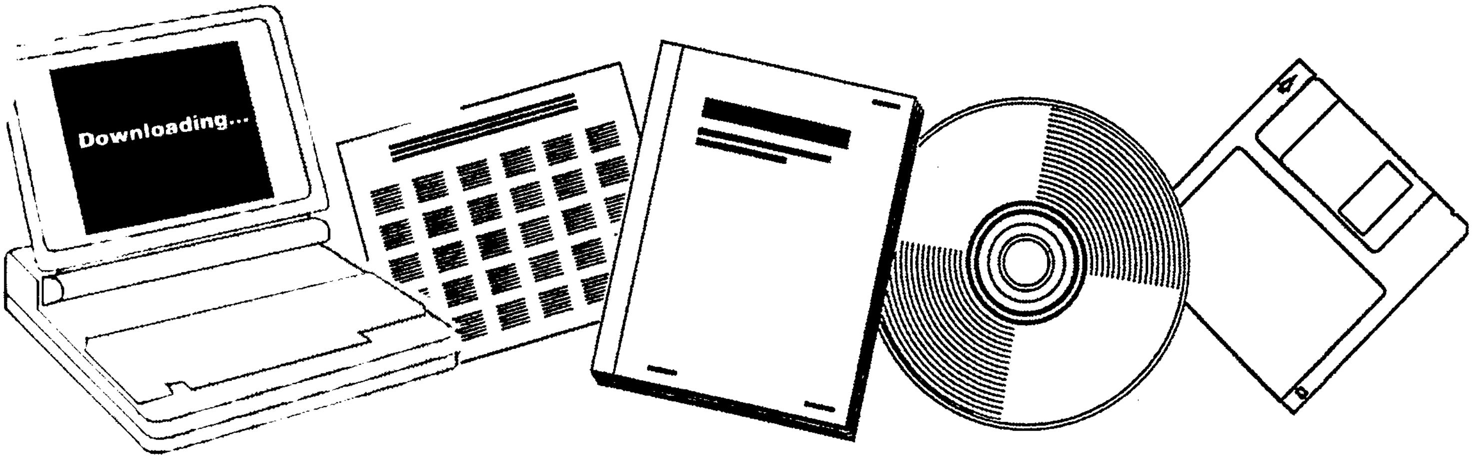
APPLIED RESEARCH AND EVALUATION OF PROCESS CONCEPTS FOR LIQUEFACTION AND GASIFICATION OF WESTERN COALS. QUARTERLY PROGRESS REPORT, JANUARY--MARCH 1978

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

JUL 1978



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

Quarterly Progress Report for the Period Jan - Mar 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

Studies of the hydrogen transfer by zinc chloride catalyst (B-3) have been completed and a final report is being prepared. Apparatus for heat transfer studies has been assembled and tested.

Presentations and Publications

Subhash Kithany and W.H. Wiser, "Equilibrium Thermodynamic Correlations in Coal Hydrogenation to Pipeline Gas," Third Rocky Mountain Fuel Symp, Albuquerque, New Mexico, Feb 1978.

John Lytle, R.E. Wood, and W.H. Wiser, "Mechanism of Coal Liquefaction: Effect of Catalyst and H_2 Concentration," Third Rocky Mountain Fuel Symp, Albuquerque, New Mexico, Feb 1978.

L.L. Anderson and D. Kang, "Analysis of Coal Extracts and Relations to Kinetics of Extraction," Third Rocky Mountain Fuel Symp, Albuquerque, New Mexico, Feb 1978.

S. Goyal and A.G. Oblad, "Production of Hydrogen and SNG from Methanol," Third Rocky Mountain Fuel Symp, Albuquerque, New Mexico, Feb 1978.

S. Cowley and D.S. Moulton, "The Acid Character of Zinc Chloride-Coal as Determined by D_2-Exchange Reactions," Rocky Mountain Fuel Symp, Albuquerque, New Mexico, Feb 1978.

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A.H. Hill, R.E. Wood and W.H. Wiser, "Recovery of Zinc Chloride Catalyst from Coal Hydrogenation Char," *Fuel Process Technol.*, Jan 1978, p 151.

W.H. Wiser, "The Chemistry of Coal Liquefaction," presented at the Coal Chemistry Workshop, Stanford Research Institute, (SRI Internat.) Menlo Park, Calif., Mar 8,1978.

C. Yang and A.G. Oblad, "Catalytic Synthesis of Light Olefinic Hydrocarbons from CO and H_2 Over Some Iron Catalysts," Symp on Advances in Fischer-Tropsch Processes, presented at Div. Pet. Chem., ACS, Anaheim, Calif, Mar 1978.

C. Yang, F.E. Massoth and A.G. Oblad, "Kinetics of CO-H_2 Reaction Over Co-Cu-Al_2O_3 Catalyst," presented at the Div. Pet. Chem., ACS, Anaheim, Calif., Mar 1978.

Project A-1

Catalytic Gasification of Coal to High BTU Gas

Single Stage Coal Gasification

Faculty Advisor: W.H. Wiser
Graduate Student: Stevan Weber

Introduction

Recently much concern and interest has been focused on the single stage reactor concept for making synthetic pipeline gas from coal. According to this concept, coal and steam, as well as catalyst, would be charged into a single reactor to generate a gas that contains methane as the primary constituent.

From thermodynamic calculations such a conversion in a single stage reactor may approach or even be autothermal. This would permit an energy savings over other more conventional multiple stage coal conversion schemes.

The objective of this work is finding a composite catalyst to give the best possible yield of methane in producing a high BTU gas. The coal is slurried in tetralin, a hydrogen-donor solvent. A continuous flow fixed bed reactor is being used.

An extensive literature search has been conducted and the parameters to be studied are

Temperature:	400-550°C
Pressure:	1000 psig

The catalysts to be studied, along with their physical properties, have been given in the previous report.

Project Status

Preliminary runs have been made with the 0.5 in. ID continuous flow reactor and the data are given in Table 1. The conversion to gaseous hydrocarbons is very low. The results indicate that such a low conversion is due to inability to bring the coal particles to reaction temperature in the rather short time in the reactor.

The coal particles were surrounded by so much solvent that the coal particles were not reaching the desired reaction temperature. Therefore, a larger reactor has been built to provide for longer residence times and some alterations in the process system have been made. A flow diagram of the present system is given in Figure 1. The new reactor is 2.25 in. ID and 20 in. long.

Preliminary runs with longer residence times have been made with this reactor and the data are given in Table 2. The results from these look promising.

Proximate and ultimate analyses of Hiawatha coal were completed and the results are given in Table 3.

Future Work

Background runs of the catalysts to be studied will be continued. To determine which two catalysts work best together, composite catalysts will be made and test runs will be carried out.

Table 1.

0.5 in CONTINUOUS FLOW REACTOR

CATALYST	Ni-Mo	Co-Mo	Co-Mo / Ni Si-Al	Ni-Mo / Ni Si-Al	Ni-Mo/ Ni-W
TEMP. °C	450	450	450	450	450
PRESSURE(PSIG)	1000	1000	1000	1000	1000
RESIDENCE TIME (MIN.)	0.51	0.51	0.51	0.51	0.51
CHAR (WT%)	9.50	8.41	8.75	8.34	5.5
GAS ANALYSIS H_2 FREE (WT%)					
CH_4	$4.0\text{X}10^{-3}$	$2.5\text{X}10^{-2}$	$1.9\text{X}10^{-2}$	$3.8\text{X}10^{-2}$	$4.1\text{X}10^{-2}$
C_2H_4	--------	$2.9\text{X}10^{-5}$	$3.8\text{X}10^{-5}$	$4.1\text{X}10^{-5}$	$1.3\text{X}10^{-4}$
C_2H_6	$1.8\text{X}10^{-3}$	$1.7\text{X}10^{-2}$	$1.1\text{X}10^{-2}$	$3.0\text{X}10^{-2}$	$3.8\text{X}10^{-2}$
C_3H_6	--------	$4.5\text{X}10^{-4}$	$4.3\text{X}10^{-4}$	$9.1\text{X}10^{-4}$	$3.1\text{X}10^{-4}$
C_3H_8	$1.0\text{X}10^{-3}$	$9.1\text{X}10^{-3}$	$1.2\text{X}10^{-3}$	$2.8\text{X}10^{-2}$	$3.4\text{X}10^{-2}$
$1\text{-}C_4H_8$	--------	$2.5\text{X}10^{-4}$	$3.1\text{X}10^{-3}$	$3.9\text{X}10^{-3}$	--------
$N\text{-}C_4H_8$	$6.3\text{X}10^{-4}$	$3.8\text{X}10^{-4}$	$1.6\text{X}10^{-2}$	$1.3\text{X}10^{-2}$	$1.1\text{X}10^{-2}$

(Ni on Si-Al contains 6% Ni by wt)

Table 2.

2.25 in CONTINUOUS FLOW REACTOR

CATALYST	Ni-Mo/Al_2O_3	Co-Mo/SiO_2-Al_2O_3	12% Ni/SiO_2-Al_2O_3
TEMP. °C	525	450	550
PRESSURE (PSIG)	1000	1000	1000
RESIDENCE TIME (MIN.)	9	9	9
GAS ANALYSIS H_2 FREE (VOL.%)			
CH_4	84.740	11.037	3.720
C_2H_4	0.242	0.273	0.293
C_2H_6	8.482	16.606	9.023
C_3H_6	0.094	0.307	0.190
C_3H_8	0.462	15.661	3.307
1-C_4H_8	0.068	2.167	0.957
I-C_4H_{10}	0.067	-----	-----
N-C_4H_{10}	0.043	9.495	1.839

Table 3.

PROXIMATE AND ULTIMATE ANALYSES OF HIAWATHA COAL

Proximate Analysis (wt%)	
Moisture	2.46
Ash	10.42
Volatile Matter	41.45
Fixed Carbon	45.67
Heating Value (BTU/lb)	13,299
Ultimate Analysis (wt%, MAF basis)	
Carbon	72.46
Hydrogen	5.43
Nitrogen	1.47
Sulfur	0.84
Oxygen	19.80
Atomic Ratio H/C	0.899

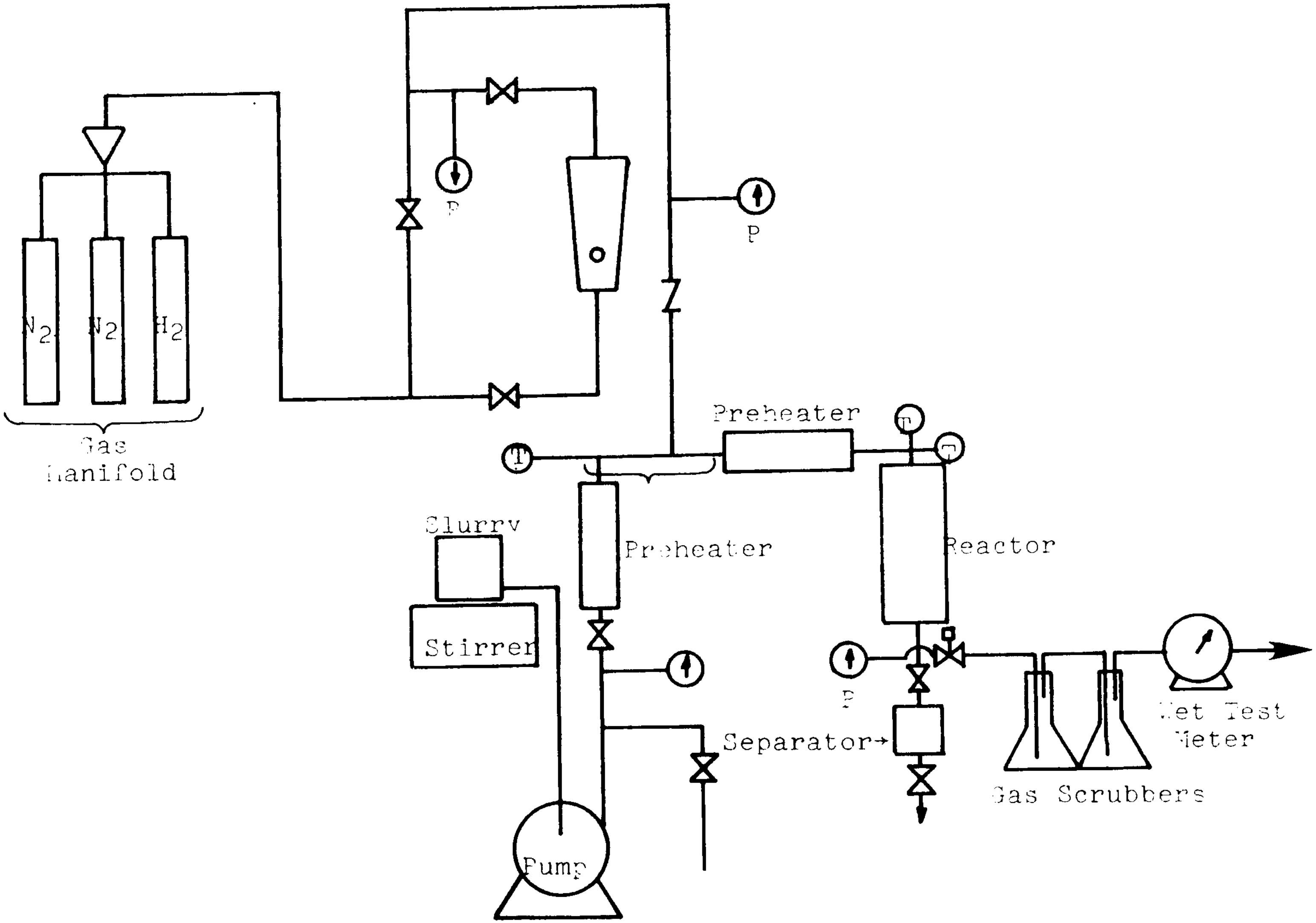

Figure 1. Flow Diagram of Continuous Mixed Bed Reactor.

Project A-1

Catalytic Gasification of Coal to High BTU Gas

Single Stage Coal Gasification

Faculty Advisor: Wendell H. Wiser
Graduate Student: Subhash Kithany

Introduction

The objective of this project is to investigate the potential for obtaining high methane yields by direct catalytic hydrogenation of coal in a single stage with a maximum temperature of 550°C. The work completed so far has included a literature search on work related to single stage coal gasification of the last 5 years. Also a thermodynamic feasibility study has been done which involved investigating the effect of various parameters, i.e., temperature, range 250-650°C; pressure, range 1000-2000 psig; and steam percent in hydrogen feed, range 0-100%.

Project Status

Preliminary experiments have been carried out to become more familiar with the reactor. The autoclave reactor was charged with 10 g of coal, 20 g of tetralin and 10 g of catalyst. The system was pressurized with either hydrogen or a hydrogen-water mixture, stirred by a Magnedrive and heated to 525°C for one hour. The products were then cooled and analyzed.

The gas products were analyzed by a gas chromatograph. The hydrogen was analyzed using dual molecular sieve columns with a helium, hydrogen (15%) mixture as carrier gas. The flow rate was 40 ml/min. The differences between the responses of the two columns was taken to correct for any base line changes during the temperature program. When analyzing the other gases (CO, CO_2, N_2, O_2), the carrier gas was pure helium. A thermal conductivity detector was used.

Hydrocarbon gases were analyzed using an alumina column and Helium as the carrier gas. A flame ionization detector was used. All gas analysis conditions are summarized in Table 1.

The instrument has been calibrated for all the following gases: hydrogen, nitrogen, oxygen, carbon dioxide, carbon monoxide, methane, ethane, propane, butane, isobutane, ethylene, propylene, butylene and acetylene.

The liquid products are being analyzed by simulated distillation using a gas chromatograph. From this the boiling point weight percent distribution can be determined.

The solid products are being analyzed by elemental analysis. Experiments without catalyst have been done and will be discussed later as more data are accumulated.

Future Work

Experiments with Ni-Mo and Ni-W catalyst systems along with alkali carbonates will be performed. The results from these experiments will determine the future direction of this project.

Table 1

Gas Analysis Conditions

	Hydrogen	CO, CO_2	Hydrocarbon Gases
Column	Molecular Sieve	Molecular Sieve	Alumina
Detector	TCD	TCD	FID
Carrier Gas	He + 15% H_2	He	He
Flow Rate	40 ml/min	40 ml/min	40 ml/min
Temp 1, °C	35	35	150
Time 1, min	1	1	16
Rate, °C/min	20	20	16
Temp 2, °C	20	20	16
Detector Temp, °C	260	260	300
Injection Temp, °C	260	260	250

Project A-2

Solvent Treatment of Coal-Derived Liquids (CDL)

Faculty Advisor: L.L. Anderson
Graduate Student: K.E. Chung

Introduction

The objective of this investigation is to separate CDL into chemically different fractions of potential industrial 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 bands in the infrared spectra of CDL fractions in dilute solutions, (4) the formulation of a new activity expression in liquid solutions, and (5) a new procedure for molecular weight determination by vapor pressure osmometry.

Project Status

The two fractions obtained by distillation revealed such interesting characteristics in molecular size and functional group contents that improvements in obtaining and comparing them with products from the cyclohexane extraction were made. Also better methods for structural analysis were examined.

Two ethanol extraction products, ES and EP-AS, similar in structure, were blended together for distillation. Before blending, ES was treated with acetone to remove residual paraffinic material. This blend, called CDL-P, represented ∿90% of CDL. The remaining portion, EP-AP, was mostly paraffinic material. To minimize possible thermal effects, the distillation was performed at ∿2 mm Hg and up to 285°C, which is approximately equivalent to 600°C at atmospheric pressure. CDL-P was extracted with cyclohexane. The cyclohexane soluble fraction, CyS, was also vacuum distilled. The average molecular weights of most fractions have been determined and additional analyses are still in progress.

The distillate was divided into three phases by physical appearance. The upper phase was isolated and designated as "light". The lower fraction was similarly separated and designated as "middle". Some distillate solidified on the condenser wall and was designated "heavy". "Light" was yellowish and fluid even at -6°C. "Heavy" had a red color.

"Middle" was reddish and somewhat fluid at room temperature, but solidified at lower temperatures. The quantity of each fraction is semi-quantitative due to the collection method. Residue in the distilling flask was called "resid". The distillation products from CDL-P were similar to the corresponding products from CyS in appearance.

Experimental data are summarized in Table 1. The distillation results of CDL-P are similar to those of ES[6], even though CDL-P included ES and EP-AS and had a distillation temperature that was ∿100°C higher than before. Taking "middle" as a mixture of "light" and "heavy", the molecular weights of "light", "heavy" and "resid" are approximately 100 units apart successively. This trend suggests that there are three component groups in CDL-P, which will be examined further as other analytical data are available.

Cyclohexane dissolves more than two thirds of CDL-P. The soluble fraction, CyS, has slightly higher molecular weight than that of CDL-P. This will be rechecked. The distillation of CyS revealed that CyS consists of all fractions observed in CDL-P. Cyclohexane extracted most of "light" and "middle" fractions out of CDL-P. It also took out ∿45% of "heavy" and ∿60% of "resid" from CDL-P.

In brief, distillation gave detailed information on molecular size distribution in CDL-P. The distribution suggested three component groups in CDL-P. Examination of the cyclohexane soluble fraction of CDL-P by distillation revealed that cyclohexane is a poor agent to fractionate CDL-P according to molecular size.

To obtain more information on the structure of CDL fractions, methods for structural analysis were studied. Methods[1-3] were designed to extract average structural parameters from NMR spectra and elemental composition, sometimes using other analytical data such as molecular weight, density,etc.[4] A few assumptions or adjustable parameters were introduced in each method, but most results from the methods have not been confirmed experimentally. Recently Whitehurst et al.[5] criticized the method by Brown and Ladner[1], which has been used extensively for coal liquids, stating that the assignments of certain bands in NMR spectra are not clear. The NMR information was used only for the determination of carbon and hydrogen aromaticities. The criticism has merit and the methods can be improved by additional experimental data.

Future Work

The remaining analytical work on the distillation products is proceeding. The NMR method for determining phenolic hydroxyl groups described in the last report will be compared with other methods. As other analytical data are available, possible characteristic component-groups will be chosen to investigate their relationships to other fractions.

References

1. J.K. Brown and W.R. Ladner, Fuel, 39, 87 (1960).
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3. G.A. Haley, ibid, 44, 580 (1972).
4. D.R. Clutter et al., ibid, 1395 (1972).
5. D.D. Whitehurst et al., "The Nature and Origin of Asphaltenes in Processed Coals," Annual Report EPRI-480, Project 410-1, Menlo Park, California, 1977.
6. W.H. Wiser et al., ERDA Contract No. E(49-18) - 2006 Quarterly Progress Report, Salt Lake City, Utah, Oct-Dec 1977.

Table 1. Results from distillation of CDL-P and its cyclohexane soluble fraction.

				Yield	
Sample	Operation	Product	Molecular Weight	Weight %	Mole %
CDL-P	-	-	258	100	100
	Distillation	Light	183	19.2	27.1
		Middle	210	15.7	19.3
		Heavy	272	17.6	16.7
		Resid	390	40.0	26.1
		Loss	-	7.5	-
CDL-P	Cyclohexane Extraction	CyS	267[a]	72.1	-
		CyP	-	29.7	-
CyS	-	-	267[a]	72.1(100)	100
	Distillation	Light	181	19.6(27.2)	40.1
		Middle	229	16.7(23.2)	27.0
		Heavy	290	7.9(11.0)	10.1
		Resid	401	23.8(33.0)	22.0
		Loss	-	4.1(5.6)	-

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[a] Tentative designation, pending further confirmation.

Project A-2

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

Solvent Extraction of Coal Utilizing Sonic Energy

Faculty Advisor: L.L. Anderson
Graduate Student: Doohee Kang

Introduction

This project involves the study of the dissolution of coal in a hydrogen donor solvent using a differential reaction system of the batch recycle type. This system affords expansion of the time scale in the rapid initial stages of reaction. The reactor also preserves the labile chemical functions, i.e., carbonyl, by rapid heat up and quench of the donor solvent system. The nature of the reaction has been detailed in previous reports.

Project Status

Figure 1 shows conversion kinetics data of three SRC fractions of Hiawatha coal run at 400°C. In Figure 2 the carbon aromaticity[1] defined as

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}}{\frac{C}{H}}$$

of these same products are plotted vs. conversion. Figure 1 shows asphaltols and asphaltenes are intermediates in the reaction of coal to lighter products. However, during the initial few minutes of the thermal reaction, direct conversion of coal to asphaltols, asphaltenes and oil is probably the dominant reaction.

The aromaticity of the products increases rapidly during the thermal reaction regime (up to about 50% conversion), but hydrogen transfer from the donor solvent is minimal (Figure 2). Hydrogens are therefore preferentially supplied by coal itself during this initial reaction period since these primary reactions are probably isolated from the solvent.

Following the initial thermal reaction, changes in product aromaticity are less pronounced as conversion continues. This indicates the active engagement of the donor solvent offsetting further aromatization of the products. This second reaction regime has been characterized by a rapid hydrogen transfer from the donor solvent.[2] The primary reaction products probably become well dispersed or dissolved in the solvent with improved chances for donor hydrogen transfer.

The aromaticity of products again increases sharply as the over-all conversion reaches the ultimate stages. This third reaction regime is characterized by the net decrease of SRC products as shown in Figure 1. The further aromatization of the SRC products is most likely due to the exhaustive reaction of the products formed in the two previous regimes. The end products are stable aromatics and gases.

Figure 3 shows three major oxygen functional groups for a typical product (benzene solubles from Kentucky #14 coal) quantified by IR spectral analysis as a function of conversion. Conversion was conducted at 400°C and 1500 psig H_2, using the same procedure as detailed in the previous reports. The abscissa is the apparent molar absorbance derived from the integration of the spectral peaks of each of the specific oxygen functional groups.

$$B = \frac{1}{C\ell} \int_{\lambda_1}^{\lambda_2} A\,d\lambda$$

where B = apparent molar absorbance

C = molar concentration

λ = wave number, cm^{-1}

ℓ = sample thickness, cm

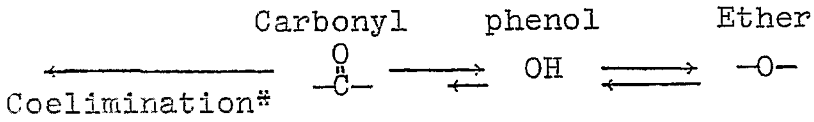
Methylene dichloride was the standard solvent utilized for the analysis for carbonyls and for OH bands. The KBr disk technique was used for the analysis of ethers (1325 ~ 1000 cm^{-1}) and insoluble products.

Nitrogen and sulfur functional groups were ignored since elemental analysis showed their minor importance compared to the oxygen contribution. Band assignments were chosen as

Total OH	3600~2200 less CH stretch bands
Carbonyl	1800~1650
Ethers	1325~1000

Alcohols (1100~1000) were negligible for the samples investigated

Band assignments will be fully discussed in the final report. Figure 3 shows that carbonyls reduce rapidly as conversion progresses; however, OH and ethers pass through maxima during the initial reaction period with OH first followed by ethers. These three functional groups may be involved in the following series reaction.



$$\xleftarrow[\text{Coelimination*}]{\qquad\qquad} \overset{\text{Carbonyl}}{\overset{O}{\overset{\|}{-C-}}} \rightleftarrows \overset{\text{phenol}}{OH} \rightleftarrows \overset{\text{Ether}}{-O-}$$

An equilibrium establishes rapidly between OH and ethers.

Figure 4 shows the correlation of the apparent molar absorbance of ether groups and molecular weights of the samples taken for the conversion of Kentucky coal. Surprisingly, molar absorbance of ethers decreases linearly as the size of the molecules decreases, indicating ethers may be a major linkage during the process of depolymerization. The distance from the intercept to the ordinate gives a unit molecular size of 257, about the size of a four-ring cluster.

Future Work

A final report on this project from 1975 is in preparation. Additional research by others will be initiated with extraction at slightly milder reaction conditions (temperature lower). Some use of the batch recycle reactor will be necessary as well as a new design. Details of the new reactor will be given in a subsequent report.

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1. J.K. Brown, W.R. Ladner and N. Sheppard, Fuel (London), 35, 79 (1959).
2. W.H. Wiser et al., ERDA Contract No. E(49-18) - 2006, Quarterly Progress Report, Salt Lake City, Utah, Oct-Dec 1977.

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*Kinetics of CO evolution appears to match the disappearance of carbonyl absorption.

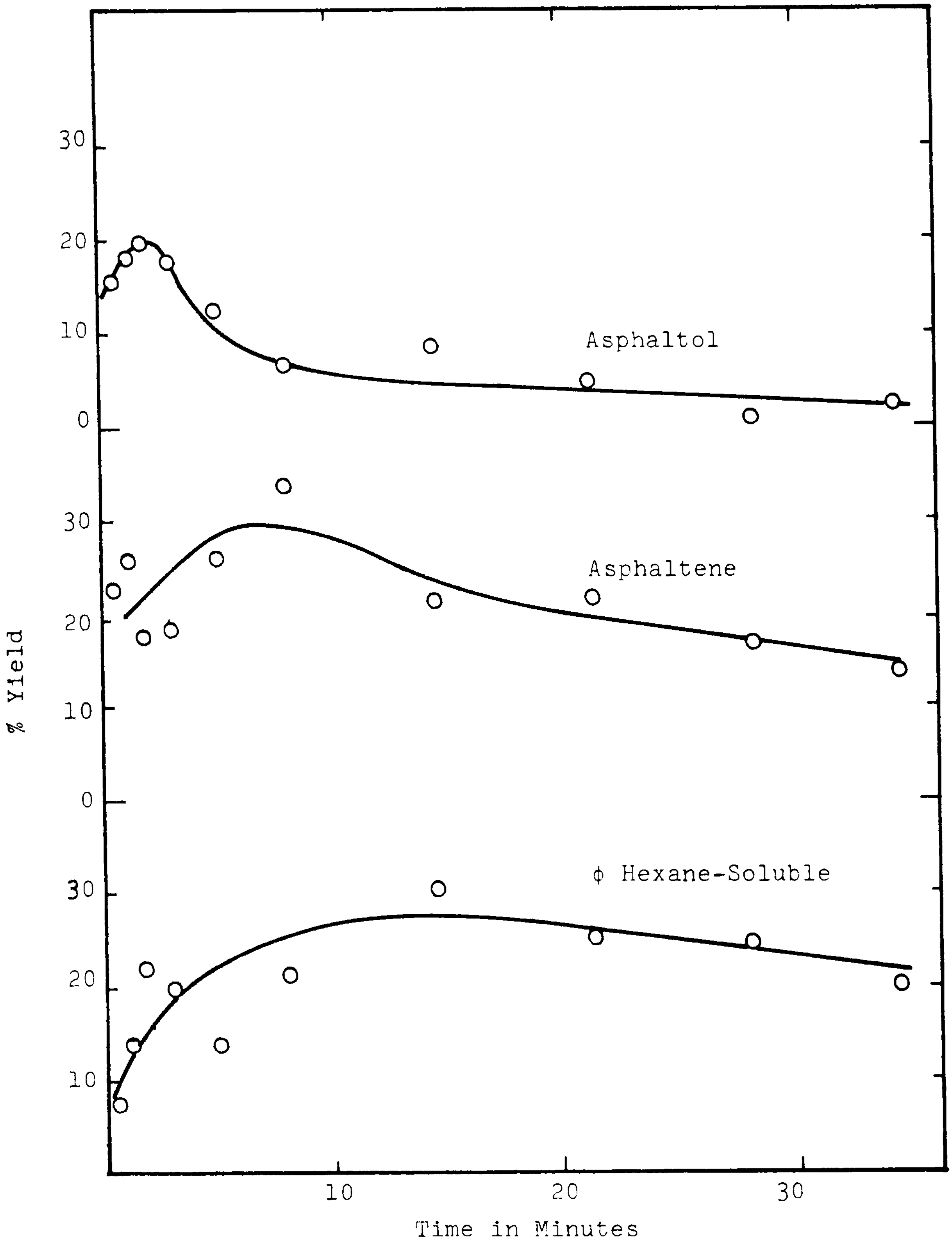


Figure 1. Percent Yield vs. Residence Time, Hiawatha Coal, 400°C, 1500 psig.

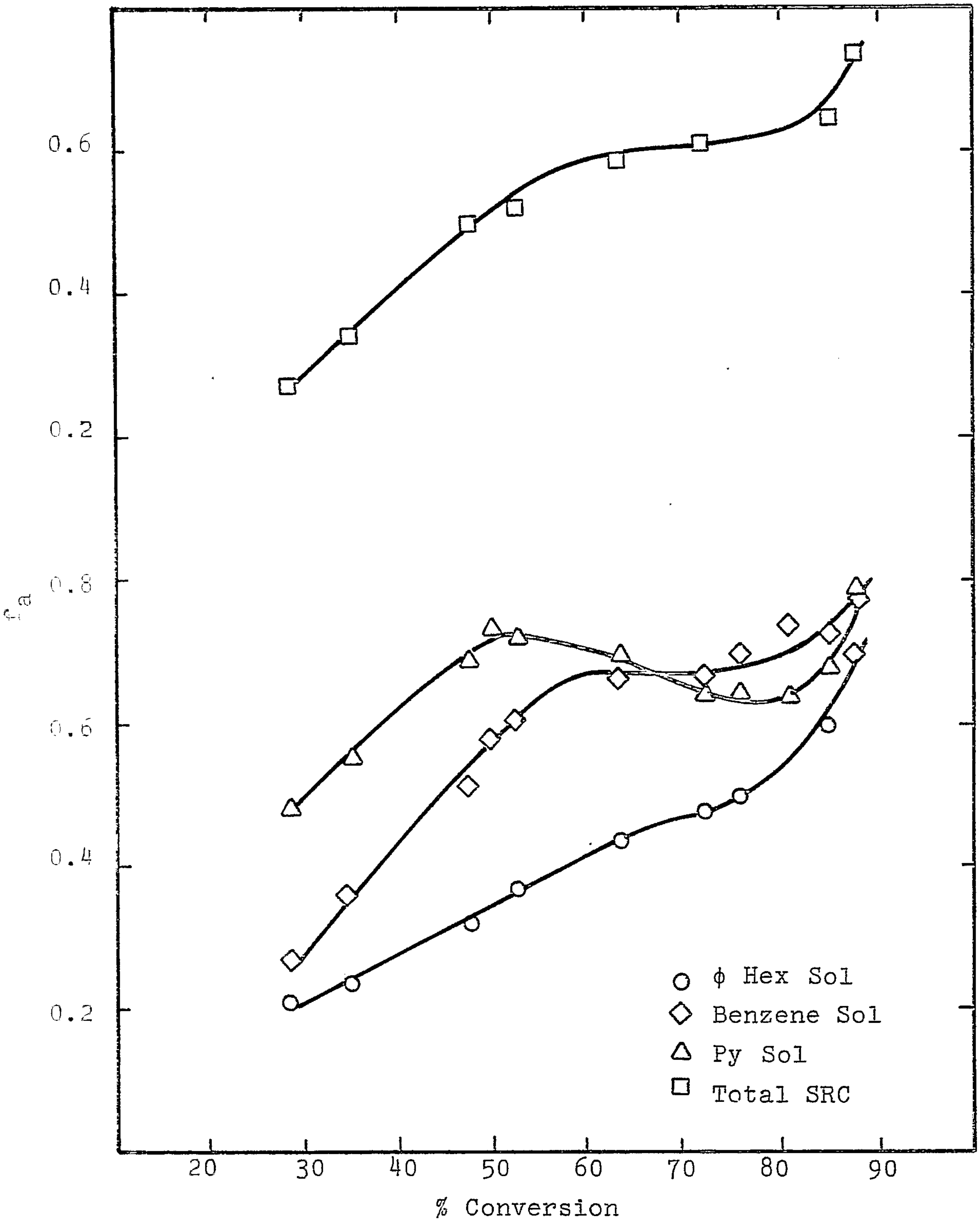


Figure 2. Aromaticity (f_a) vs. Conversion, Hiawatha Coal, 400°C, 1500 psig.

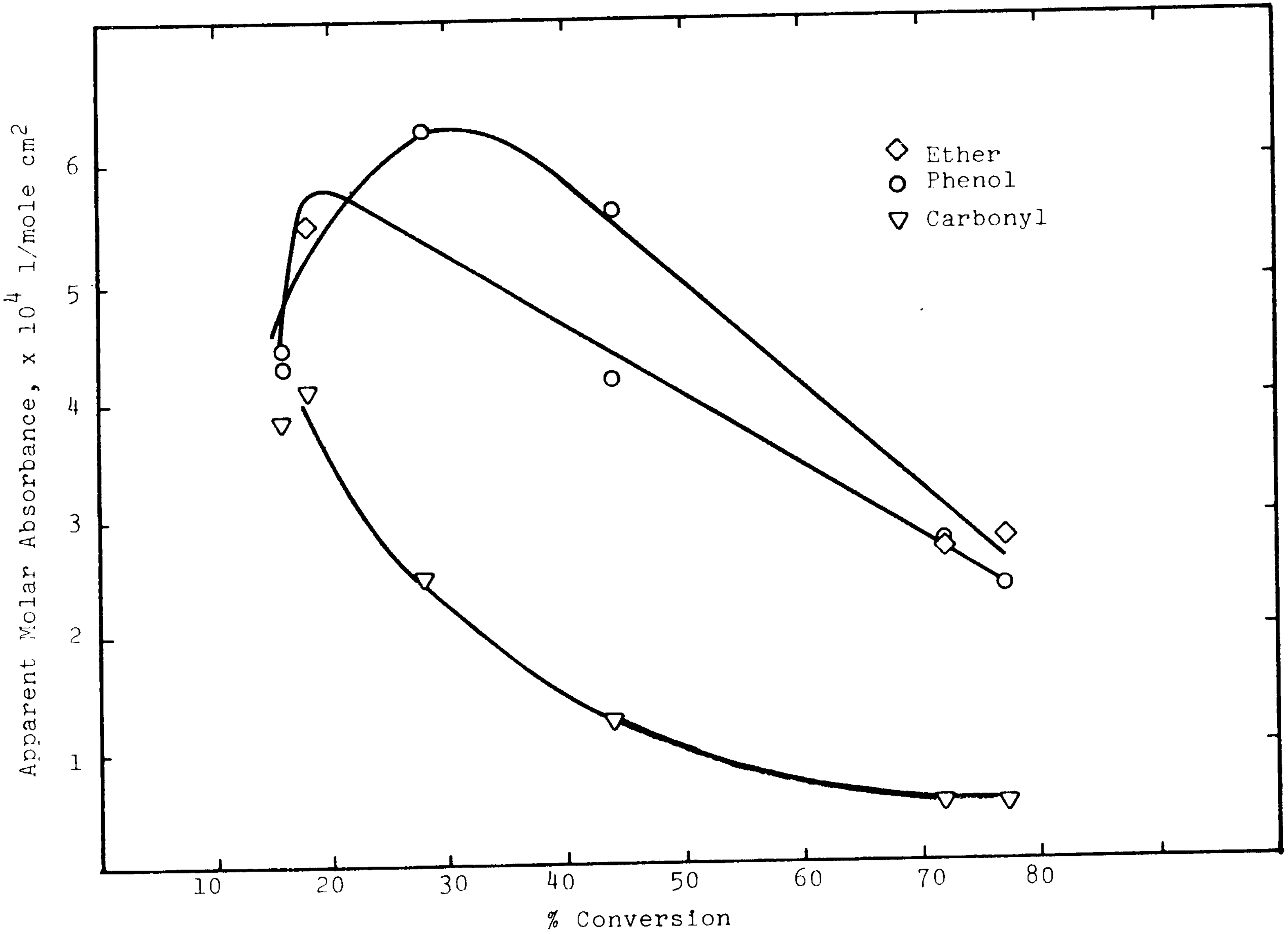
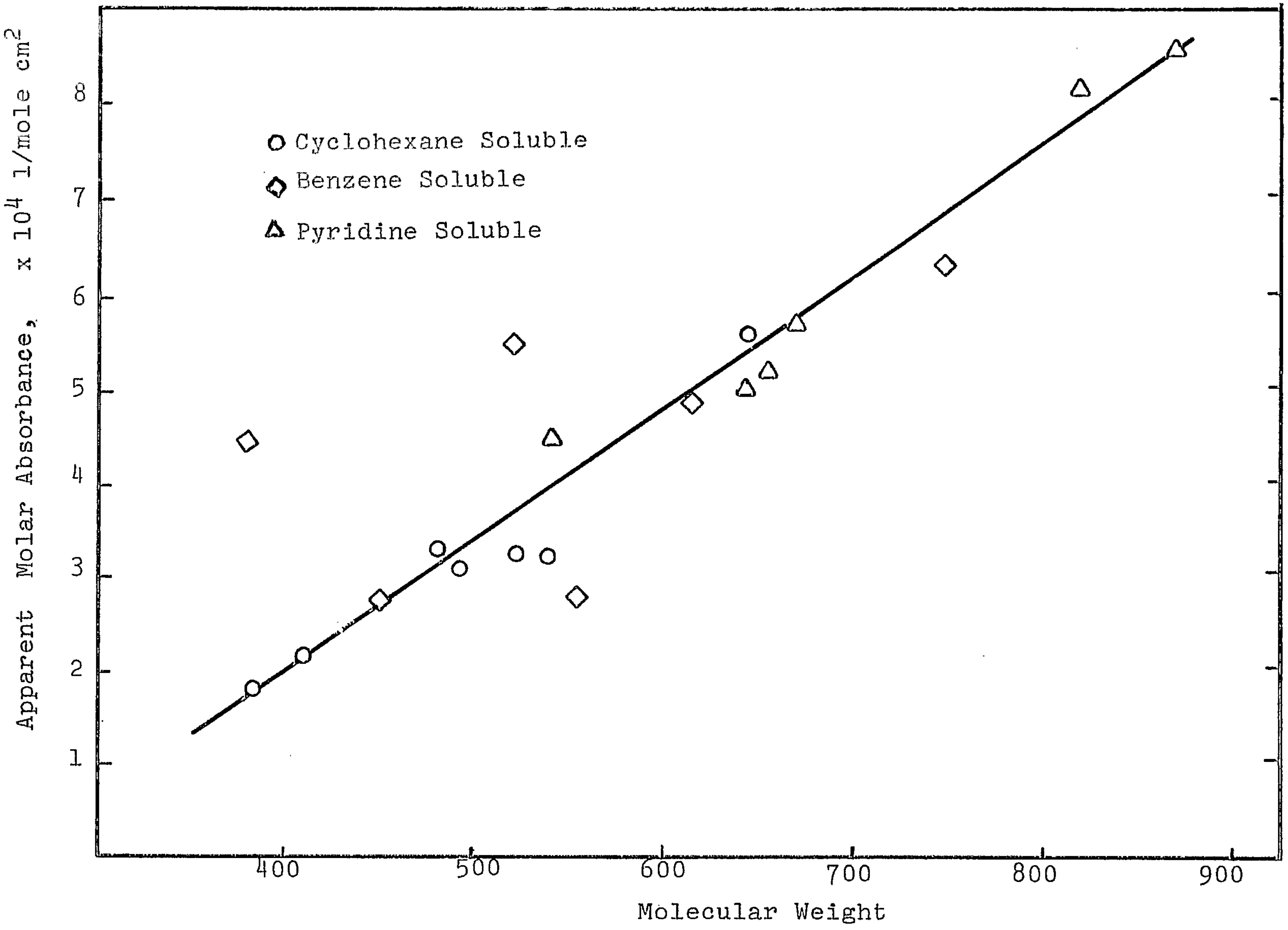


Figure 3. Apparent Molar Absorbance vs. Conversion. Benzene Soluble Product, Kentucky #14 Coal, 400°C, 1500 psig H_2.

Figure 4. Apparent Molar Absorbance of Ether vs. Molecular Weight, Kentucky #14 coal.



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.

Project Status

An appropriately designed reactor needed for the study is presently under construction, and a preliminary screening of homogeneous catalysts, using simple extractive equipment and techniques, has been initiated.

Future Work

With completion of the reactor construction, systematic studies on selective catalytic cleavage or transformation of carbon-oxygen bonds present in coal will be undertaken.

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

Benzene has been steam reformed on G56B Girdler catalyst. The experimental parameters and results are shown in Table 1. Benzene did not react with steam below about 600°C on the catalyst. Despite an increase in the steam ratio, no coking was observed during experiments B002 to B006. (Coking is detected by the differential pressure gauge across the reactor and the material balance.) None of the product gases contained methane.

To find the base point (without catalyst) for benzene and toluene, the reactor was packed with α-Al_2O_3 pellets only. Benzene and toluene were steam reformed separately at different temperatures and the results are shown in Tables 2 and 3, respectively. Benzene did not decompose or react with steam below 725°C and coking did not occur, even though the steam ratio as kept constant at 4.07. Only traces of methane were present in the product gases. The conversion was not 100% even at 940°C as compared to 100% conversion on Ni-catalyst at 800°C.

Steam reformed toluene on α-Al_2O_3 produced no gases below 750°C. At higher temperatures about 1% of methane was produced. Coking was not observed and the conversion was not complete.

Future Work

The above results suggest that Ni-catalyst increases the reaction rate. However coking occurs. In an attempt to decrease coking, the Ni-catalyst will be impregnated with different amounts of sodium.

Table 1

STEAM REFORMING OF BENZENE ON G56B

Run No.	B002	B003	B004	B005	B006
Benzene Feed Rate cc/min.	2.44	0.645	0.820	0.780	0.770
Water Feed Rate cc/min.	9.80	10.34	8.85	7.57	9.87
Steam Ratio	3.30	13.17	8.87	7.97	10.53
Space Velocity hr^{-1}	8869	2344	2980	2835	2798
Catalyst Temp. °C	650	800	800	800	775
Conversion %	56	76	100	100	100
Product Gas					
% H_2	71.9	74.4	71.6	72.9	73.0
% CO	8.3	5.0	7.4	6.5	4.8
% CH_4	0.0	0.0	0.0	0.0	0.0
% CO_2	19.8	20.6	21.0	20.6	22.2
Carbon Balance %	70.2	87.6	63.6	67.6	65.7
Coking	Yes	Yes	Yes	Yes	Yes

Table 2

STEAM REFORMING OF BENZENE ON PACKING $\alpha-Al_2O_3$

Run No.	B007	B008	B009	B010
Benzene Feed Rate cc/min.	2.22	2.22	2.22	2.22
Water Feed cc/min.	11.00	11.00	11.00	11.00
Steam Ratio	4.07	4.07	4.07	4.07
Pressure psig	0	200	200	200
Maximum Temp. °C	725	845	890	940
Conversion %	0	33	53	68
Product Gas				
% H_2	0	65.0	63.6	63.2
% CO	0	10.0	11.6	12.6
% CH_4	0	0.0	0.5	1.0
% CO_2	0	25.0	24.6	23.2
Carbon Balance %	100	109	105	98
Coking	No	No	No	No

Table 3

STEAM REFORMING OF TOLUENE ON PACKING $\alpha-Al_2O_3$

Run No.	T001	T002	T003	T004
Toluene Feed Rate cc/min.	2.00	2.00	1.23	1.23
Water Feed Rate cc/min.	11.00	11.00	11.25	11.25
Steam Ratio	4.6	4.6	7.7	7.7
Pressure psig	0	100	100	100
Maximum Temp. °C	750	800	850	900
Conversion %	0	51	73	94
Product Gas				
% H_2	0	70.3	69.4	69.4
% CO	0	9.5	9.6	9.6
% CH_4	0	1.0	1.0	1.0
% CO_2	0	19.2	20.0	20.0
Carbon Balance %	100	102	98	101
Coking	No	No	No	No

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 zeiolite-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] 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.

Project Status

Preliminary Results

The catalytic cracking reactor system is shown schematically in Figure 1. Gaseous products are collected quantitatively in a gas holder and analyzed by gas chromatography. Liquid products are identified and then quantitatively analyzed by a combination of gas chromatography, NMR and mass spectral methods.

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.

For example, in the mild temperature range of 350-450°C and conversion levels of up to 80%, decalin yields 75-90 wt % of light liquids and only 10-25 wt % of gaseous products (mainly C_3-C_4 components). The liquid product mixture consists mainly of C_6-C_{10} alkylcyclohexenes and cyclohexanes and C_5-C_8 open chain olefins and paraffins, together with smaller amounts of C_6-C_8 aromatic hydrocarbons. The change in product composition as a function of temperature shows that the cleavage of the bicyclic system in decalin is a stepwise process. Splitting of the first ring produces 1-butylcyclohexene (1) and 1-methyl-2-propylcyclohexene (2) as primary products. This is followed by additional cracking steps, involving splitting of the second ring as well as cleavage of alkyl groups in (1) and (2), to yield C_5-C_8 open chain (mostly branched) hydrocarbons and C_6-C_8 cyclohexenes and cyclohexanes as well as small amounts of C_6-C_8 arenes and other low boiling components. The depth of cracking is easily controllable by variation in the experimental conditions, and coke formation is very low in the 350-450°C range. Similar cracking patterns are indicated with higher polycyclic naphthenes and with hydrotreated coal liquids. Such feedstocks are presently under systematic investigation.

Future Work

The systematic catalytic cracking study of polycyclic naphthenes and hydrogenated coal liquids will be continued.

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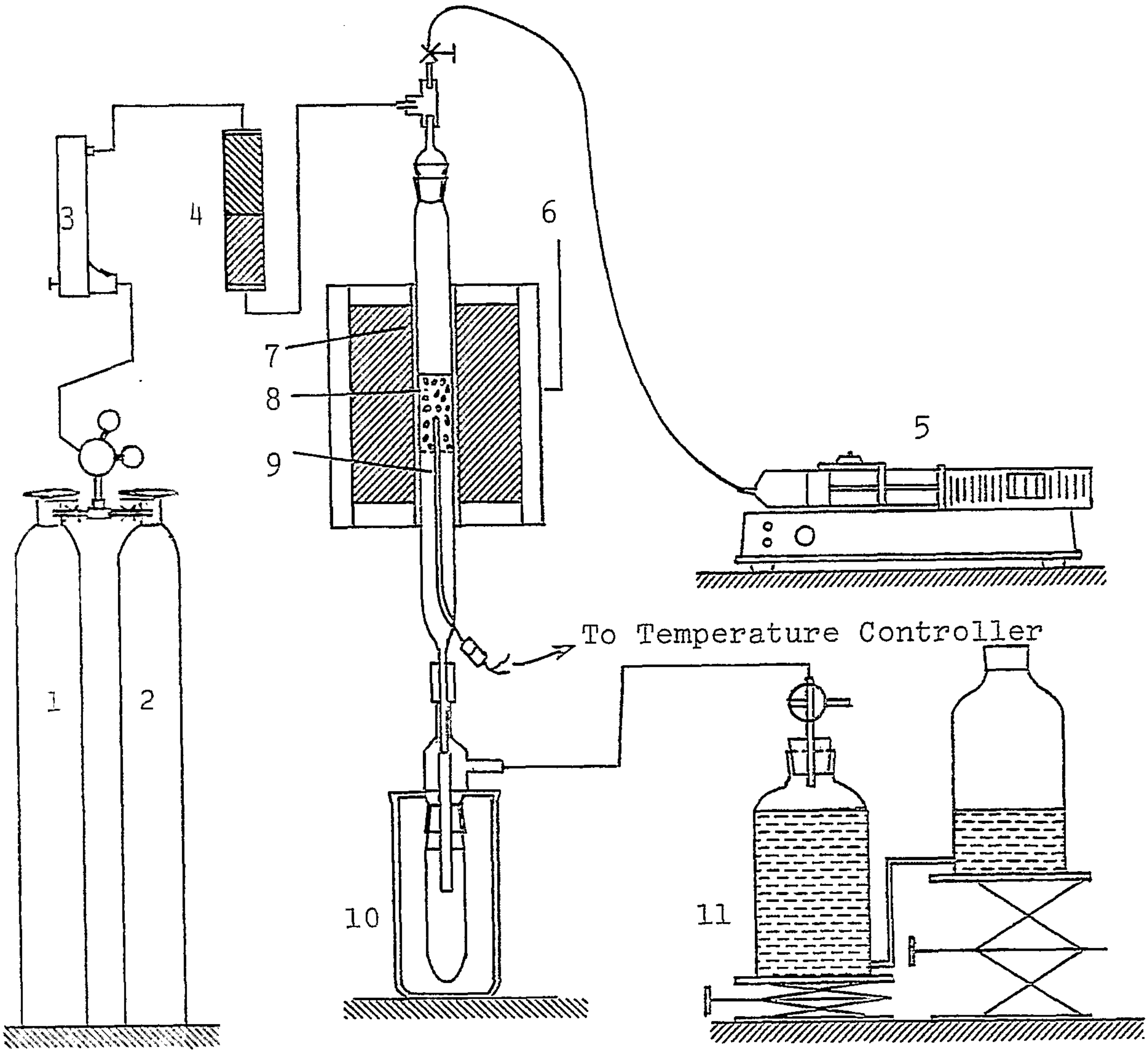
2. J. Shabtai and N. Lahav, Israel Patent 50548 (1976); U.S. Patent, pending.

Figure 1. Schematic of Catalytic Cracking Apparatus.



1. N_2 Cylinder
2. Compressed Air Cylinder
3. Flow Meter
4. Moisture Adsorber
5. Syringe Pump
6. Furnace
7. Quartz Reactor
8. Catalyst Bed
9. Thermocouple
10. Cold Trap
11. Gas Holder

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. Furthermore, recent extractive coal liquefaction studies under relatively mild operating conditions indicate that oxygen-containing functional groups play an important role in the structure of bituminous coal as bridging units between polycyclic aromatic-hydroaromatic clusters.[1] Consequently, a systematic catalytic hydrodeoxygenation study of coal-derived liquids and related model compounds, as a function of catalyst structure and experimental conditions, is being undertaken with the following objectives:

(1) To determine the direction and mechanism of hydrodeoxygenation of representative oxygen-containing compounds present in coal-derived liquids.

(2) To develop efficient process conditions for controllable removal of oxygen from different coal liquids.

(3) To contribute to the understanding of the chemistry and catalysis of extractive coal liquefaction.

Project Status

Hydrodeoxygenation Apparatus

The hydrodeoxygenation autoclave system constructed for this study is shown in Figures 1 and 2. Basically, this system consists of four identical autoclaves, equipped with separate heaters, a shaker assembly, a gas injection apparatus, and controlling equipment for measurement of reaction pressure and temperature.

Each autoclave has a ∿30 ml capacity and is designed to withstand pressures of up to 5000 psig and temperatures of up to 600°C. The autoclaves, valves, connecting tubing and thermocouple well are made from type 306 stainless steel.

The entire reactor assembly is mounted on a box-type shaker. Agitation within the autoclaves is provided by horizontal shaking. The major axes of the autoclaves coincide with the vibrational axis of the assembly. This is necessary to keep the catalyst suspended in the reactor.

Preliminary Experiments.

Some preliminary hydrodeoxygenation experiments with model compounds, in particular methyl benzoate, are being carried out with the purpose of selecting appropriate hydrodeoxygenation catalysts and defining a suitable range of experimental conditions.

Future Work

Systematic hydrodeoxygenation studies of coal liquids and related oxygen-containing compounds, e.g., esters, ethers, O-heterocyclics (in particular condensed polycyclic systems), ketones, condensed quinones, etc. will be carried out.

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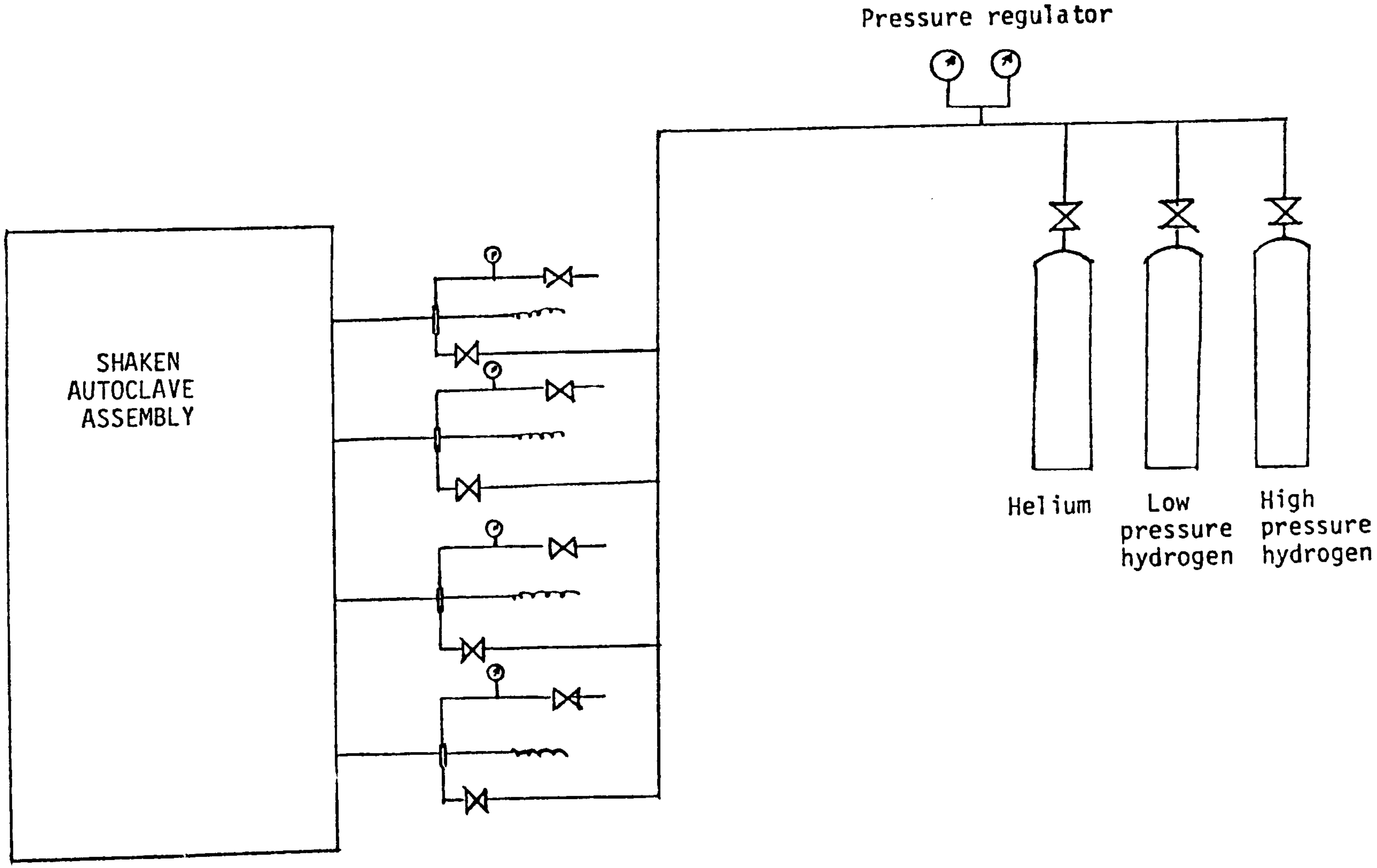

Figure 1. Shaken Autoclave Reactor System

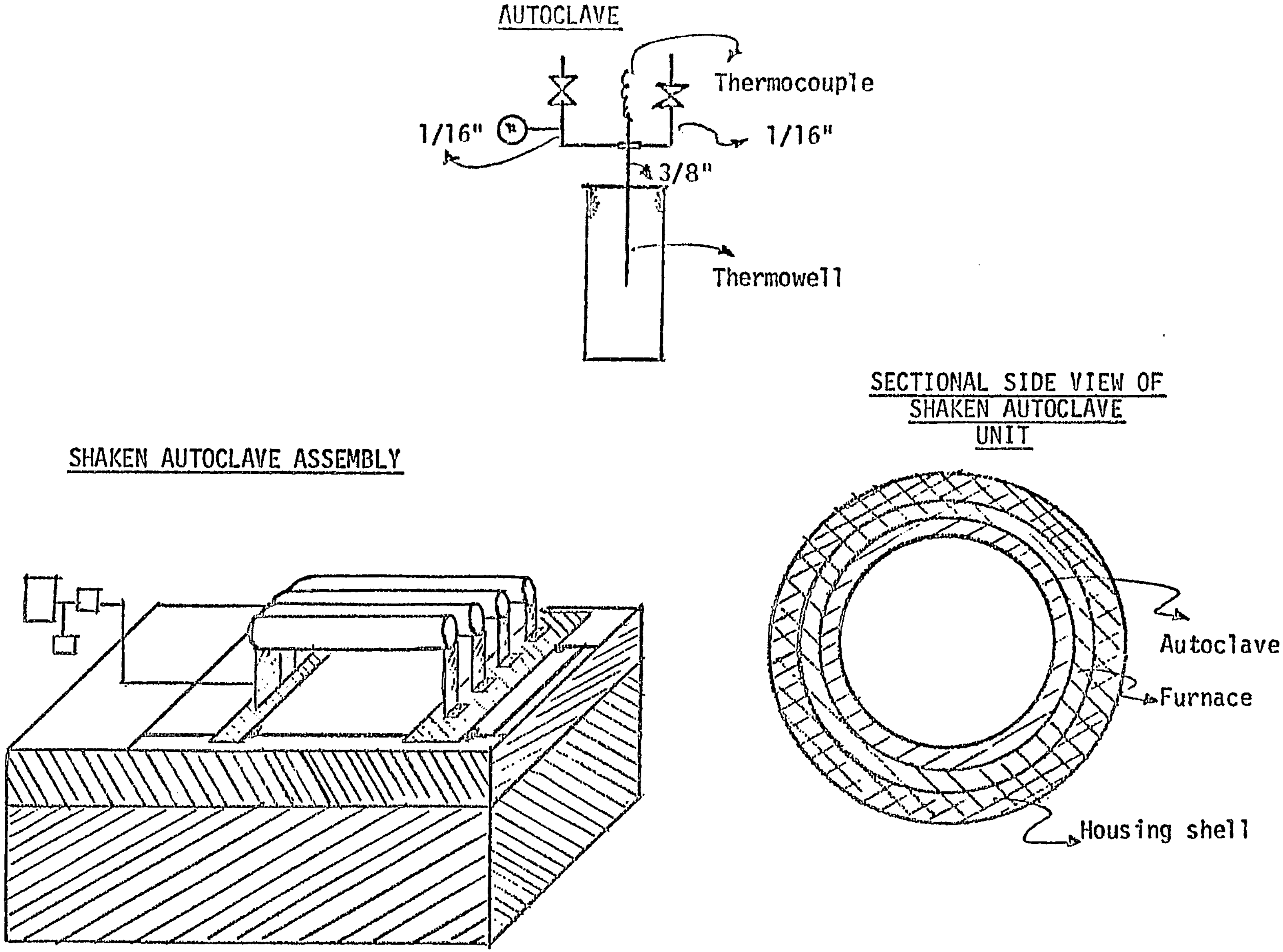

Figure 2. Components of Shaken Autoclave Reactor System

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 experimental apparatus has been designed, the component parts have been ordered and the nonstock items are being fabricated.

Future Work

The equipment will be assembled as the parts arrive, after which testing will begin. A typical catalytic cracking feedstock will be used to shake down the experimental apparatus and will provide a reference point for the study on coal-derived liquids. Commercially available amorphous and crystalline aluminosilicate catalysts will be evaluated in this investigation at catalyst-to-oil ratios ranging from 2 to 5 (by weight) in the temperature range of 723-873°K at atmospheric pressure.

Project A-8

Fischer-Tropsch Reaction 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 Boudard 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

Several manganese-iron catalysts have been prepared and are undergoing preliminary testing in a fixed-bed system to map the process variable space for the production of low molecular weight olefins from H_2 and CO. The slurry reactor is being designed and the component parts are being acquired.

Future Work

The slurry reactor apparatus will be fabricated and preliminary equipment testing will be completed. The most promising fixed-bed catalyst will be tested in the slurry reactor to map the process variable space. Process variables such as temperature, pressure, catalyst-slurry ratio, H_2/CO ratio and gas flow rate will be studied.

Project A-8

Synthesis of Low Molecular Weight Olefins From H_2 and CO

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

Introduction

The development of a catalyst for the hydrogenation of carbon monoxide to maximize the production of low molecular weight unsaturated hydrocarbons ($C_2^=$ to $C_4^=$) would be commercially significant. Previous studies indicated that a multimetallic iron-based catalyst gave the desired selectivity; however, the preferred catalyst composition was not determined. The objective of the present investigation is to develop a multimetallic, unsupported iron-based catalyst that will selectively produce low molecular weight hydrocarbons.

Project Status

An initial catalyst (90 wt % Mn and 10 wt % Fe) has been prepared by coprecipitation from a mixture of manganese nitrate solution (as purchased) and iron nitrate in a basic medium (pH 9). The bulk composition was determined by atomic absorption and X-ray fluorescence spectroscopy. The calcined catalyst (773 K) is undergoing preliminary testing in a fixed-bed reactor system.

Future Work

Unsupported manganese-iron catalysts of different Mn/Fe ratios will be prepared and subjected to a variety of calcination and/or fusion pretreatments. These catalysts will be characterized as to total surface area as determined by BET adsorption, and the nature of the surface will be probed by selective chemisorption. The catalytic behavior of the catalysts will be determined by the H_2-CO reaction under a wide variety of process conditions. The most selective catalyst for the production of low molecular weight olefins will then be prepared in the form of a supported catalyst and its catalytic and adsorptive properties will be investigated.

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 + H_2 Fischer-Tropsch reaction. 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 this quarter was spent completing construction of the temperature programmed desorption (TPD) apparatus. Some difficulties in operation were resolved by minor alterations. The apparatus was tested with a nickel kieselguhr catalyst. Results obtained for H_2 chemisorption on the reduced catalyst compared favorably with an adsorption isotherm measured on the same catalyst in a volumetric adsorption system.

Preliminary results on the $Co-Al_2O_3$ catalyst gave very little H_2 chemisorption. This is puzzling since this catalyst showed about 40% reduction of the cobalt and exhibited O_2 chemisorption in the microbalance apparatus. Reasons for this discrepancy are being investigated. This problem must be resolved since this technique will be used to measure active cobalt surface area in the presence of copper (which should not retain irreversibly adsorbed H_2).

Future Work

TPD runs will continue with other catalysts of interest to measure active metal areas using H_2. In addition, CO will be used as absorbate to detect any differences in bonding strength between catalysts having various Cu/Co ratios. Complementary studies are planned with the infrared cell.

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 runs of benzothiophene hydrodesulfurization over a sulfided $CoMo/Al_2O_3$ catalyst revealed the following:

1) An increase in temperature increased conversion only to a small extent.

2) An increase in benzothiophene partial pressure decreased conversion.

3) An increase in hydrogen sulfide partial pressure decreased conversion.

4) An increase in hydrogen partial pressure increased conversion.

5) Change in ethylbenzene partial pressure had no effect on conversion.

6) The presence of water had a negligible effect.

7) The presence of pyridine decreased conversion to a large extent.

8) Benzothiophene and ethylbenzene formed coke in the absence of hydrogen.

Project Status

To study the effect of pyridine on the adsorption characteristics of the catalyst, temperature programmed desorption of thiophene was employed. A schematic of the system is shown in Figure 1. A Hewlett Packard 5730 Gas Chromatograph was modified by replacing the chromatographic column with a reactor tube which was constucted from 1/4" O.D. 12" stainless steel tubing. About 0.5 g of catalyst was taken for the experiment. A reference tube filled with γ-alumina was placed in the oven to compensate for base line drift.

Helium carrier gas was split into two streams, one lead directly to the reference tube and the other to the reactor tube. For the adsorption cycle, another stream of helium passed through a series of two bubblers and entered the reactor tube just before the oven. This stream was shut off during the desorption cycle. The flow through the reference tube and reactor tube were adjusted to be the same.

The experimental sequence is as follows: (1) The catalyst is sulfided **for** 2 hours at 400°C using H_2S/H_2 and cooled to room temperature in helium. (2) Helium is bubbled through the thiophene bubblers and to the reactor until the rate of adsorption of thiophene by the catalyst is small. (3) The helium through the bubbler line is closed and the catalyst is allowed to desorb in He at room temperature to remove weakly adsorbed material from the catalyst surface (about 2 hours). (4) Then, the oven temperature is increased at various programmed rates to 350°C to desorb the chemisorbed thiophene still retained.

From the desorption data, the temperature at which the peak maximum appeared was obtained and using the analysis of Amenomiya et al.,[1] the activation energy of desorption was calculated. The governing equation is

$$2 \log T_m - \log \beta = \frac{E_d}{2.303\ RT_m} + \log \frac{E_d V_m}{Rk_o}$$

Figure 2 shows the plot of $2 \log T_m - \log \beta$ vs. $\frac{1}{T_m}$ from which the activation energy of desorption of thiophene on 8% Mo on alumina catalyst was calculated to be 10.9 kcal/mole. In the above equation

E_d = activation energy of desorption

β = rate of heating °C/min

T_m = peak temperature ^{o}K

V_m = amount of gas adsorbed at a surface coverage = 1.

Future Work

The thiophene adsorption experiments will be carried out to study the effect of catalyst poisoning with a known amount of pyridine. The whole series will be repeated with the Co-Mo catalyst.

After the metal reactor has been assembled, initial runs will be made on mixing efficiency prior to making kinetic studies on benzothiophene.

Referencec

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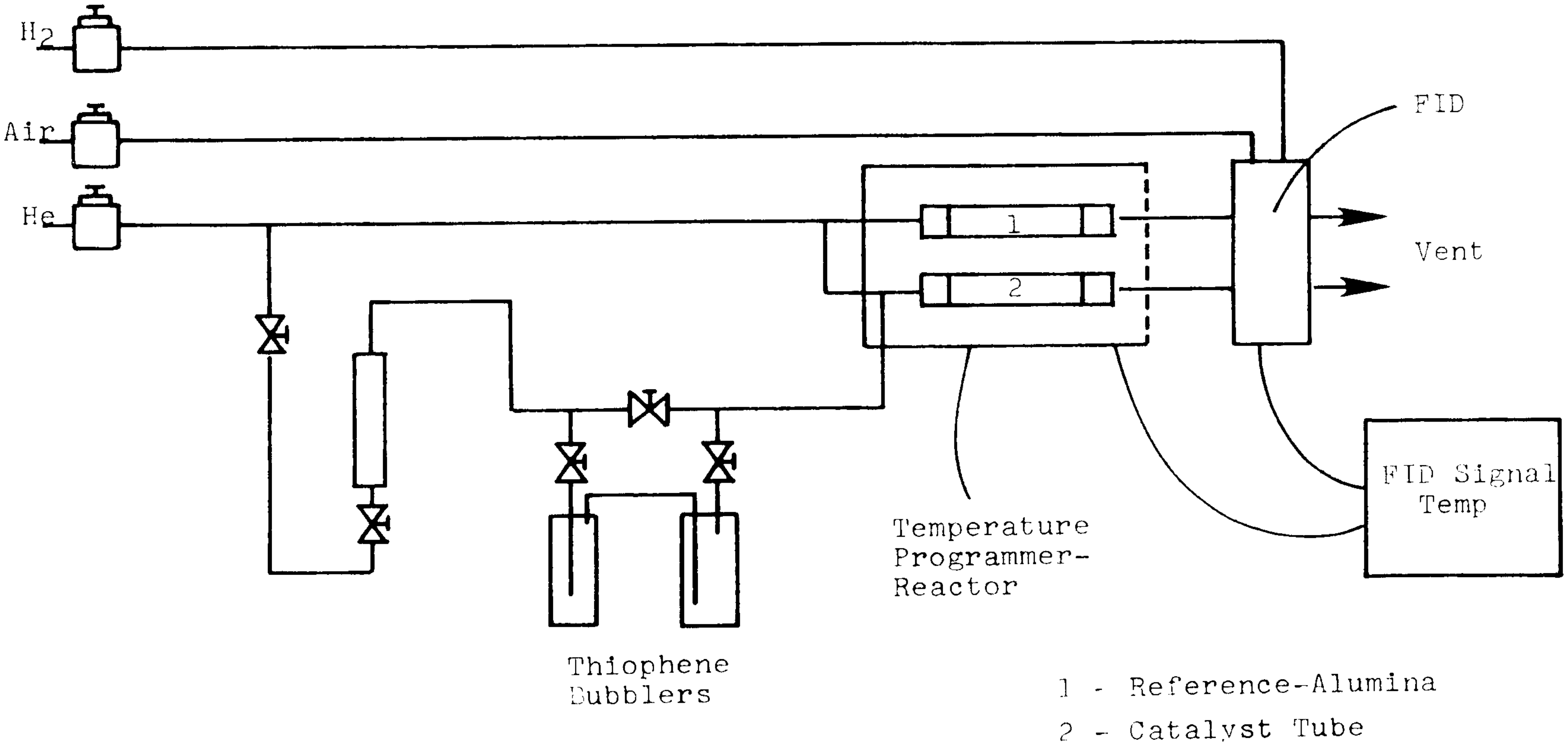
Figure 1. Temperature Programmed Desorption Schematic



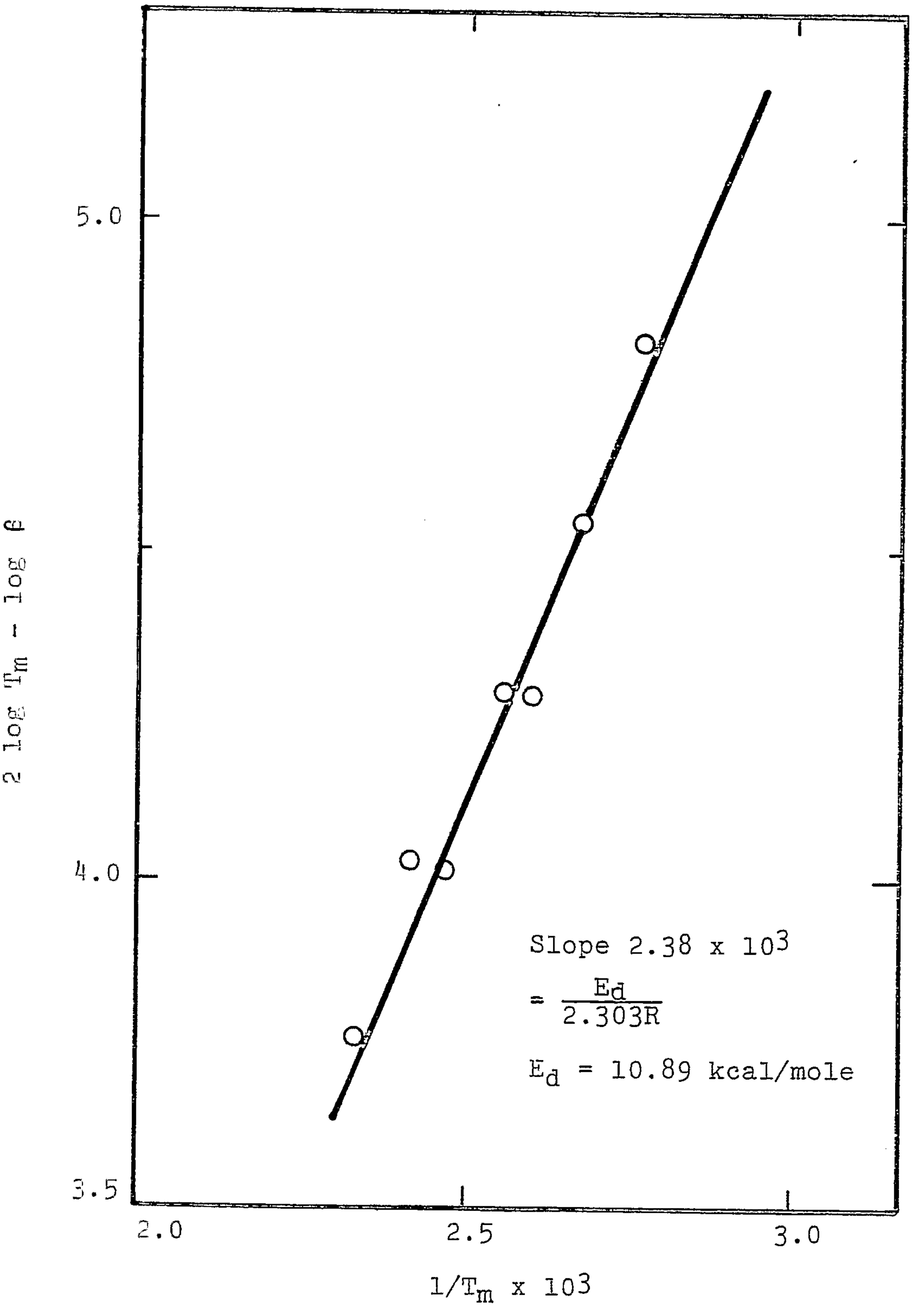


Figure 2. The activation energy of desorption of Thiophene.

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.[1,2] 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.[3-6]

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.[7-9] 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.[10-12]

Pyrolysis and dissolution of a high-volatile Utah coal have been discussed and compared with hydrogenation.[13-16] 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.[16] 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.[17] The yield of these molecules is proportional to volatile matter content.

The postulate of a dual structure in coal is consistent with the results of mass spectrometry[18] and solvent extraction[19-21] 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.[22] Zinc chloride, Co-Mo/Al_2O_3, red-mud plus sulfer and presulfided red-mud were used as catalysts. The partical 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 with out catalyst. The temperature ranged from 400°C to 500°C and the hydrogen pressure was 1800 psi. Residence time (8 - 21 sec) was varied by choice of the tube length (40 - 120 ft).

Future Work

Products will be separated by stepwise extraction using hexane, toluene and pyridine. Structural analysis of the various products will be performed.

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Project B-4

Mechanism of Catalytic Hydrogenation by Metal Halide Catalysts

ESCA Studies on Coal Metal-Salt Interactions

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

Introduction

The relatively new techniques of ESCA (Electron Spectroscopy for Chemical Analysis) and Auger Electron Spectroscopy are being used to investigate the catalytic hydrogenation of coal by metal halide catalysts. The two "new" peaks in the Auger spectra of a zinc chloride impregnated coal are due to the presence of calcium rather than an interaction between coal and zinc chloride. The gradual change in these peaks as a function of reaction conditions is now interpreted as a gradual migration of calcium to the coal surface as zinc chloride diffuses away from the surface.

The purpose of this work has been to detect changes in the zinc electron spectrum and to correlate these changes with interactions of zinc chloride and coal. The zinc electron spectrum can be divided into three areas: electrons originating from core levels in the atom, electrons originating in valence levels of the atom and Auger electrons. Zinc photoelectron spectra for core level electrons showed no change for various coal samples or zinc compounds. The zinc photoelectron spectra for valence level electrons were not examined because of the very low intensities of these spectra when using X-rays for excitation. Although zinc Auger spectra obtained from zinc compounds showed a small range of variation between samples, they did not give much information on zinc chloride - coal systems.

Project Status

Emphasis this quarter has shifted from zinc spectra to spectra of other elements found in coal, such as carbon, hydrogen, oxygen, nitrogen and sulfur. All except hydrogen have electron spectra of sufficient intensity to be observed by the ESCA technique, if found in high enough concentrations in the sample.

Utah Beehive coal and its char were examined by ESCA. The carbon and oxygen peaks were easily observed in both the coal and char with no significant differences. The sulfur and nitrogen were below the concentration levels for practical observation.

Limitations of the present ESCA unit (no insitu sample preparation facilities) and the nature of the zinc chloride-coal system make further studies using the ESCA and Auger Electron Spectroscopy techniques impractical. The zinc core level electron spectra and the Auger spectra of zinc contribute little to understanding the system. Zinc valence level electron spectra may contain useful information but are very expensive in terms of time because of the low signal intensities. Spectra of other elements gave no useful data.

Future Work

Further work with the zinc chloride-coal system is unlikely. However if insitu etching were possible in the ESCA unit, the diffusion of zinc chloride into the coal particle might be studied. The increased zinc peak intensity upon sample grinding is evidence of such a diffusion. Sulfur forms in high sulfur coal have been studied using ESCA. Similar studies for low sulfur coals are possible but would be expensive because of the instrument time involved.

Studies of nitrogen in coal might also be possible but expensive. Nitrogen has been observed in Kaiparowitz Utah coal with seventy-three scans (carbon was evident on the first scan).

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 or 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

Because of vaporization problems of the model compound 9-benzyl, 1,2,3,4-tetrahydrocarbazole in the TGA system, a more fundamental approach has been taken. About 50 mg of sample were vacuum sealed in a 25 mm x 900 mm pyrex tube. The presence of toluene, carbazole, tetrahydrocarbazole and benzyl carbazole in the products from the initial two runs indicated the occurrence of pyrolysis. These pyrolysis products were identified by GC-MS. Several more sample runs at 475°C for 60 min were analyzed and indicated the presence of benzene, toluene, dibenzyl, carbazole, tetrahydrocarbazole, benzyl carbazole, methyl tetrahydrocarbazole (traces) and benzyl tetrahydrocarbazole (unpyrolyzed model compound). The chemical reactions that could produce these products are shown in Figure 1. The reactions involving H as a reactant or product are abstraction reactions involving the hydroaromatic portion of the model compound, as molecular hydrogen does not appear in the gas phase.

Pyrolysis was studied at 5 different temperatures from 375° to 475°C at approximately 25° intervals. At each temperature, seven or eight samples were heated and then removed successively at 5 min intervals. The reaction tubes were cooled in liquid nitrogen to quench the reactions.

Since the heavy-walled pyrex tube required more than 30 min to heat up, smaller tubes were used (6 mm x 100 mm). The furnace temperatures were monitored by a millivolt recorder.

At pyrolysis times greater than 40 min, several products were formed due to secondary reactions, i.e. toluene formation increased with time reaching a maximum at 40 min and then decreased thereafter.

Future Work

To maintain uniform temperatures and reduce the heat-up time (to with 90 sec), a fluidized sand bath will be used. A 12 ft 1/4" SP 2250 column will be used in the HP 5830A GC. Gas chromatographic standardization will be done for benzene, toluene, carbazole, tetrahydrocarbazole, dibenzyl and 9-benzyl tetrahydrocarbazole.

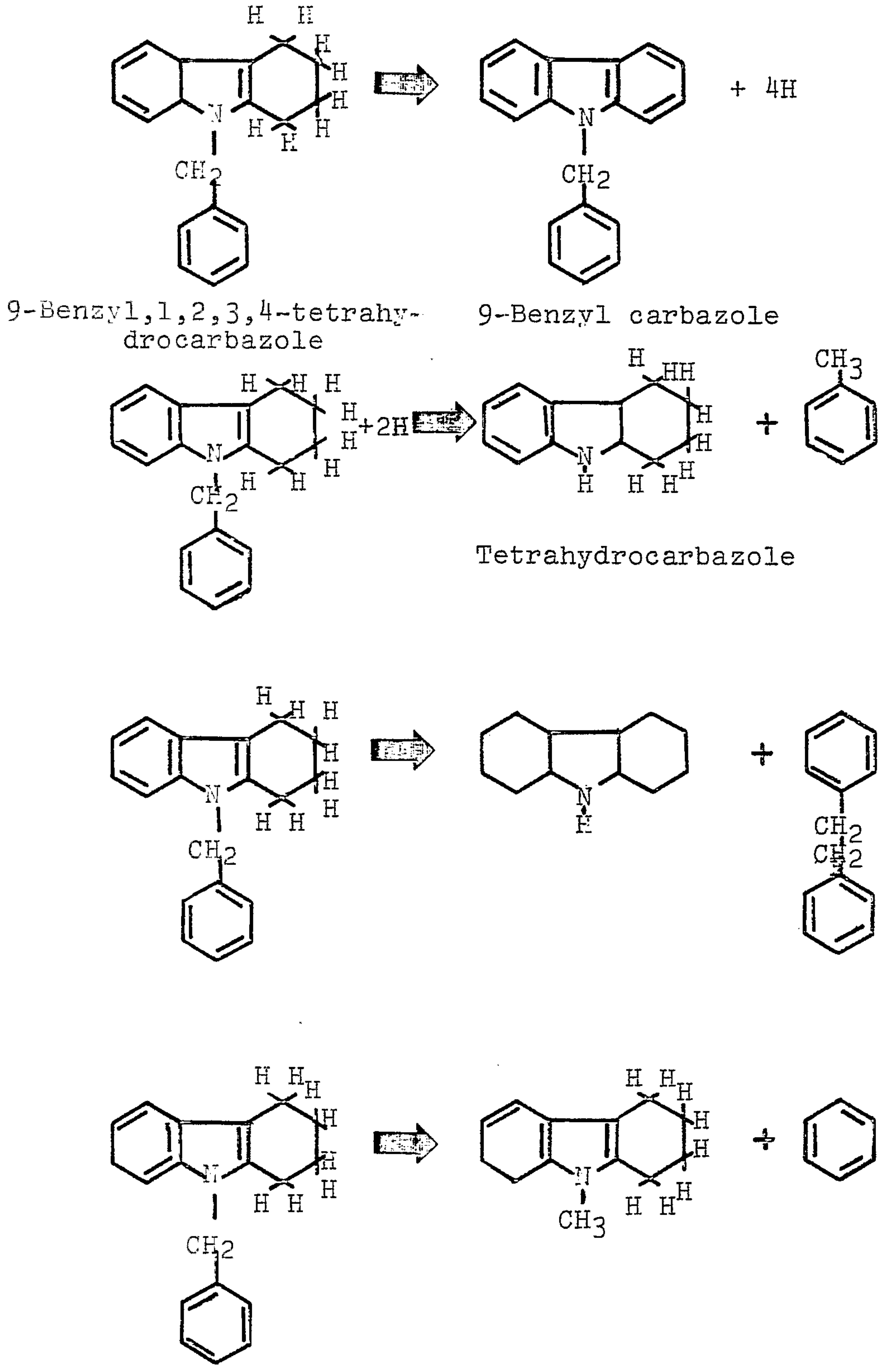


Figure 1. Possible Pyrolytic Reactions

Project C-2

Heat Transfer to Gas-Solid Suspensions in Vertical Co-Current Downflow

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

Introduction

This project is a two-part study of the flow behavior and heat transfer characteristics of a two-phase gas-solid mixture as it flows downward through a vertical, heated tube. The first set of experiments using uniform glass beads is nearing completion. The second set of experiments with actual coal particles has been started. This study will be applied to the design of advanced, short-residence-time, continuous hydrogenation reactors for coal liquefaction, where heat transfer may be the rate-limiting factor.

Project Status

Modifications to the experimental apparatus for heat transfer studies with the glass bead-air system have been completed, and the system has been checked for operability. The heat transfer test section was made of a type-304 stainless steel seamless tubing, 0.625 in. x 0.51 in. x 36 in. long, with copper flanges silver-soldered at both ends. As the heated section was used directly as an electrical heating element, it was separated by phenolic insulators from the other sections.

Alumel-Chromel thermocouples were installed at 15 axial positions on the outside surface of the tube and electrically insulated by sheets of mica approximately 0.001 in. thick. The thermocouple lead wires were then wound tightly around the tube to reduce temperature gradients in the wires near the junction and wrapped with a high-temperature tape. Finally, two layers of asbestos tape and fiber glass thermal insulation were taped around the tube. Two sets of thermocouples imbedded in the fiber glass insulation and copper bus bar at the bottom acted as indicators to check the heat loss from the insulation and end flanges.

For the power source, a DC rectifier-transformer-type welder (Miller SRH 404) with a main current adjustment knob and an additional fine controller was used to heat the tube. It can deliver up to 300 amperes continuously.

The voltage drop across the tube and the shunt connected in series to one of the electrical leads from the welder was monitored by d'Arsonval meters to control the voltage and current needed for heating the tube. These voltage taps were also connected to a Hewlett Packard 3450-A multifunction meter with an automatic scanner and a digital recorder for accurate measurement. The schematic diagram of the test section and instrumentation are shown in Figure 1. The multimeter was interfaced to a Wang computer, which was programmed to accept and average at least three readings of the input data from the meter and process it to get final results such as flow rates, heat fluxes, local heat transfer coefficients and Nusselt numbers.

To check the operation of the system and to determine the heat loss correction for the gas-solids suspension flow, initial runs were made with gas alone at various gas flow rates.

Experimental asymptotic Nusselt numbers adjusted for variable properties are compared with the analytical expression of Sparrow in Figure 2. The experimental results agree to ± 5 percent with the analytical expression. Higher deviation of Nusselt numbers above gas Reynolds number of 25000 may be caused by errors in the outlet gas bulk temperature measurement.

The variation of local Nusselt numbers with the axial distance is shown in Figure 3. The gas Reynolds number appears to have little or no influence on thermal entrance effects. The thermal entry length defined as that value of x/D at which the Nusselt number approaches to within 5 percent of the asymptotic value is about 38 tube diameters.

A diagram of the present test section being used for coal-air studies is shown in Figure 4. Twelve pressure taps are located along the length of the tubing. Two photomultiplier tube detectors are fixed between taps P5 and P6 and between P9 and P10. The injection point for the phosphor-tagged coal samples has been moved to a point located below the 3/4 to 5/8 inch reducing union on the 5/8 inch tubing itself. The overall length of the 5/8 inch section of tubing is approximately 25 feet, providing an L/D ratio of more than 500 at the outlet.

An attempt was made to correlate the solids feed rate from the vibratory feeder with the controller setting at each gas flow rate. Instabilities in the feeding mechanism made this approach unreliable. Although the feed rate is fairly constant at given conditions, it is not reproducible each time at the same conditions. A more successful approach has been to correlate the feed rate in terms of the pressure drop at the top of the tubing, where acceleration effects are important and make up a large portion of the entire pressure drop. The acceleration pressure drop varies more dramatically with solids loading than does the frictional pressure drop. At a given controller setting and constant gas flow rate, some undesirable fluctuation still occurs in the two-phase pressure drop. However, this may be caused by a fluctuating solids feed rate or a nonuniform distribution of solids in the flow.

The particle densities of both the coal and phosphor were measured by water displacement and equaled 79.1 lbm/ft^3 and 253 lbm/ft^3, respectively. Because of the large density difference between the coal and phosphor, the effect of the phosphor coating on the bulk density of the tagged coal particles was investigated. An increase of approximately 25 percent was noted for a sample of -24/+28 mesh particles. Inspection of the phosphor-coated particles under the microscope also revealed that the phosphor was caked on the surface of the large particles (-28/+24 mesh) rather heavily and was not adhering much at all to the smaller particles (-42/+48 mesh). A new technique which involves spraying dry coal particles with a fine mist of sodium silicate solution and then dusting sparingly with phosphor appears to have solved these problems.

Pressure drop measurements for air alone have yielded friction factors which agree rather well with those predicted by the modified Colebrook equation for a roughness ratio, e/D, of 0.00020. This value is typical of the values that have been reported by other researchers for seamless stainless steel tubing. A plot of the average of the measured friction factors for all of the pressure tap intervals versus the Reynolds number is shown in Figure 5. The results of error analysis calculations are also indicated by the brackets and represent the estimated uncertainty due to random reading errors. In all cases, this uncertainty is less than 3 percent. The pressure taps and manometer system are functioning normally.

Pressure drop as a function of axial location is shown in Figure 6 for Reynolds numbers of 10,000 and 29,000 with and without solids flowing. The effect of the solids on lengthening the entry length can be clearly seen. In both cases, approximately 350 to 400 tube diameters are required before steady flow conditions are achieved.

More particle velocity measurements were taken for a Reynolds number equal to 10,000 by injection of -28/+42 mesh coal particles tagged with phosphor by the former method. The injection was performed for several different solids loadings, and no variation was detected. A typical photograph of the oscilloscope trace of the outputs of detectors D1 and D2 is shown in Figure 7. The measured particle velocity was, in all cases, approximately equal to the gas velocity, 47 feet per second. The injection point for these measurements was located in 3/4 inch tubing above the 3/4 to 5/8 inch reducing union. The pulses were not quite as sharp as had been obtained previously, and the injection point was relocated to a point below the reducer to avoid the unnecessary turbulence.

Future Work

Plans for next quarter are to complete the heat transfer experiments for the glass bead-air suspension flow and to analyze the data and compare it with literature data for the upflow regime. For the coal-air system, plans are (1) to determine the cause of the fluctuations in the measured pressure drop, (2) to correct the problem and stabilize the flow and (3) to finish taking the pressure drop and particle velocity data. Small amounts of dust have been removed in the system's filter bags, and a screening experiment will be performed to determine whether attrition has had an appreciable effect.

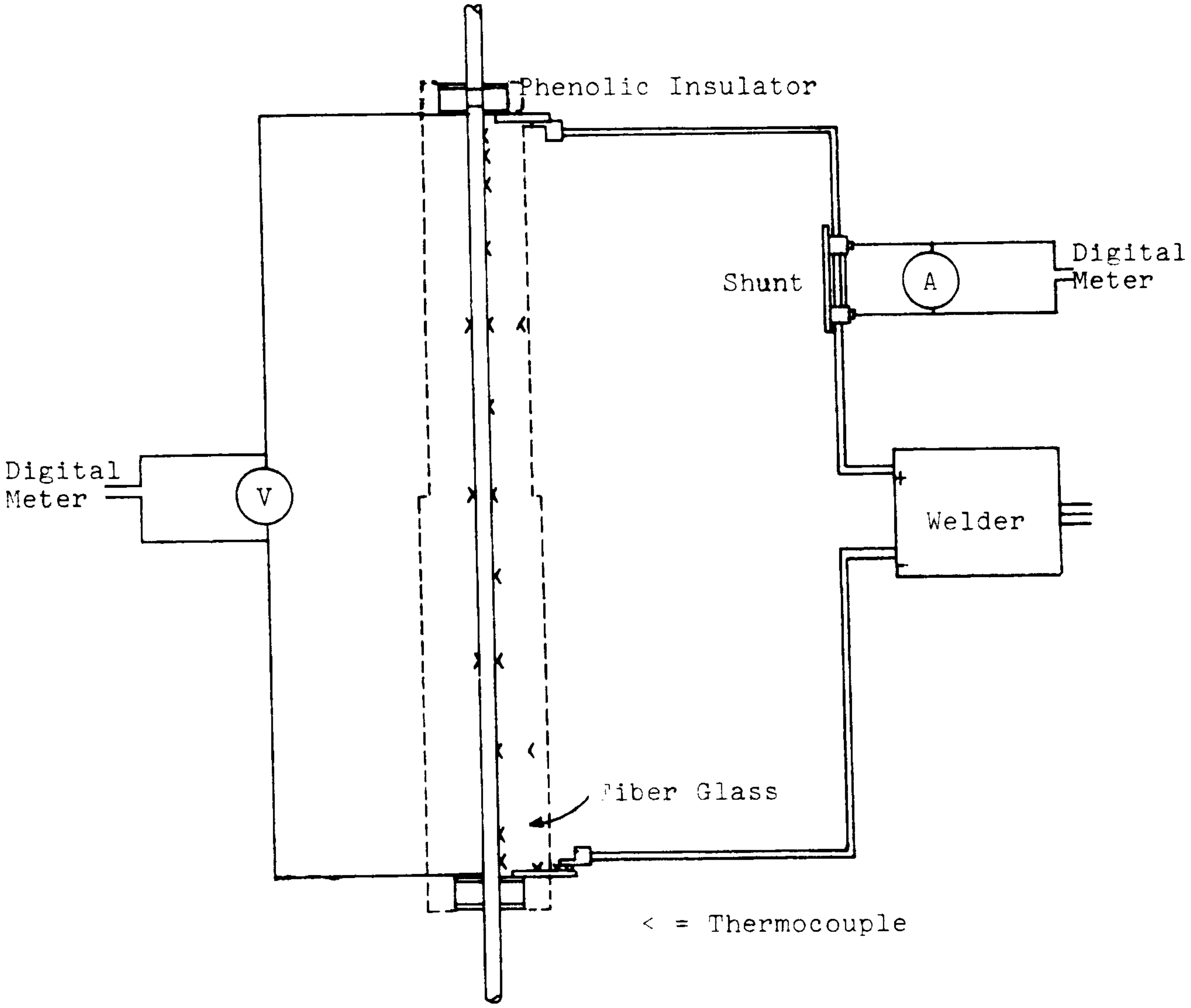


Figure 1. Schematic Diagram of Test Section for Heat Transfer Studies.

Figure 2. Asymptotic Nusselt Numbers

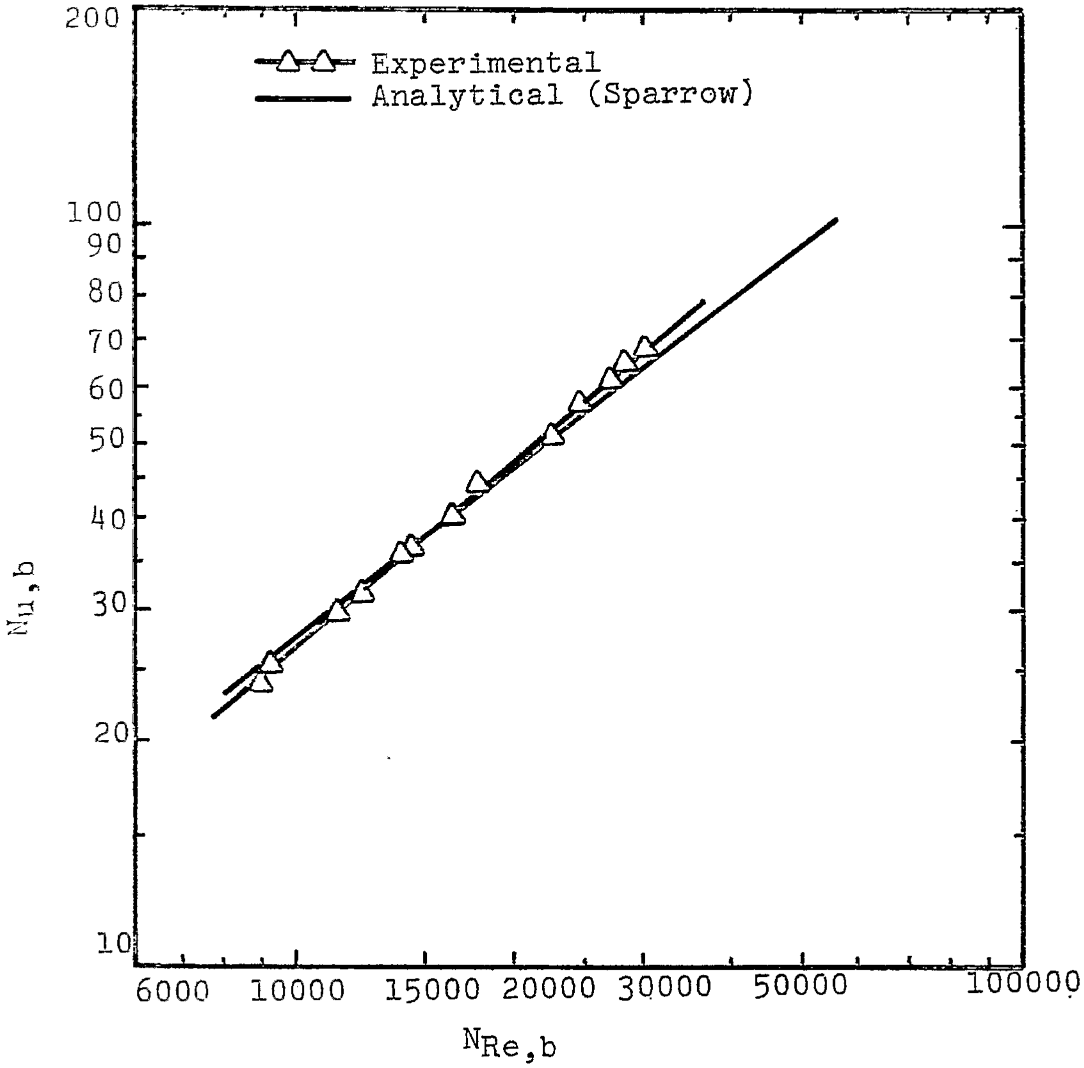
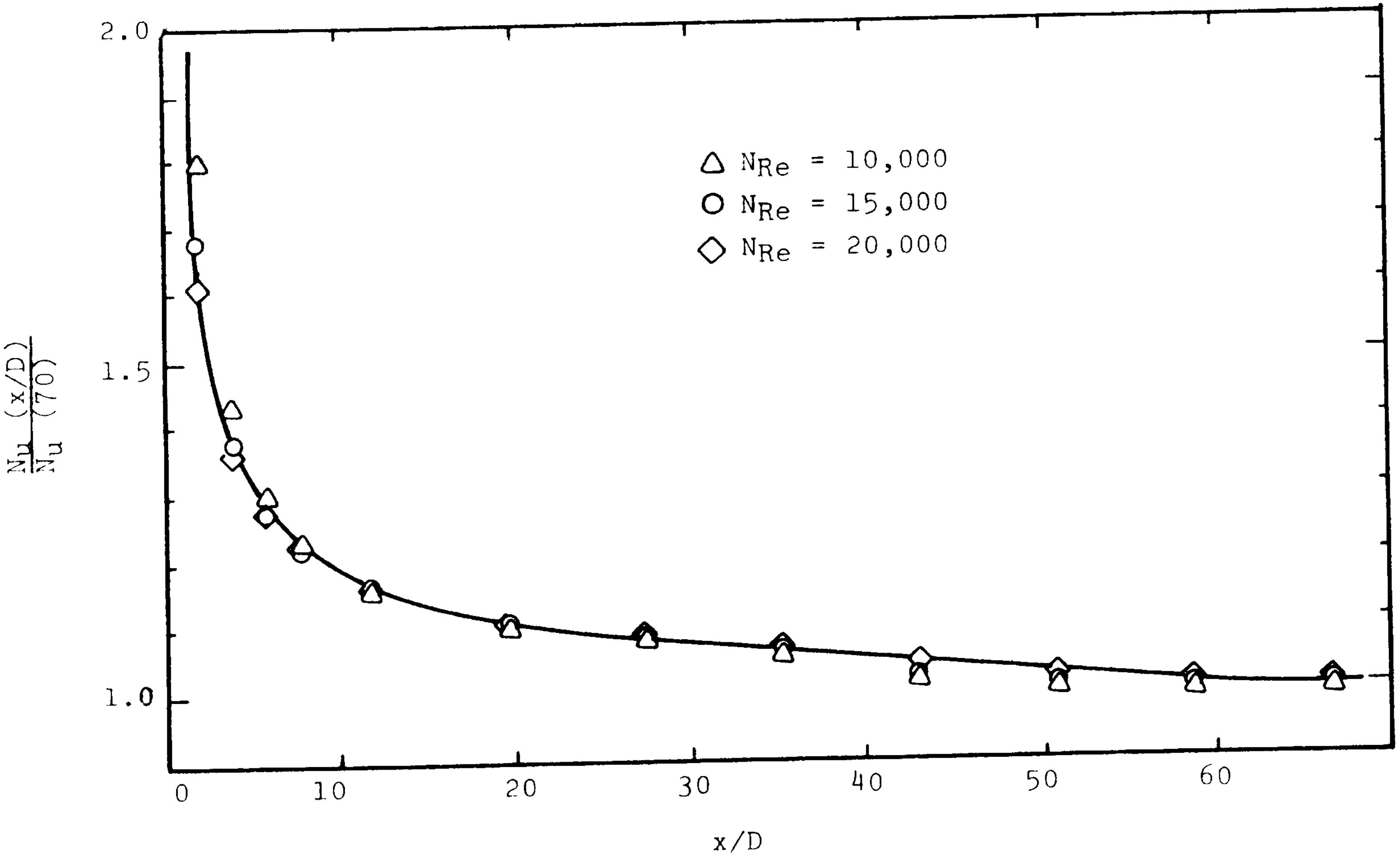
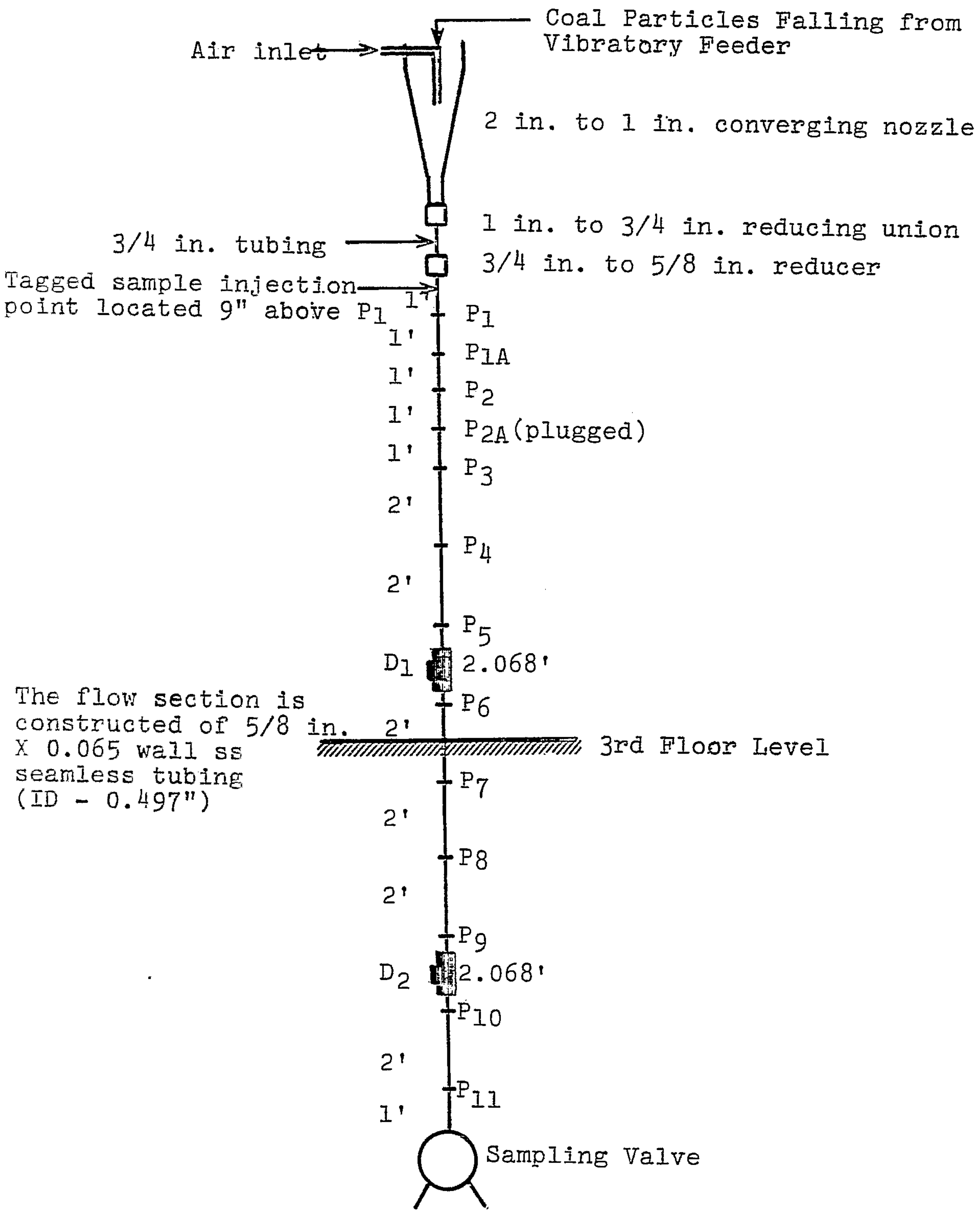


Figure 3. Development of Local Nusselt Number Ratio.





The flow section is constructed of 5/8 in. X 0.065 wall ss seamless tubing (ID - 0.497")

Photomultiplier Tube Detectors D_1, D_2
Pressure Taps P_1, P_{1A}, P_2..., P_{11}

Figure 4. Flow System Diagram.

Figure 5. Average Friction Factor for All Pressure Taps With Only Air Flow (Air Alone).

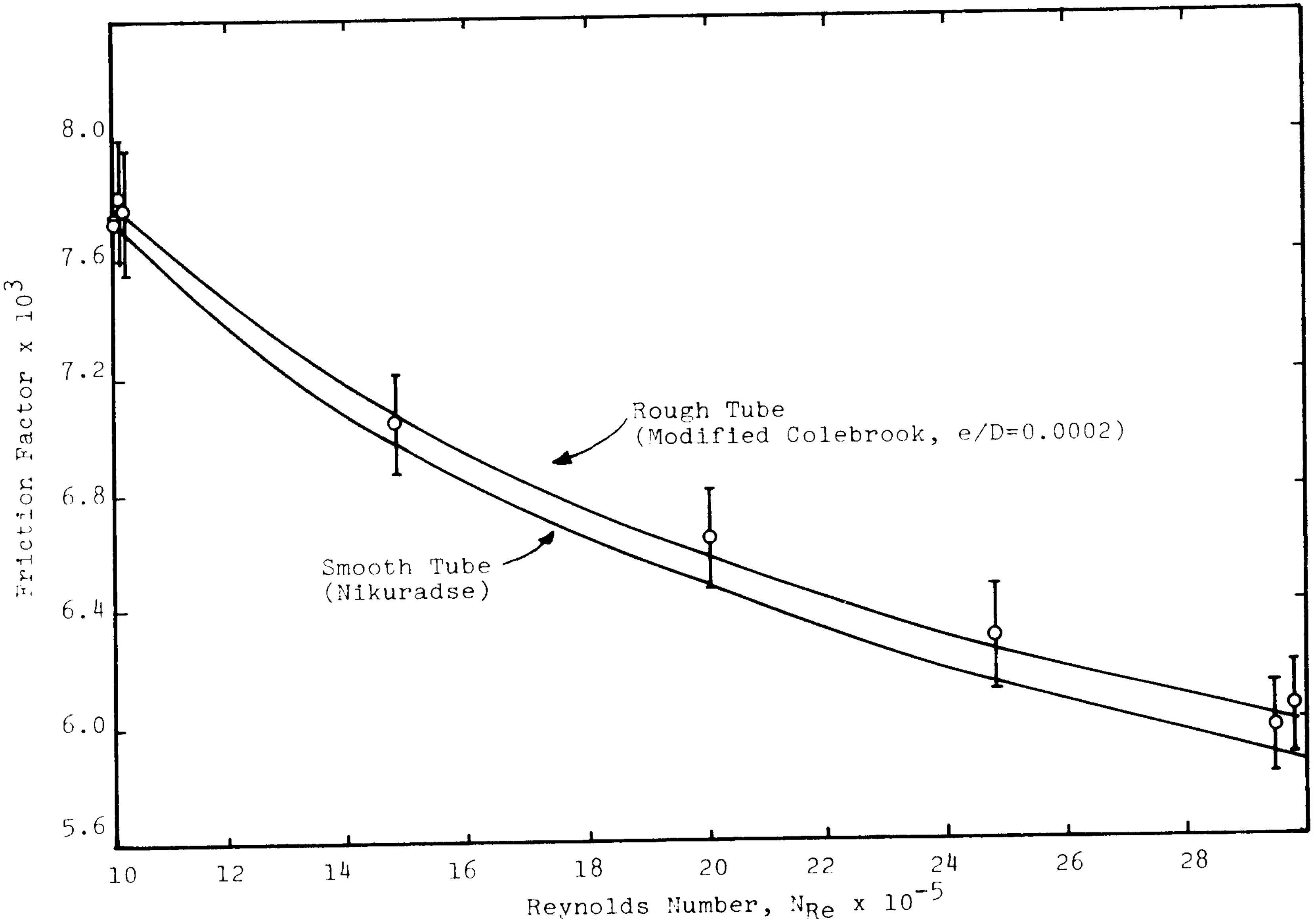
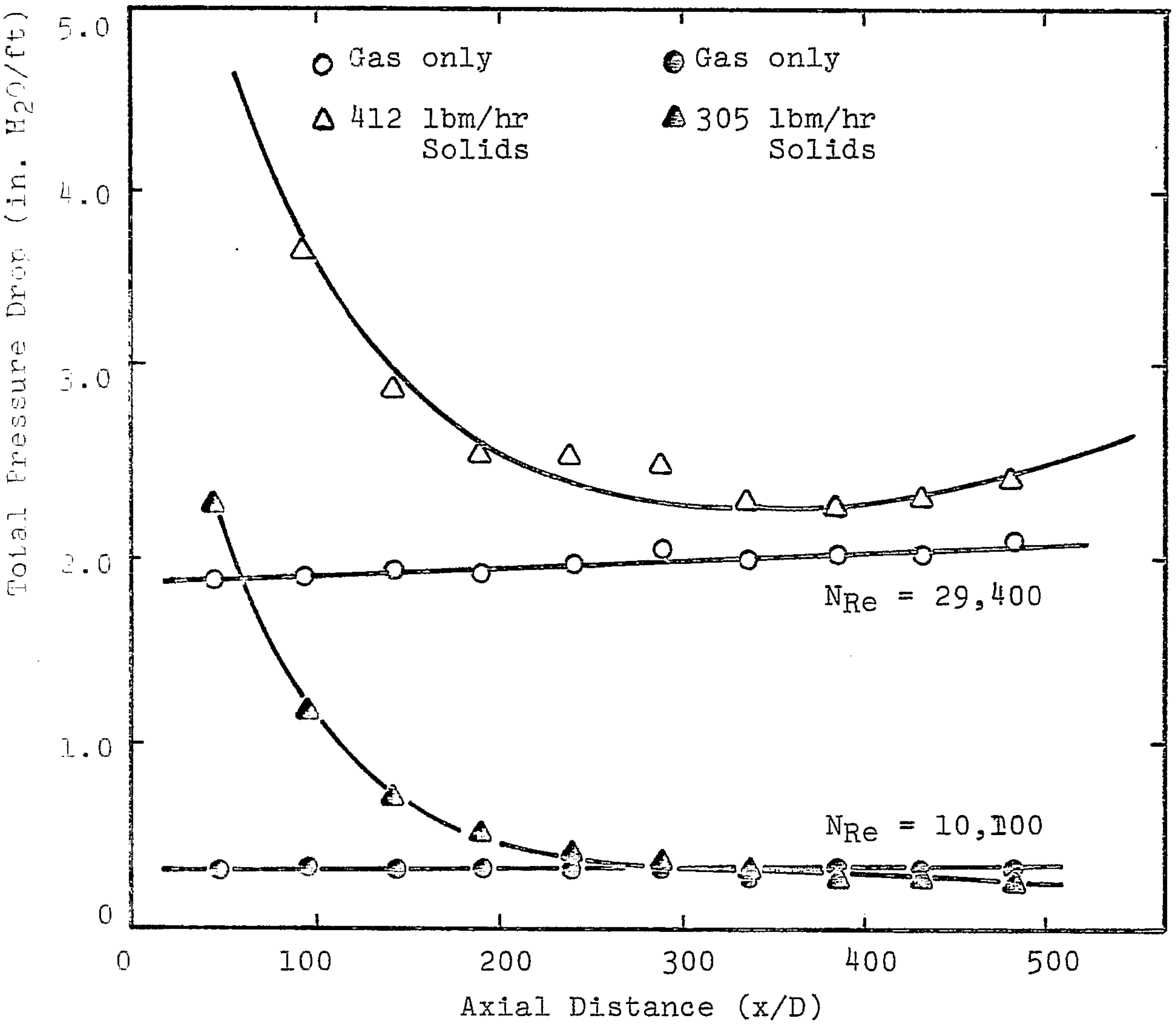


Figure 6. Total Pressure Drop (Two-Phase) as a Function of Axial Distance.



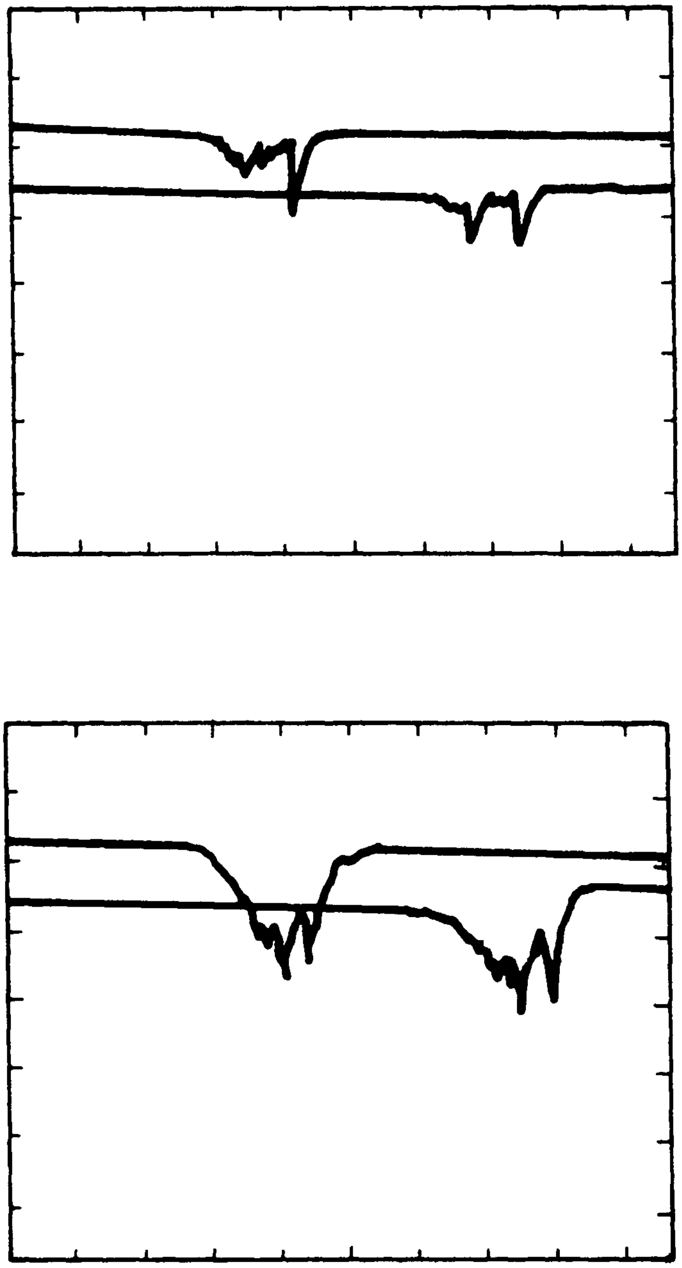


Figure 7. Typical Photographs of the Oscilloscope Trace of Outputs from Detectors D1 and D2.

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 on coal hydrogenation. The existing hydrogenation equipment from ERDA Project FE (49-18) - 1200 is being used. The reaction vessel consists of a series of coiled tubes, each approximately 20 feet long. The reaction zone consists of a preheat and a reactor section. The preheat section contains two coiled tubes in series containing 44 feet of 3/16 inch ID tubing. The reactor section is in series with the preheat section and contains three tubes with a total length of 64 feet of 1/4 inch ID tubing.

The residence time of the coal in the reaction area is of major importance. For this reason a magnetic detection device has been developed. Using this device, iron powder may be detected by a coil of copper wire which is placed inside the reactor 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 residence time measurement will be used to help determine reactor stability or resistance to plugging with respect to the coal particle size, gas velocity, temperature and percent of catalyst applied.

With a continuous feed of coal the effect of residence time on coal conversion will be studied. This study will also include an examination of variables such as coal particle size, catalyst percentage, temperature and pressure.

Project Status

The data presented in Figure 1 of the previous report was reviewed and interpreted again. The figure showed the percent conversion vs. residence time for three particle size ranges. The residence time measurement was taken as peak to peak. Typical residence time information is shown in Figure 1 of this report. In this example peak to peak residence time is indicated as 57 sec. However, the residence time based on half the total area under the curve is indicated as 64 sec.

The curve of Figure 1 was obtained by use of the residence time measurement device developed in this laboratory.[1] Powdered iron as tracer was detected at two points, i.e., at the beginning of the preheater and at the end of the reactor, by an induced alternating magnetic field around the stream of coal and hydrogen. As the iron passed through, the frequency of this alternating magnetic field changed and was electronically processed to yield the voltage output (Figure 1).

There are some difficulties in determining the actual coal residence time from this measurement. The vapor residence time is not indicated by the iron, although, the residence time of the hydrogen is from 1 to 2 sec. The coal vapors produced tend to move with the hydrogen to the condensers. The vapor residence times are less than that of the coal residues depending on when the vapors are produced. Generally, these vapors constitute 60 % or more of the original mass of the feed. Since the iron remains with the coal residue, the values reported are based on the coal residue residence times. These residence times are therefore longer than the average residence time of the coal mass.

In spite of the above problem, this two phase system does have some advantages. As the vapors are evolved and are rapidly removed from the reactor, they have less opportunity to react with the residues and hydrogen. This decreases hydrogen consumption and increases the effectiveness of the reactor.

The residence time based on 1/2 of the total area (Figure 1) is significant. This probably represents what the average mass residence time would be if the vapors were transported at the same rate as the residues. Data is evaluated on this basis and plotted in Figure 2. Residence times on this basis are longer than those in Figure 1 of the previous report. Also some of the scatter has disappeared and some data points were eliminated because determination of the area of the curve was not possible. This was usually due to a changing base line.

Figure 3 shows the results of plotting points taken from Figure 2 at various conversion levels. A linear relationship is noted when particle diameter to the 2.5 power is plotted vs. the average residence time. If the surface area is based on spherical particles, it will be proportional to the diameter squared. However, other powers of the diameter may be related to the surface area in nonuniform particles. Similarly, the volume of a coal particle is not necessarily related to the cube of the particle diameter. The actual significance of the data in Figure 3 has not yet been determined.

Future Work

A high pressure Thermal Gravimetric Analysis (TGA) apparatus is now being set up. This will permit more rapid gathering of kinetic data with respect to coal hydrogenation in the presence of various metal salt catalysts.

Reference

1. W.H. Wiser *et al.*, ERDA Contract No. E(49-18) - 2006 Quarterly Progress Report, Salt Lake City, Utah, Oct-Dec 1975.

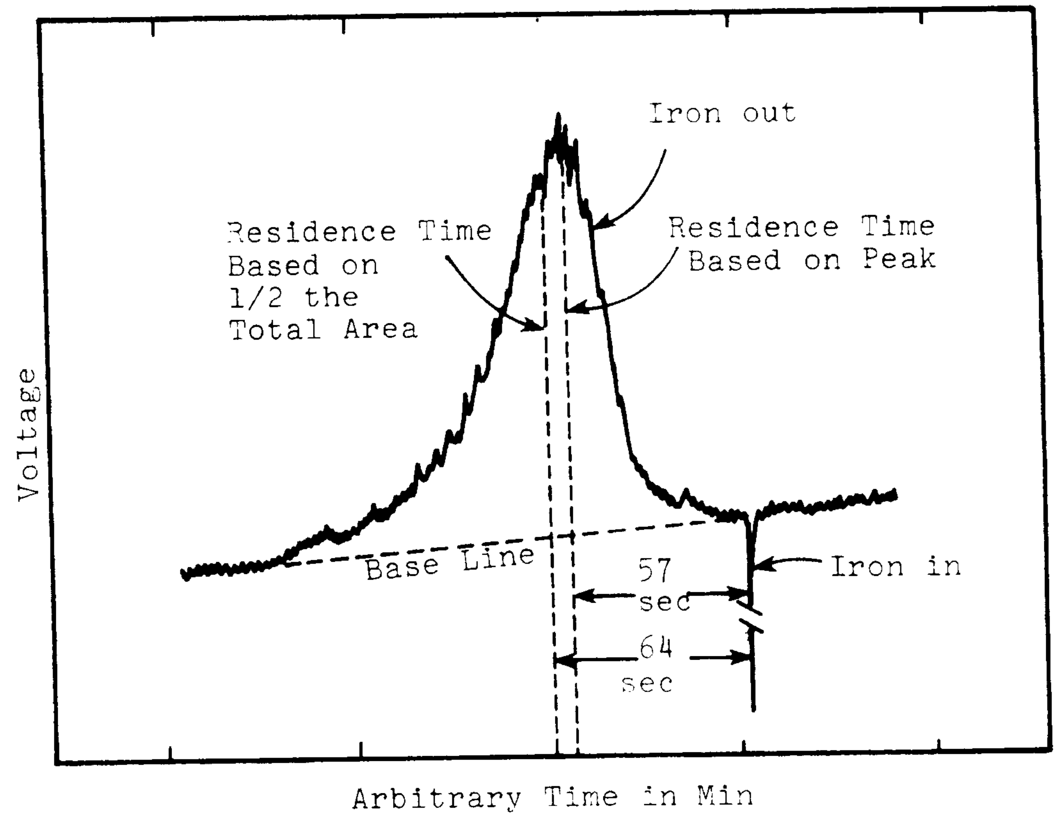


Figure 1. Typical Residence Time Information.

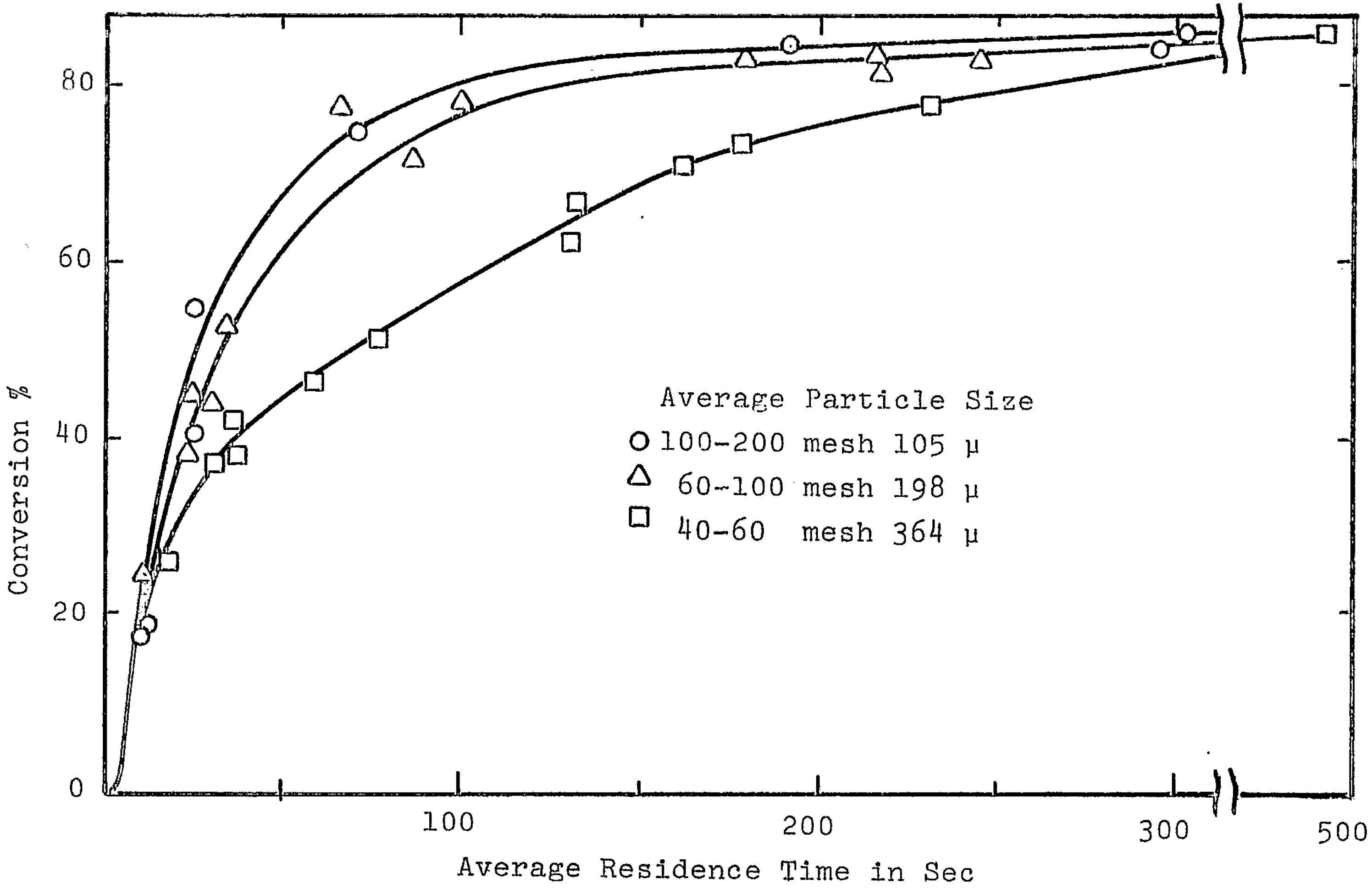


Figure 2. Average Residence Time vs. Conversion of Clear Creek, Utah Coal to Liquids and Gases in the Coiled Tube Reactor. Pressure - 1800 psig H_2, Temperature - 920°F.

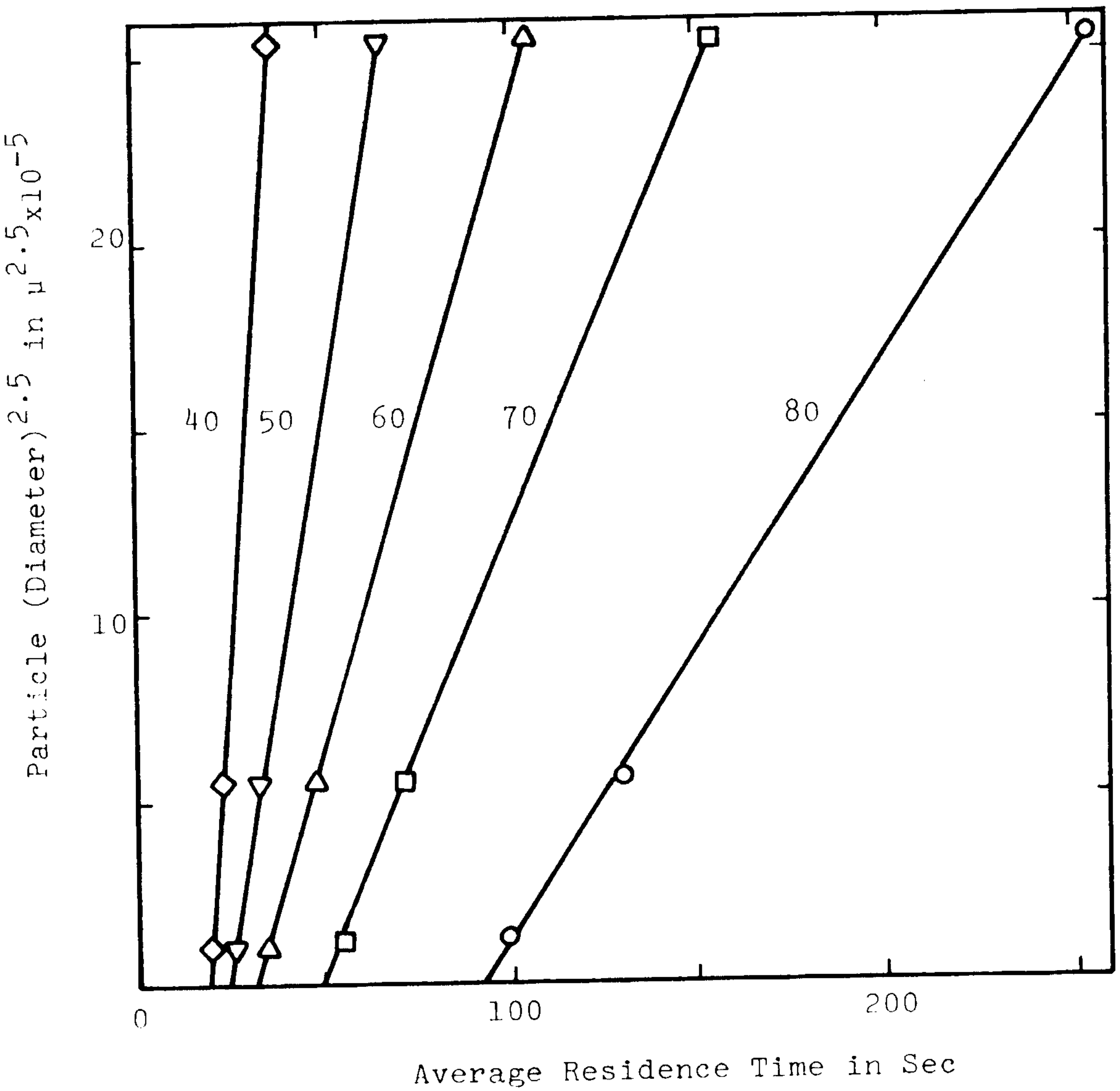


Figure 3. The Relation Between Coal Residence Time and Particle Diameter to the 2.5 Power is Nearly Linear. The numbers on the Lines Indicate the Percent Conversion.

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

A coal derived asphaltene sample was prepared for separation using GPC with column packings of polystyrene, S-X1 and S-X2. Once dried, a 0.6979 g sample was introduced into the separation system. The conditions and results are summarized in Table 1 and Figure 1.

A sample of coal derived asphaltene was prepared for dehydrogenation.[1] Conditions of this run are summarized in Table 2 and are similar to the previous runs, except that the gas samples to be analyzed were taken in stream and analyzed at close time intervals throughout the first portion of the run. The gas constituents were separated using a Hewlett Packard Model 5180 GC and a molecular sieve column at 100°C isothermal. The gas was about 95% hydrogen.

Future Work

A second coal asphaltene will be separated using GPC and the resulting elution curve used to varify previous results. The dehydrogenated asphaltene will be separated using GPC and compared to the original coal asphaltene elution curves. If structural differences are evident, further characterization of products will follow using NMR and GC-MS studies.

The acid-base nature of coal asphaltenes will also be studied by dissolving the asphaltenes in toluene and passing dry HCl gas through the solution. The products of this reaction will be studied using the same scheme as the dehydrogenation products previously mentioned.

References

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

Table 1.

GPC of Coal Asphaltene

Solvent	Benzene-methanol solution, 5%
Column Packings	Column 1, styrene-dioinylbenzene copolymer S-X2 Column 2, styrene-dioinylbenzene copolymer S-X1
Column Length (packed bead)	72 cm
Flow Rate	1.07 ml/min
Inlet Pressure	180 psi
Aliquot Size	11.5 ml

Table 2.

Dehydrogenation of Asphaltene

	Run 3
Sample Size	3.2678
Phenanthridine, g (vehicle)	2.5681
Catalyst, g (1% Pd on $CaCO_3$)	1.3019
Reaction Temp, °C	353.0
Reflux Time, hr	24
Vol gas evolved, cc	233.0

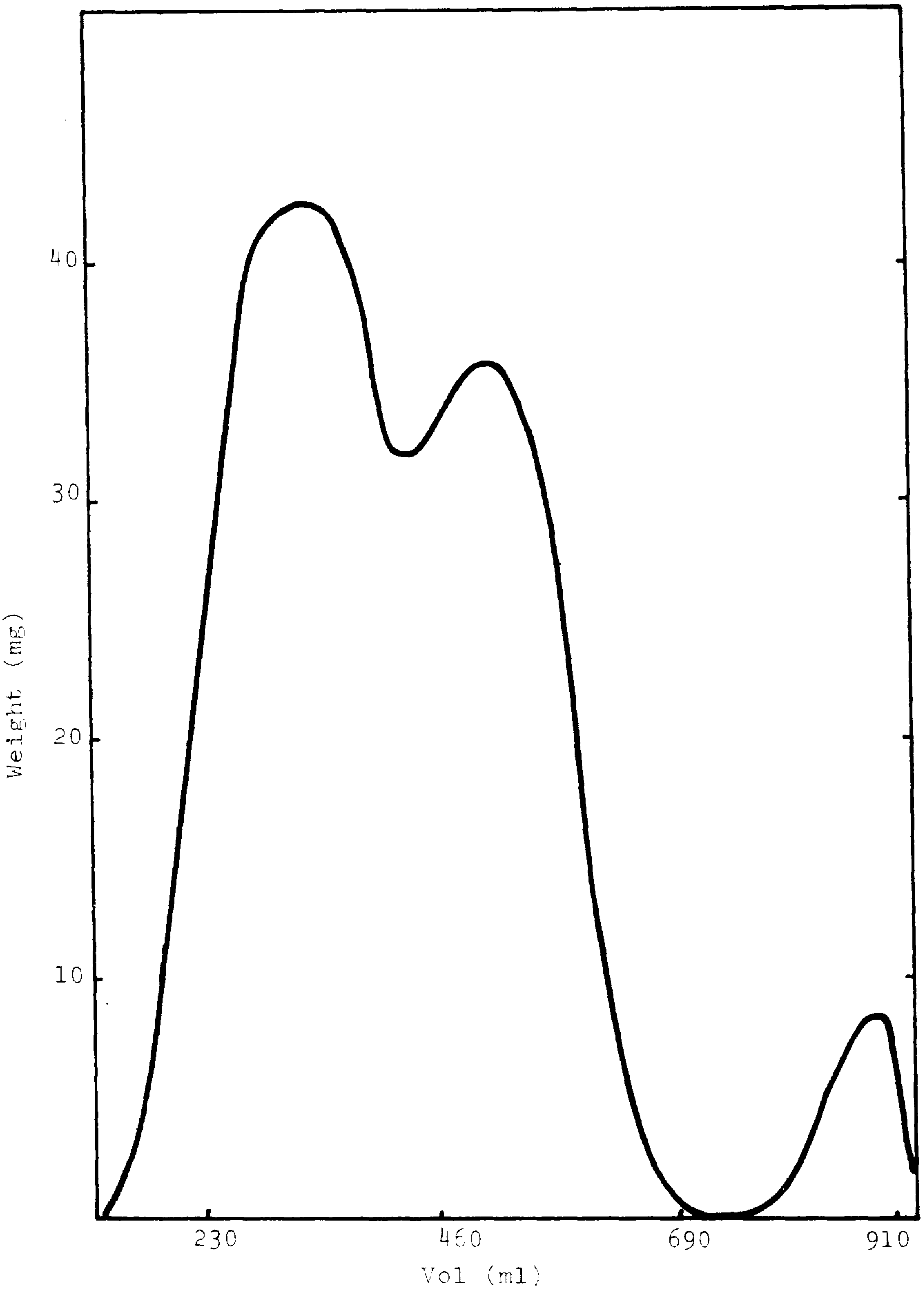


Figure 1. Elution Curve of Coal Asphaltene.

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 fractions 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° (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.)

A general analytical scheme for the characterization of light, coal-derived liquid mixtures is now being developed.

Project Status

A good separation of the ambient-80°C (A-80) SB fraction of coal liquids can be obtained on a carbopack C/0.19% picric acid GC column.[1] This sample has been analyzed on a GC-MS instrument at the Flammability Research Center at the University of Utah, and the results are shown in Table 1. The peak numbers in Table 1 are keyed to those given in the typical gas chromatogram of the A-80 fraction shown in Figure 1. The molecular weights and therefore the empirical formulas of the compounds in question were given by the GC-MS analysis, but many of the specific isomers were not identified. A number of unknown isomers have now been identified by peak enhancement (addition of known compounds to the total coal liquid sample, and observation of the GC peaks that increase in size). The results of this work are also shown in Table 1.

Carbowax 20 M can retard the GC elution of aromatics and alkenes relative to saturates. To determine whether the identification of GC peaks in the A-80 fraction would be facilitated by separating the total sample into the two simpler fractions and to determine the nature of the separation which Carbowax 20 M would effect, the A-80 fraction has been cut in half on a Carbowax 20 M GC prep column, i.e., the hydrocarbon mixture was passed through the column and the peaks in the first half of the eluent were collected in one receiver,,while those peaks eluting thereafter were collected in a second receiver. The results of this work are shown in Table 2. There data indicate that, in general, saturates elute before unsaturates of the same carbon number. There appears to be no great advantage to half-fractionation with respect to the A-80 coal fraction, but the procedure could have considerable merit depending on the specific nature of the mixture being separated.

The analysis of the light hydrocarbons formed in the hydrogenation of five different Utah coals has previously been reported by GC retention time only.[2] The GC calibrations have now been done to identify the compounds in the mixture and are given in Table 3. The peak numbers referred to in Table 3 are those given in Figure 1.

Future Work

The reproducibility of the SB distillation and GC analysis of the A-80 fraction will be assessed, and some additional samples will be run.

References

1. R.R. Beishline and W.H. Wiser, ERDA Contract No. E(49-18)-2006, Quarterly Progress Report, Salt Lake City, Utah Jan-Mar 1977.

2. *ibid.*, July-Sept, 1977.

Table 1. Compounds in the Ambient to 80°C Coal Liquid Fraction.

Peak Number	Molecular Weight (GC-MS)	Empirical Formula (GC-MS)	Identity	
			GC-MS Analysis Method	Peak Enhancement Method
1	70	C_5H_{10}	pentene[a]	
2	68	C_5H_8		
3	72	C_5H_{12}	pentane[a]	
				1-pentene[c]
4	84	C_6H_{12}	hexene[a]	
5	84	C_6H_{12}		Cyclohexane, methylcyclopentane
6	84	C_6H_{12}	ethylcyclobutane	
				2,3-dimethylbutane[c]
7	82	C_6H_{10}		1-methylcyclopentene
				Cyclohexene[c]
8	86	C_6H_{14}		3-methylpentane
9	82	C_6H_{10}	dimethylbutadiene[a]	
10	82	C_6H_{10}	hexyne[a]	
				2-methyl-1-pentene[c], n-hexane[c]
				2-methylpentane[c]
11	84	C_6H_{12}		trans-2-hexene
12	84	C_6H_{12}		cis-2-hexene
13	86	C_6H_{14}	hexane[a]	
				1-hexene
14	86	C_6H_{14}	hexane[a]	
15	78	C_6H_6	benzene	
16	98	C_7H_{14}	dimethylcyclopentane[a]	
17	98	C_7H_{14}	dimethylcyclopentane[a]	
				methylcyclohexane[c]
18	96	C_7H_{12}	heptyne[a] or heptadiene[a]	2,4-dimethylpentane[b]
19	96	C_7H_{12}	heptyne[a] or heptadiene[a]	
20	100	C_7H_{16}		3-methylhexane
21	100	C_7H_{16}	methylhexane[a]	
				2-heptene[c,d]
				1-heptene[c]
22	98	C_7H_{14}		trans-3-heptene
				toluene[c]
23	100	C_7H_{16}		n-hpetane

[a] specific isomer unknown

[b] eluted on top of sample peak but was not present in original sample

[c] eluted between peaks in sample

Table 2. Half-Fractionation of the Ambient to 80°C Coal Fraction by Preparative GC-Carbowax 20M Column.

First Fraction

Peak Number	Molecular Weight (GC-MS)	Empirical Formula (GC-MS)	Identity	
			GC-MS Analysis	Peak Enhancement Method
1	70	C_5H_{10}		
2[b]	68	C_5H_8		
3	72	C_5H_{12}		
4	84	C_6H_{12}		
6	84	C_6H_{12}	ethylcyclobutane	
11	84	C_6H_{12}		trans-2-hexene
12	84	C_6H_{12}		cis-2-hexene
13	86	C_6H_{14}	hexane[a]	
14	86	C_6H_{14}	hexane[a]	
20	100	C_7H_{16}		3-methylhexane

Second Fraction

5	84	C_6H_{12}		cyclohexane, methylcyclopentane
7	82	C_6H_{10}		1-methylcyclopentene
8	86	C_6H_{14}		3-methylpentane
9	82	C_6H_{10}	dimethylbutadiene	
10	82	C_6H_{10}	hexyne[a]	
15	78	C_6H_6	benzene	benzene
16	98	C_7H_{14}	dimethylcyclopentane[a]	
17	98	C_7H_{14}	dimethylcyclopentane[a]	
18	96	C_7H_{12}	heptyne[a] or heptadiene[a]	
19	96	C_7H_{12}	heptyne[a] or heptadiene[a]	

[a] specific isomer unknown

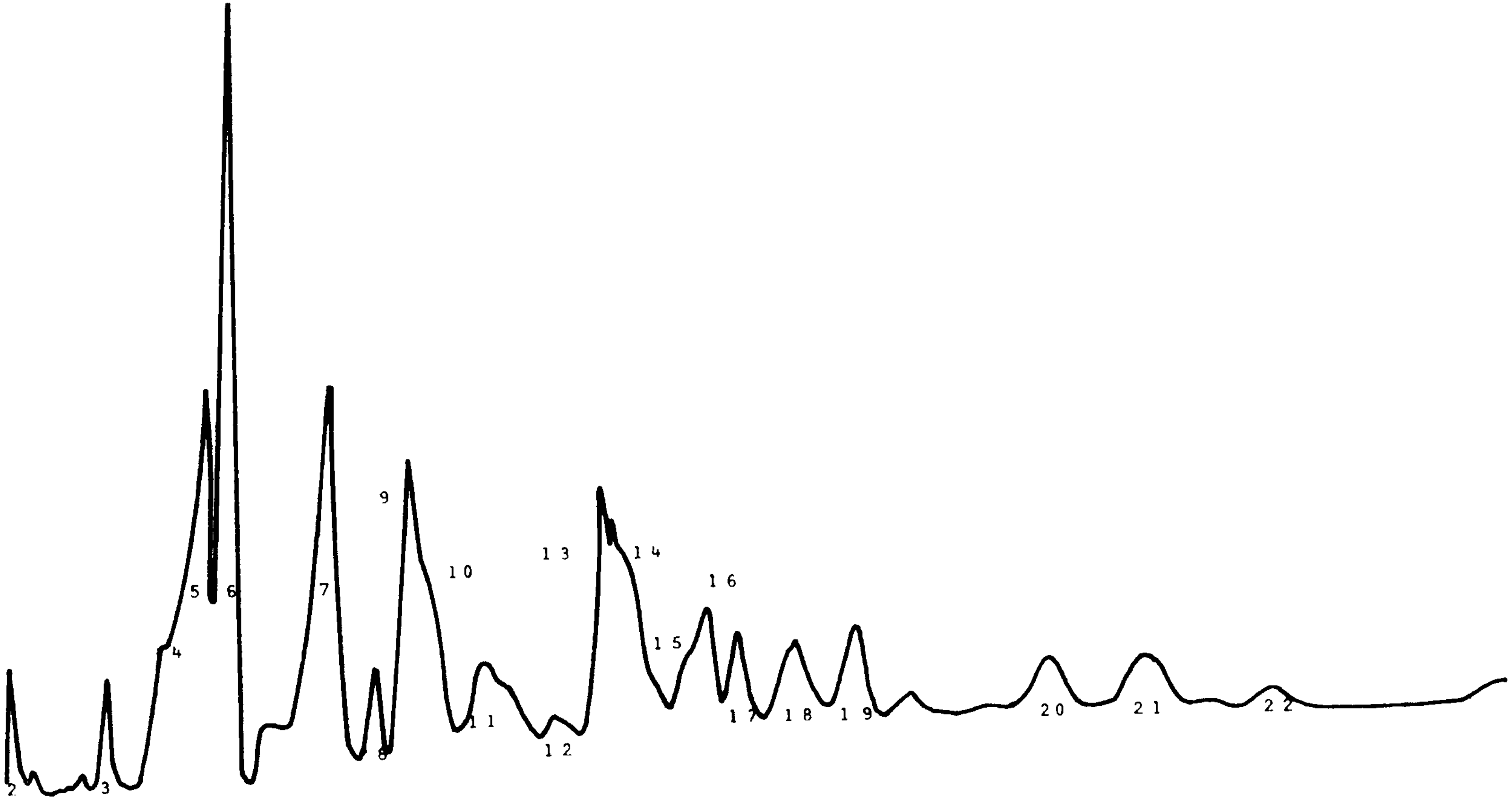
[b] appeared in both fractions

able 3. Compounds in Ambient to 80°C Coal Liquid Fractions of Some Utah Coals.

Peak umber	AREA PERCENT Swisher #4	Braztah #3	Consolidated Coal #6	Beehive-Emery Co.	Swisher #2	Identity (GC-MS and Peak Enhancement Method)
1	3.595	4.322	1.431	2.317	2.304	pentene^a
2	1.667	1.791	0.3495	1.003	1.020	$C_5H_8{}^a$
3	5.347	5.341	0.6822	1.476	2.108	pentane^a
4	10.94	11.81	14.05	12.09	7.801	hexene^a
5						cyclohexane, methylcyclopentane
6	16.43	16.78	12.78	15.04	11.96	ethylcyclobutane
7	11.24	10.88	11.31	15.39	9.201	1-methylcyclopentene
8	2.008	2.068	1.288	1.812	1.466	3-methylpentane
9	13.96	12.30	8.298	12.39	11.28	dimethylbutadiene^a
10						hexyne^a
11	2.547	4.445	4.210	5.443	4.604	trans-2-hexene
12	1.491	1.680	1.720	1.320	0.6619	cis-2-hexene
13	8.687	13.30	12.68	10.93	6.286	hexane^a
14						hexane^a
15	--	--	--	1.047	0.8200	benzene
16	6.371	3.092	5.590	4.254	3.410	dimethylcyclopentane^a
17	2.143	1.382	4.794	2.087	6.549	dimethylcyclopentane^a
18	1.722	1.288	2.602	2.969	4.733	heptyne^a or heptadiene^a
19	2.221	1.980	4.898	3.811	7.397	heptyne^a or heptadiene^a
20	1.381	0.6326	2.178	2.382	2.216	3-methylhexane
21	1.488	0.9104	1.833	2.078	1.234	methylhexane^a
22	--	0.2259	1.087	0.8051	1.267	trans-3-heptene
23	--	1.091	6.868	0.4717	6.515	n-heptane

[a] specific isomer unknown

Figure 1. Gas Chromatogram of the Ambient-80°C Coal Liquid Fraction: Carbopack C/0.19% Picric Acid Column.



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 reaction 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 mechanism shown in Figure 1 is consistent with the experimental results that have been obtained.

Project Status

The 300 MHz ^1H NMR spectrum of dimer 1 has been obtained (Dr. Don K. Dalling, University of Utah) and is summarized in Table 1. The 300 MHz instrument was able to resolve several multiplets that are merged in the 60 MHz spectrum, but the specific assignments of many of the peaks cannot be made without additional work (^{13}C NMR and deuteration studies). Since the structure of dimer 1 has been defined well enough to distinguish it from all other $C_{20}H_{20}$ structural isomers, no further NMR studies of dimer 1 are contemplated.

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

$$\text{1,2-DHN} \xrightarrow{k_1} \text{naphthalene} + H_2$$

$$2(\text{1,2-DHN}) \xrightarrow{k_2} \text{tetralin} + \text{naphthalene}$$

To test this hypothesis, a series of reactions have been carried out in small calibrated sealed glass tubes, each containing a different initial concentration of 1,2-DHN. The tubes were heated at 390°C for approximately thirty minutes, then cooled and opened, and their contents quantitatively analyzed by GC.

The rate expression for proposed simultaneous first and second order reactions is

$$-d[1,2\text{-DHN}]/dt = k_1[1,2\text{-DHN}] + k_2[1,2\text{-DHN}]^2$$

This expression was integrated and the antilog of the integrated equation was taken and algebraically rearranged to give

$$1/[1,2\text{-DHN}] = e^{k_1 t}/[1,2\text{-DHN}]_0 + k_2/k_1(e^{k_1 t}-1)$$

Since the tubes were heated for the same length of time, t is constant. A plot of $1/[1,2\text{-DHN}]$ vs. $1/[1,2\text{-DHN}]_0$ should give a straight line with a slope of $e^{k_1 t}$ and an intercept of $k_2/k_1(e^{k_1 t}-1)$. After the value of k_1 is obtained from the slope, k_2 can be obtained from the intercept.

Surface reactions may be involved. Therefore, one of the tubes was half filled with small glass beads to evaluate the effect of surface area on the reaction rate.

The results of the tube reactions are shown in Table 2, and the rate plot of the data is given in Figure 2.

The rate plot is precisely linear, furnishing evidence for the proposed simultaneous first and second order reactions. The data point for the tube containing the glass beads (tube 3, Table 2) falls on the line with the other data, indicating that the rate of the reaction is not a function of the surface area.

The data in Table 2 indicate that the percent reaction in a given time increases as the initial concentration increases. This eliminates the possibility of a simple first order reaction, since for a first order reaction, the percent reaction in a given time is independent of the initial concentration. The possibility of a simple second order reaction is also eliminated, since a plot of $1/[\ ]$ vs. $1/[\ ]_0$ at constant t must give a slope of 1.0 for a simple second order reaction. The slope of the rate plot in Figure 2, however, is 1.22.

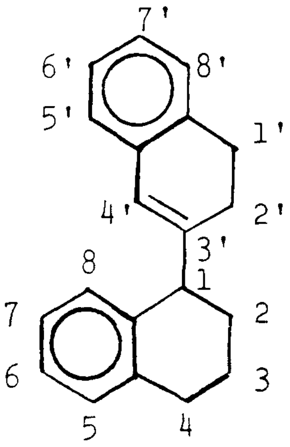
Future Work

The synthesis of 2-methyl indene will be completed. The need for 2-methyl indene was discussed in the previous report. The pyrolysis of 1,2-DHN will be further studied. Activation energies will be obtained, and hydrophenanthrene analogues of 1,2-DHN will be synthesized for studies intended to delineate the scope of these hydrogen transfer reactions.

Table 1.

300 MHz 'H NMR Spectrum of Dimer 1

Chem Shift S, ppm	No. of Protons	Peak Shape[a]	Assignment
7.18	1	d	Aromatic
7.09	6	m	
6.96	1	d	
6.19	1	s	4'
3.68	1	poorly resolved doublet of doublets	1
2.76	4	m	1', 4
2.13	2	m	2,2', 3
1.92	2	m	
1.78	2	m	



[a] s=singlet, d=doublet, m=complex multiplet.

Table 2.

Pyrolysis of 1,2-DHN for 29.23 min at 390°C

Tube	Vol (ml)	Internal Area (cm^2)	$[DHN]_0$ ($m \times 10^2$)	$[DHN]_t$ ($m \times 10^2$)	% Reaction
1	0.576	5.50	5.4	3.5	35
2	0.526	5.56	8.9	5.1	43
3	0.387	8.52	12.0	6.2	48
4	0.557	5.70	13.0	6.5	50

Figure 1. $H_2O + ZnCl_2 \rightleftharpoons H^+ + HOZnCl_2^-$

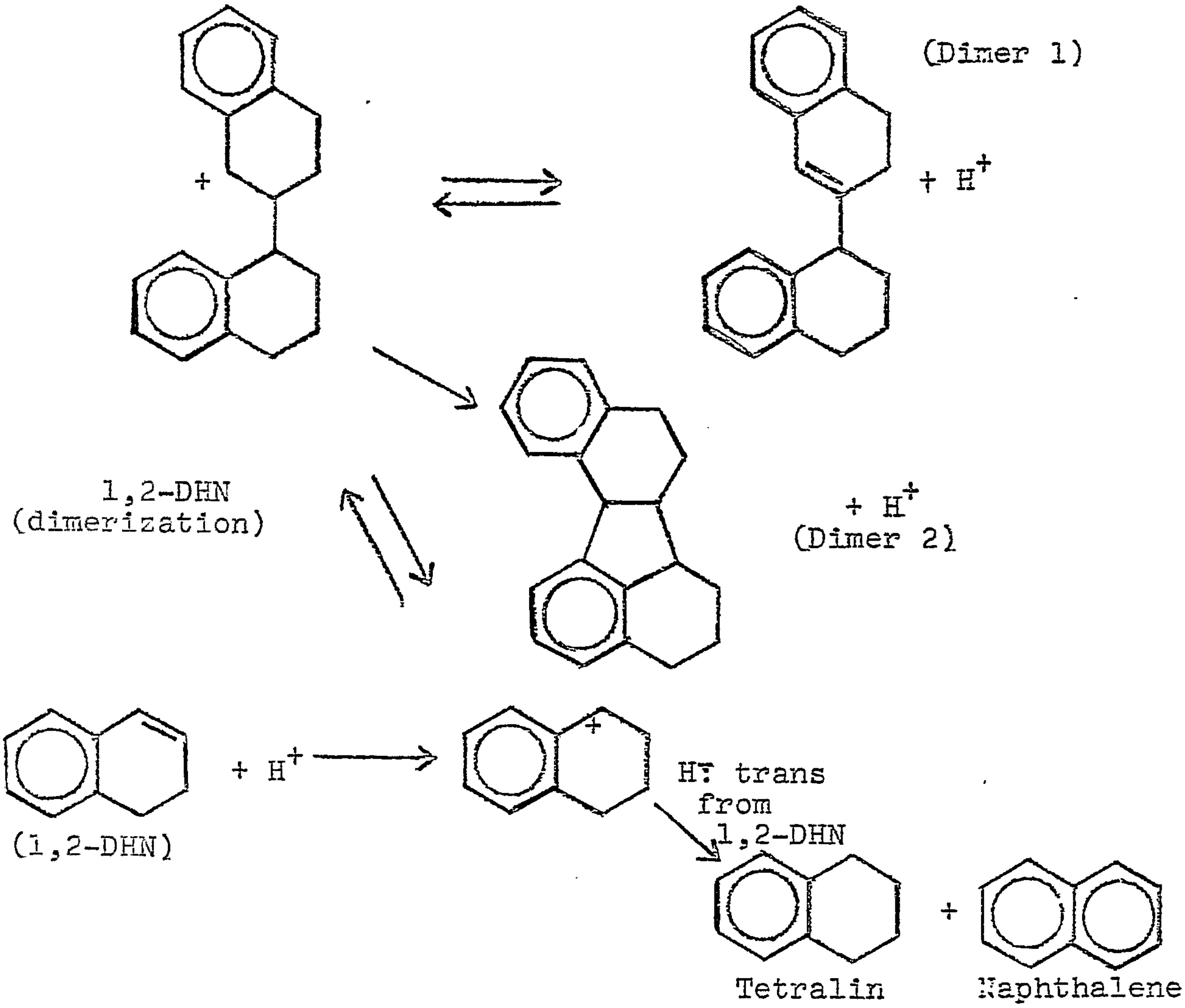
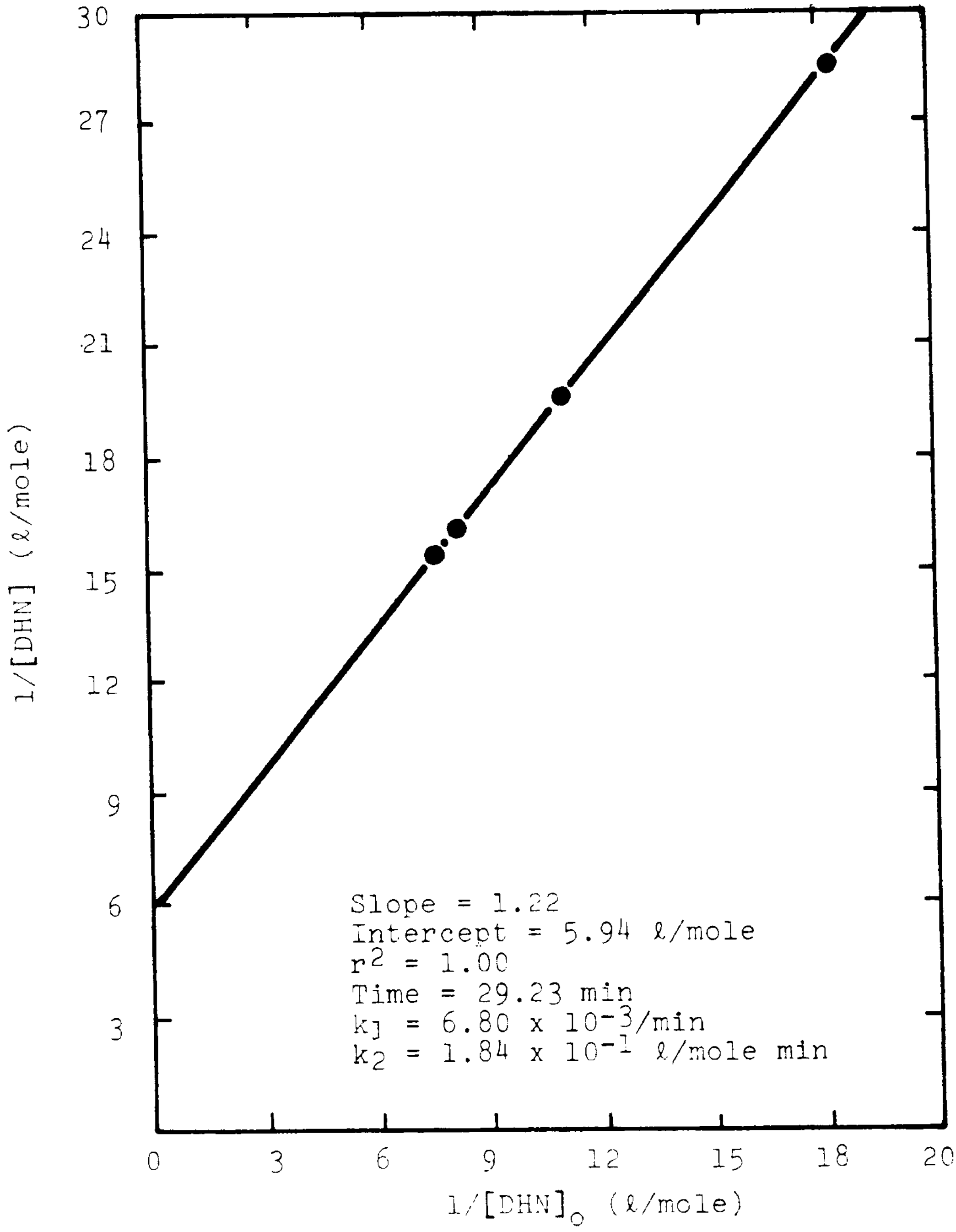


Figure 2. Kinetics of the Pyrolysis of 1,2-DHN at 390°C.



Slope = 1.22
Intercept = 5.94 ℓ/mole
r^2 = 1.00
Time = 29.23 min
k_1 = 6.80 x 10^{-3}/min
k_2 = 1.84 x 10^{-1} ℓ/mole min

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

Faculty Advisor: W.H. Wiser
Graduate Student: Hsiang-Yun Kung

Introduction

In catalytic hydrodesulfurization the rate of diffusion of sulfur-bearing oil molecules from the external surface of the catalyst pellets towards the center is frequently slower than the chemical reaction rate.[1] Consequently, the majority of the molecules are already desulfurized in the outer parts of the pellet before they reach the center, and only part of the internal catalyst surface is effectively used. If the accessibility of the internal surface of catalyst pellets to the reactant molecules could be increased, the allowable space velocity would be higher for the same degree of desulfurization. The most effective method to obtain better utilization of the catalyst internal surface area is to decrease pellet size.

For a continuous flow tubular reactor containing a fixed catalyst bed in which there is plug flow, the following equation holds for a reaction presenting first order kinetics:

$$\ln\frac{C_{in}}{C_{out}} = \ln\frac{1}{1-x} = \frac{k}{S_v}\,\rho_p\eta \qquad (1)$$

$$\text{with } \eta = \frac{1}{h}\left[\frac{1}{\tanh 3h} - \frac{1}{3h}\right] \qquad (2)$$

$$\text{and } h = \frac{R}{3}\sqrt{\frac{k\rho_p}{S_v D_e}} \qquad (3)$$

where

C_{in} and C_{out} = concentration of sulfur in feed and product, respectively

x = fraction of sulfur compounds converted

k = reaction rate constant $\left(\frac{\text{cm}^3 \text{ vol of oil}}{\text{sec g of cat}}\right)$

S_v = liquid space velocity of the oil (vol of oil/unit time and unit vol of catalyst)

S_g = specific surface area of the catalyst

ρ_p = pellet density of catalyst

η = effectiveness factor (factor of catalyst surface effectively used during the reaction)

2R = average pellet diameter

D_e = effective diffusion coefficient of the sulfur compounds inside the pores.

The quantity h defined by Eq (3) is called the Thiele modulus.

If relatively large pellets of an active catalyst are used and if the diffusion of sulfur compounds through the pores towards the center of the pellet is relatively slow, the reaction is strongly diffusion limited and the catalyst is used inefficiently. Therefore, the Thiele modulus h is high and η is low. If h is large, **Eq** (2) tends to

$$\eta = \frac{1}{h} = \frac{3}{R}\sqrt{\frac{S_v D_e}{k \rho_p}} \qquad (4)$$

and Eq (1) tends to

$$\ln \frac{C_{in}}{C_{out}} = \ln \frac{1}{1-x} = \frac{3}{R}\sqrt{\frac{D_e k \rho_p}{S_v}} \qquad (5)$$

This expression shows that in the case of diffusion limited kinetics the conversion strongly depends on the pellet diameter and less strongly on the diffusion coefficient.

The objective of this project is the study of diffusional effects of hydrodesulfurization of (1) straight run gas oil and (2) coal derived oils, with various sizes of catalyst in a vapor phase fluidized bed reactor.

Project Status

The equipment has been ordered and is being assembled as it arrives. The gas oil feedstock was obtained from the Salt Lake Refinery of the American Oil Compnny. The properties of the oil are

API Gravity, at 60°F	29.3
Sulfur, percent by weight	1.6

ASTM D-86 Distillation

Distillation, vol %	Temp, °C
IBP	272
10	330
30	350
50	367
70	376
90	380

Residua and Loss

90

Since it is necessary to maintain vaporization 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.

Future Work

The equipment will be assembled as the components arrive. Thereafter, testing and experimental runs will proceed.

Reference

1. J.W. Le Nobel and J.H. Choufoer, Proc. Fifth World Petrol. Congr., 1959, Section III, Paper 18.

V Conclusions

Twelve projects were active during this quarter. Projects A-6 and A-9 have not been initiated. Project B-3 has been completed. The student on Project B-1 has completed his work and is writing his thesis. A new student will continue this work. One report on supplemental work is included in this report. Conclusions for each project are included in the individual report.

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