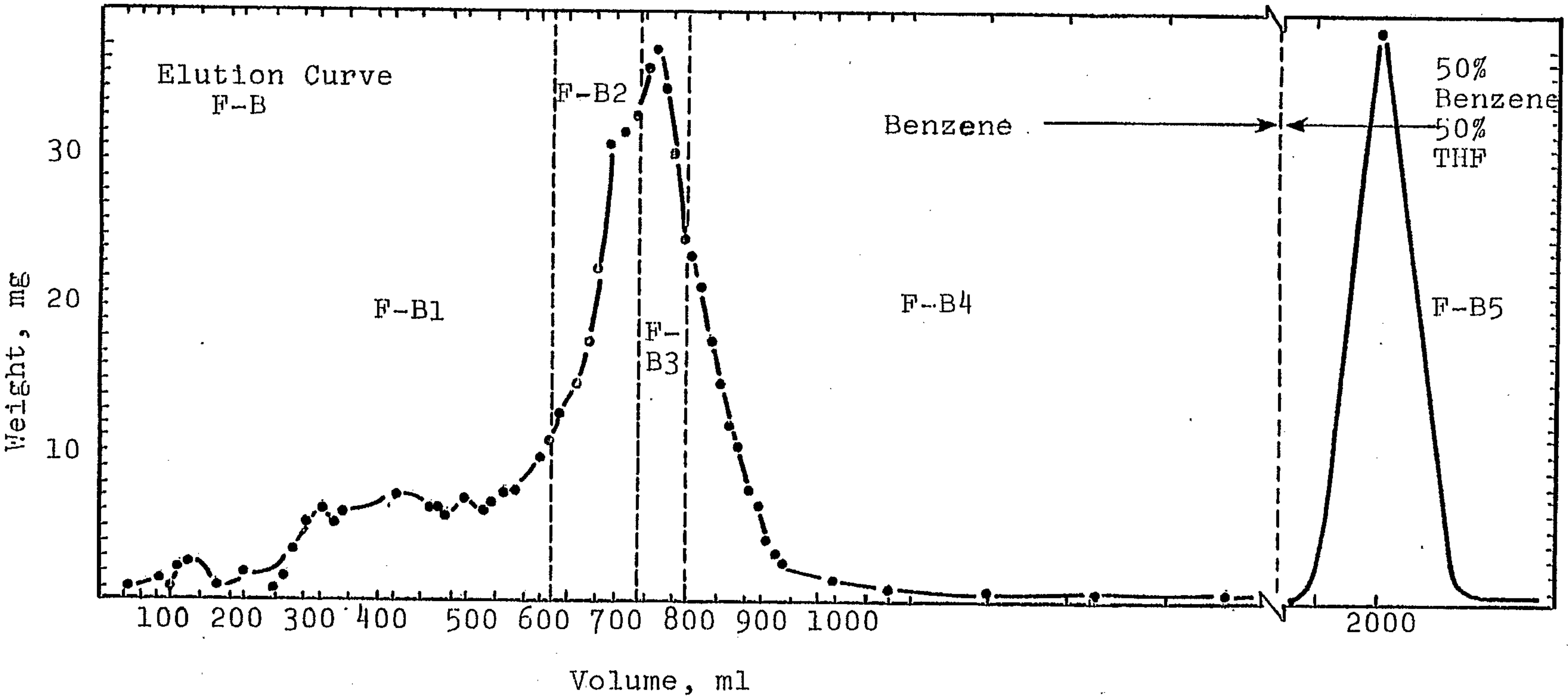


Figure 2. Elution curve for dehydrogenation reaction.

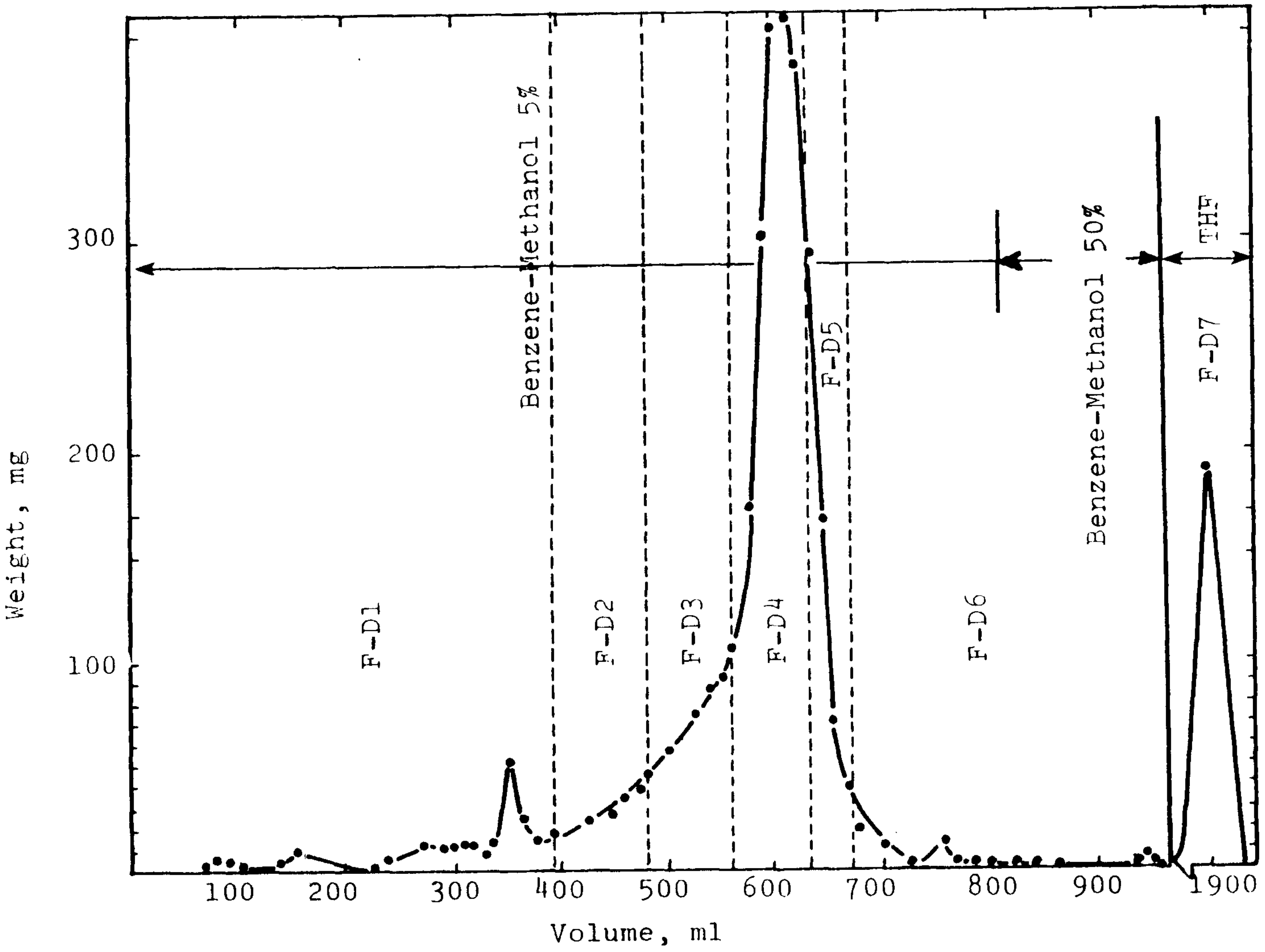


Figure 3. Elution curve for asphaltene.

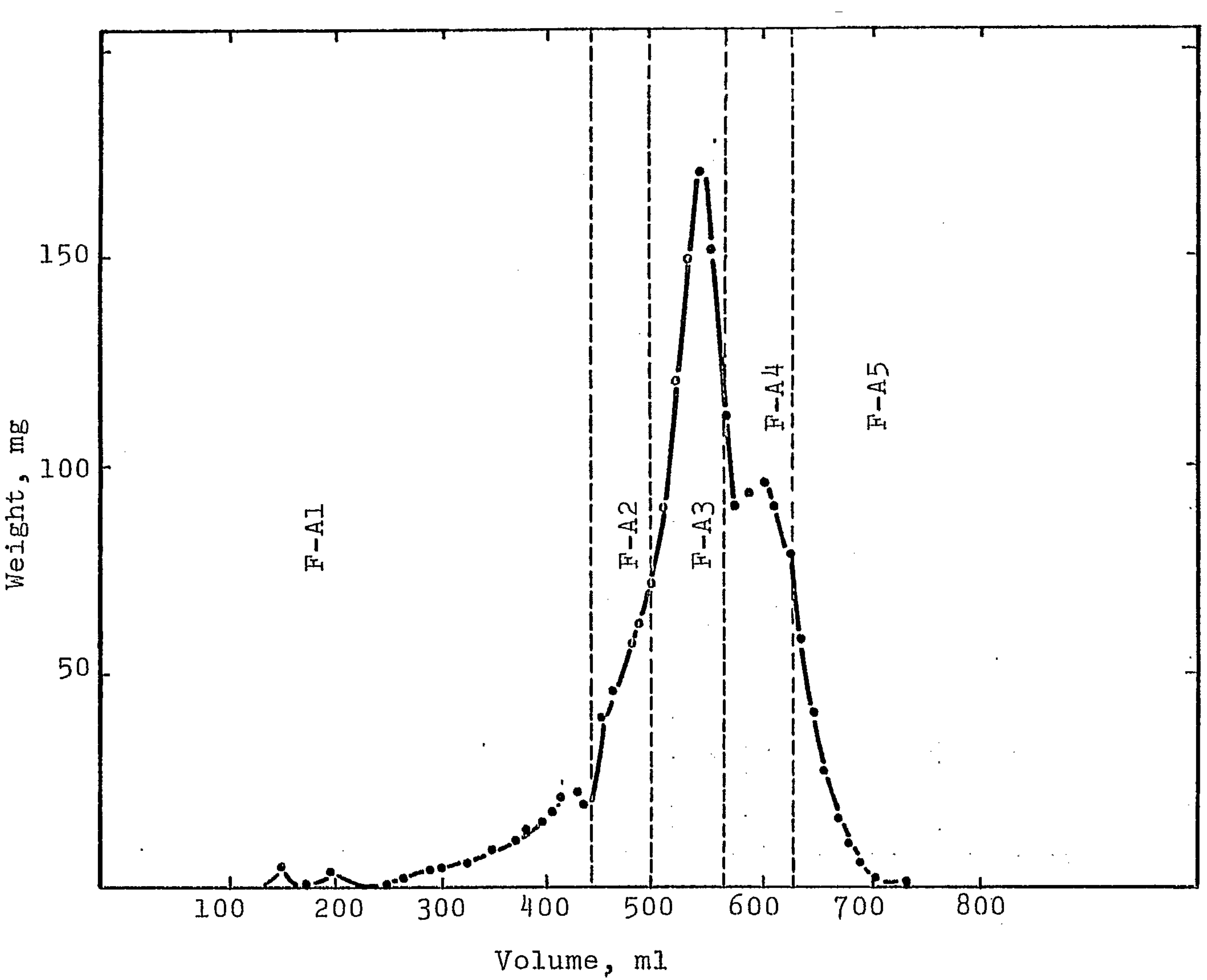


Figure 4. Elution curve for acid/neutral fraction.

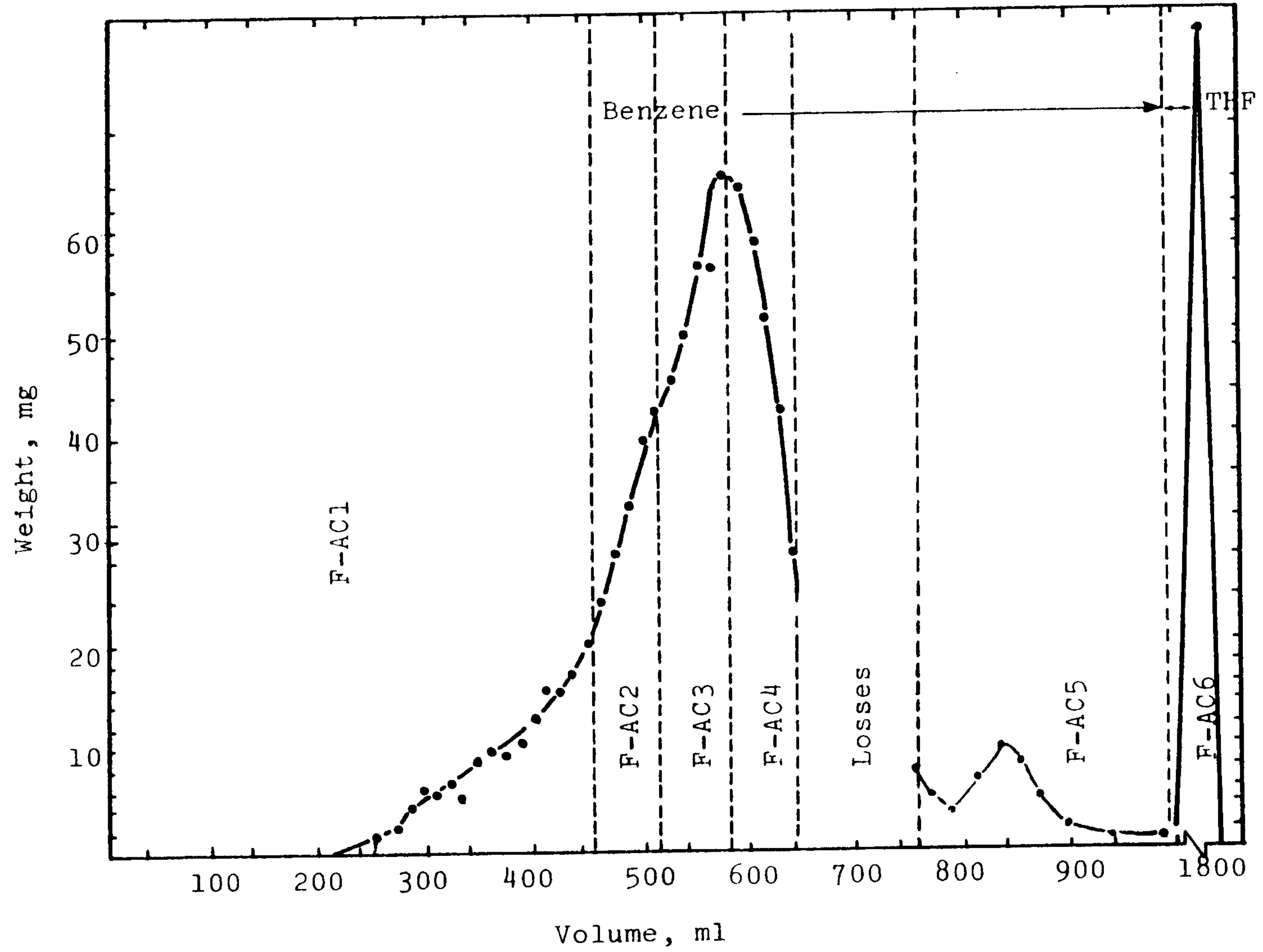
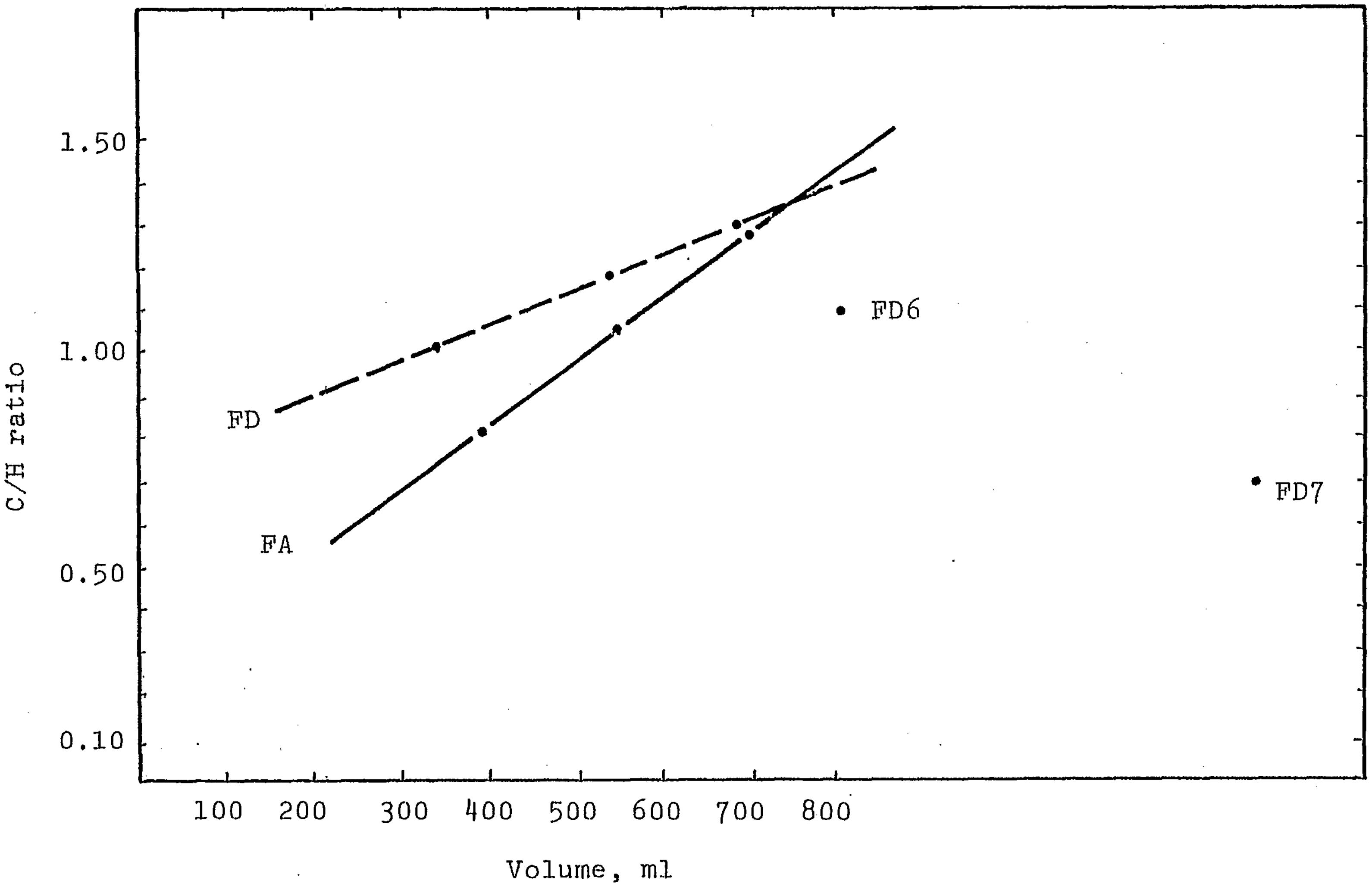


Figure 5. Regression analysis on C/H ratios for asphaltene (FA) and dehydrogenation reaction (FD) products.



Project D-4

Pyrolytic Studies and Separation and Characterization of Coal-Derived Liquids

The Separation and Characterization of Coal-Derived Liquids

Faculty Advisor: R.R. Beishline

Introduction

This project deals with the investigation of promising methods for analyzing and identifying the lighter fraction of coal hydrogenation liquids. A spinning band (SB) distillation column (> 200 theoretical plates at atm press) is being used to determine whether fractionation can separate pure components directly from complex coal-derived liquids. Also SB distillation in combination with preparative gas chromatography (PGC) is being tested.

SB fractionation of crude material boiling up to 150°C (atm) did not give distillates consisting of pure components, but did effectively cut the pot charges into smaller less complex fractions.

Using SB distillation in combination with PGC, the components in an 80-100°C (atm press) coal liquid fraction have been separated and isolated, and compounds representing about 70 volume % of the fraction have been spectroscopically identified (MS, IR, NMR). (Identification by GC-MS is more time economical.)

The development of a scheme for the analyses of the ambient 80°C (A-80) fraction of coal liquids is nearly completed.

Project Status

As part of the development of the analysis scheme for the A-80 coal liquid fraction, the reproducibility of the SB distillation and GC analysis of the A-80 fraction has been determined. Three identical distillations were carried out to obtain three samples of ambient-80° distillate which, theoretically, should be identical (see Table 1). Three samples of each distillate were subjected to GC analyses and electronic integration of the GC peak areas. The mean area percent and standard deviation of each peak in the three chromatograms of the respective three distillates were calculated. This evaluated the reproducibility of the GC analysis of each separate distillate. A typical set of results (for distillate #1) is shown in Table 2.

The F test was applied to the mean data for the three separate distillations. This test calculates the statistical probability that the three distillates are really three samples of the same mixture, where the degree of "sameness" is based on the degree to which the analyses of the separate distillates show the same statistical variances. The F test was significant at the 1% level, i.e., there is a 99% chance, based on the above criteria, that the three distillates are of essentially identical composition.

The pot charges for the distillations (Table 1) were aliquots of a single coal liquid sample (crude ambient-150^oC fraction from liquefaction of Clear Creek, Utah coal produced in the University of Utah coal reactor). The apparent loss of lower boiling components indicated by the increasing initial boiling points of distillates 1,2 and 3 is not real, since the lighter components (first peaks to elute) are present in almost equal amounts in distillates 1,2 and 3 (see Table 2).

The average of the standard deviations for distillates 1, 2 and 3 was 0.74%. Examination of the data indicates that larger integration errors are associated with the area percents of peaks that are merged (see peaks 4, 5 and 6; 9 and 10; and 14, 15 and 16 in Table 2). The average standard deviation of nonmerged peaks in distillates 1, 2 and 3 is 0.53. The mean data for distillates 1, 2 and 3 and the calculated F values are shown in Table 3.

Future Work

The separation of the A-80 coal fraction on a capillary GC column has been scheduled to be done at the Flammability Research Center at the University of Utah. This work will be reported once it has been completed. An overall analysis scheme for the A-80 coal liquid fraction will be formulated and reported.

Table 1. Reproducibility of the SB Distillation of Aliquots of a Single Coal Liquid.

Distillation #	Pot Charge (ml)	Reflux Ratio	Boiling Range of Distillate (°C)	Volume of Distillate (ml)
1	25	200:1	51-80	1.25
2	25	200:1	53-80	1.38
3	25	200:1	57-80	1.21

Table 2. GC Analysis of Distillate #1.

Peak #	Chromatograph # 1	2	3	Mean	Standard Deviation
1	2.90	2.59	2.72	2.74	0.15
2	1.40	1.23	1.23	1.29	0.10
3	2.20	1.81	1.89	1.97	0.21
4, 5 merged	14.12	11.32	11.71	12.38	1.52
6	18.37	18.10	19.05	18.51	0.49
7	16.57	14.99	16.71	16.09	0.96
8	1.90	1.72	1.72	1.78	0.11
9,10 merged	17.79	17.54	15.78	17.04	1.10
11	4.55	4.99	5.95	5.16	0.72
12	2.39	1.31	1.94	1.88	0.54
13	10.06	8.21	9.43	9.23	0.94
14,15,16merge	5.08	6.67	6.12	5.96	0.81
17	1.14	0.93	0.59	0.89	0.28
18	2.08	2.15	1.94	2.06	0.11
19	0.69	2.98	2.53	2.08	1.22
				ave. std. dev. =	0.62

Table 3. Mean Data and F Values for GC Analysis of Distillates 1, 2 and 3.

Peak #	Distillate # 1	Mean Data Distillate # 2	Distillate # 3	F
1	2.74	2.78	2.75	9.00
2	1.29	1.42	1.34	9.01
3	1.97	2.81	2.07	9.00
4, 5 merged	12.38	12.12	18.16	9.00
6	18.51	17.13	11.05	9.00
7	16.09	14.40	13.10	9.00
8	1.78	1.74	2.63	9.00
9, 10 merged	17.04	17.81	12.16	9.00
11	5.16	3.98	9.08	9.00
12	1.88	1.52	2.74	9.00
13	9.23	7.41	7.14	9.00
14, 15, 16 merged	5.96	8.14	8.59	9.00
17	0.89	0.78	0.44	9.01
18	2.06	1.78	1.43	9.00
19	2.08	2.01	2.09	9.00

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 the following scheme of simultaneous first and second order reactions is operative.

$$\text{1,2-DHN} \xrightarrow{k1} \text{naphthalene} + H_2 \qquad \text{(I)}$$

$$2(\text{1,2-DHN}) \xrightarrow{k2} \text{tetralin} + \text{naphthalene} \qquad \text{(II)}$$

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 donor scheme,

$$\text{coal} + \text{tetralin} \xrightarrow{\text{heat}} \text{hydrogenated coal} + \text{naphthalene}$$

and are of considerable interest.

Project Status

Additional kinetic data for reactions (I) and (II) are being obtained with the objectives of determining activation energies and working out a scheme to kinetically handle side reactions. A report of these results will be made after collection of the data.

The synthesis of 1,2-dihydrophenanthrene, 3,4-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene is now being carried out, using standard literature procedures. These compounds will be used in a study to determine whether or not the reaction

$$2 \text{ dihydroaromatic} \longrightarrow \text{aromatic} + \text{tetrahydroaromatic}$$

occurs in the phenanthrene system as well as in the naphthalene system.

Future Work

The kinetic study of reactions (I) and (II) will be continued, and the sysnthesis of the di- and tetrahydrophenanthrenes will be completed.

Reference

1. 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

Faculty Advisor: A.G. Oblad
Graduate Student: Hsiang-Yun Kung

Introduction

The hydrocatalytic desulphurization of partly vaporized gas oils in a fixed bed using small diameter pellets of cobalt molybdena alumina is an established commercial process which is operated with once-through up or downflow of liquid through the reactor. Hydrogen rich gas flows cocurrently and is recycled. Reaction temperatures are 680-780°F and reaction pressures are between 600 and 1000 psig. Heavier feedstocks are very difficult to process with this process scheme.

More efficient processes are needed to desulphurize higher molecular weight coal-derived liquids, residual petroleum feedstocks, native bitumens and black oils. The more important chemical engineering problems facing the designer of any new process will be

1) A higher proportion of sulphur will be present in the feedstock with relatively more of it locked within large polycyclic molecules. Each ton of oil will therefore need to react with more hydrogen and the intrinsic chemical reaction rate might be restricted by the permissible rates of molecular diffusion of reacting molecules to and from the active catalyst sites. Any such tendency would be accentuated by the simultaneous demand for hydrogen for hydrocracking, denitrogenation, and partial saturation of polycyclic aromatics.

2) Carbon laydown during processing will be considerable and contaminants originally present in residual feedstocks will also give rise to deposits of nickel, vanadium and salts of sodium on the catalyst. These deposits will result in a decline of catalytic activity and in a progressive increase in pressure drop across a fixed bed reactor and might necessitate the use of other reaction techniques.

Anticipating this need, the objective of this project is to study the diffusional effects of the hydrodesulphurization of straight run gas oil and coal-derived oils, with various sizes of catalyst in a vapor phase fluidized bed reactor.

Project Status

In the beginning work, the feedstock will be in the vapor phase under HDS reaction conditions and H_2/oil feed ratios. Dew points were theoretically estimated for the high pressure H_2/HC system. The dew point for a H_2/oil feed ratio of 4000 std cc/cc at 1500 psig is 775°F. Later, studies will be made to determine the extent the operation is possible in mixed liquid-vapor phase.

The equipment has been assembled and pressure tested at 1700 psi and 24°C with nitrogen. The parameters to be studied have been tentatively set as follows:

Temperature: 400 - 500°C

Pressure: 1000 - 1500 psig

The catalyst to be used is a cobalt molybdenum alumina selected for proper pore size. Pressure drop across the distributor and top solids retaining plate was determined for the velocity range studied. Figure 1 shows the pressure drop across the distributor and top solids retaining plate was negligible.

Future Work

The catalyst will be ground to the required mesh size and sulfided. The system will be tested as a whole, and experimental runs will begin.

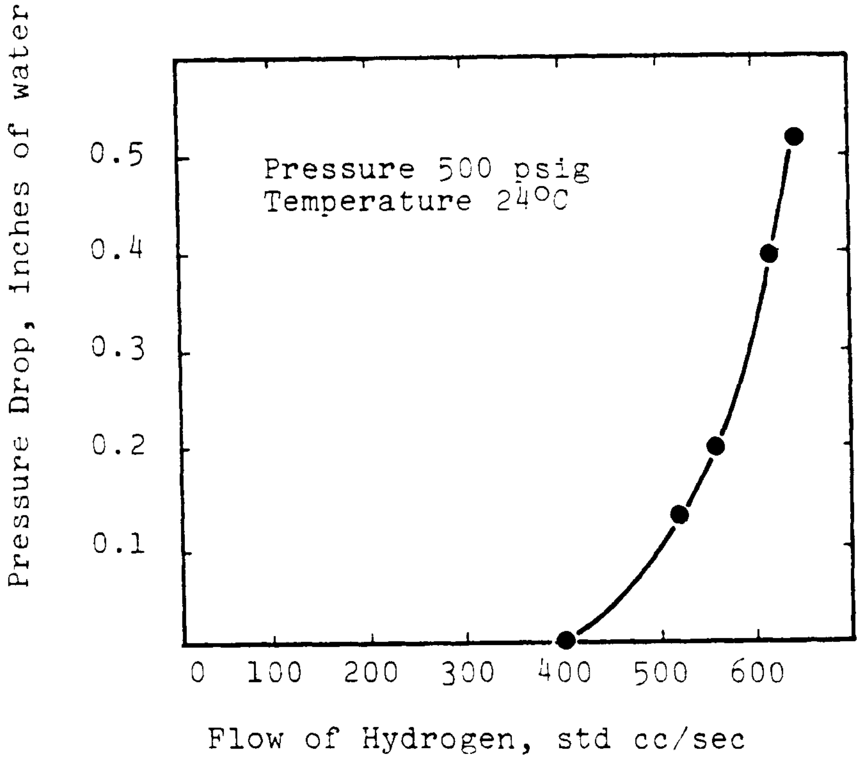


Figure 1. Total pressure drop across the distributor and the solids retaining plate at the top of the reactor.

V. Conclusion

Twelve projects were active during the quarter. Projects A-6 and A-9 have not been initiated and Project B-3 has been completed. Students on Project A-1 have completed their degrees. New students will continue these projects.

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