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STUDY OF COAL REACTIVITIES

Final Report for the Period June 1, 1976—September 30, 1979

By

John C. Angus
Nelson C. Gardner
Frank J. Kocjancic, Jr.
Sunggyu Lee

Joseph J. Leto
Steven M. Shine
Chi-Kang Tien
Robert J. Williams

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Date Published

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Case Western Reserve University
Department of Chemical Engineering
Cleveland, Ohio

U. S. DEPARTMENT OF ENERGY

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APPLIED RESEARCH AND EVALUATION OF
PROCESS CONCEPTS FOR LIQUEFACTION
AND GASIFICATION OF WESTERN COALS

FINAL REPORT

CONTRACT PERIOD 1 JUNE 1975 - 31 JULY 1980

WENDELL H. WISER
PRINCIPAL INVESTIGATOR

DEPARTMENT OF MINING AND FUELS
ENGINEERING
UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH 84112

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Catalytic Gasification of Coal to High-BTU Gas

Faculty Advisor: W.H. Wiser

Introduction

Technologies for the conversion of coal to high-BTU gas are usually initiated by reacting the coal with steam and oxygen in the temperature range of 950°C or higher. Direct reaction of coal with steam is practiced because water must ultimately be the primary source of hydrogen for such processes. The steam-coal reaction is highly endothermic and requires temperatures of the order of 950°C or higher if the reaction is to proceed at a reasonable rate without an externally applied catalyst. The molecular oxygen is introduced to react with carbon in the coal to produce the energy necessary to achieve and maintain the temperature for the reaction.

The carbon monoxide thus produced from the oxygen and from the steam is to be hydrogenated to produce principally methane. The ratio of hydrogen to carbon monoxide must be greatly increased to accomplish this. Thermodynamic considerations demand that the reaction of carbon monoxide and more steam to produce molecular hydrogen must be conducted at temperatures of 450°C or lower, if a hydrogen-carbon monoxide ratio of 3 or greater is to be achieved. This reaction must proceed with the help of a catalyst. Following cleaning of this gas to remove H_2S , CO_2 and other impurities, the carbon monoxide is catalytically hydrogenated in the temperature range of 450°C to produce methane. The hydrogenation reaction is exothermic.

In a system such as this the introduction of molecular oxygen to react with carbon to achieve the necessary elevated temperatures for the steam-carbon reaction represents a severe energy penalty to the process. As much as $1/3$ of the heating value of the coal, or perhaps more, is lost to the process through this sequence of events. It has been noted, however, that the overall process of converting coal to methane approaches thermal neutrality, if the entire process could be achieved at temperatures in the range of the methanation reaction. Inasmuch as thermodynamics demand that the methanation reaction must occur at temperatures below 500°C if high methane yields are anticipated, it would be attractive to conduct the full process at temperatures below 500°C and do it in a single reactor to gain the maximum benefit from the energy of the methanation reaction and to most nearly approach thermal neutrality in the process. This work is intended to investigate the various parameters and factors, including commercially available catalysts, which might make such a process possible.

Experimental

All of the available catalyst combinations considered to be practical for hydrogenating coal to a gaseous product high in methane are solids in the temperature range of the reactions. It therefore is necessary to disperse the coal in a solvent to provide for intimate contact between the coal material which is to be hydrocracked and hydrogenated and the internal pore surface of the catalyst. It therefore was decided initially to dissolve the coal in a hydrogen donor solvent. This was performed in the first stage of a two-stage system. Tetralin was used as the solvent.

Two catalysts were tested in the first stage, namely, sulfided Ni-W/SiO₂-Al₂O₃ and sulfided Ni-Mo/Al₂O₃. This portion of the work was conducted in a batch autoclave with temperatures of the order of 480°C and pressures of the order of 2000 psi. The liquids produced in this stage were passed to a second hydrogasification stage which was a continuous reactor with a fixed catalyst bed of sulfided Ni-W/SiO₂-Al₂O₃ or sulfided Ni-Mo/Al₂O₃. The temperatures in the hydrogasification stage were of the order of 600°C with pressures of about 1750 psi.

Results and Discussion

The Ni-Mo/Al₂O₃ catalyst yielded the highest conversions to liquids and gases in the first (hydrosolvation) stage. This may be due in part to the larger pore diameter of the Ni-Mo/Al₂O₃ (114 Å) compared with the Ni-W/SiO₂-Al₂O₃ (65 Å). Yields of gases and light oils increased with temperature while heavy oil yield increased then decreased above 420°C due to cracking. This is illustrated in Figure 1. Yields of all conversion products increased with pressure, as illustrated in Figure 2. A typical yield from the hydrosolvation process, using a sulfided nickel-moly catalyst supported on alumina with a temperature of 480°C and hydrogen pressure of 2000 psi, was: 22% gases, 63% liquids and 15% char.

The liquids were then passed through the hydrogasification stage with a catalyst of nickel-moly sulfide on alumina at a temperature of 600°C and hydrogen pressure of 1750 psi. Yields of gases increased while liquid yields decreased with increasing temperature in the second stage, as shown in Figure 3. A high ratio of methane to other hydrocarbon gases was achieved and this ratio increased with temperature as illustrated in Figure 4. A typical yield from the hydrogasification process was: 40% gases, 19% liquids and 4% char based upon the 63% liquids introduced to the hydrogasification stage. When the gases and solids were combined with those from the first or hydrosolvation stage and the liquids from the second or hydrogasification stage were fractionated into three fractions, a typical overall yield of the two processes combined was: gases (C₁-C₄) 62% (48 of the 62 being methane), gasoline (C₅ to 200°C) 10%, middle oil (200°C to 300°C) 7%, heavy oil (> 300°C) 2%, and char 19%. These results are summarized in Table 1.

When it was demonstrated that the coal gasification operation with maximum temperature of the order of 600°C could be conducted in two stages with the same catalyst in each of the two stages, it appeared possible to attain results similar to those obtained in the two stages by combining the operation into a single stage. A flow system with a fixed catalyst bed was constructed to pursue these studies. The coal was slurried in tetralin, a hydrogen donor solvent, for reasons explained above. From consideration of the general concepts of the chemical structure of coal as understood today, it was concluded that an appropriate and effective catalyst must contain both strong hydrogenation function and strong cracking function. In a bituminous coal approximately 65-75% of the carbon appears as aromatic carbon. An average condensed configuration is about 3 rings per cluster. These aromatic configurations must be hydrogenated, then cracked, with further hydrocracking of the fragments, to maximize the single carbon structure of methane. Catalysts on an alumina and a silica-alumina support were tested to obtain the cracking function. Catalysts containing nickel, combinations of nickel and tungsten, combinations of nickel and molybdenum and these combinations coupled with palladium were tested in various ratios in search of the maximum effectiveness in producing methane from coal.

Typical results from the single stage gasification process, with nickel-moly on alumina as catalyst, a reactor temperature of 500°C and hydrogen pressure of 1000 psi are: gases 41.3%, liquids 39.4%, char 19.3%. The overall conversion to liquids and gases is comparable to the conversion in two stages; however, the liquid yields are higher in the single stage process and the yields of ethane are slightly higher than the yields of methane.

A catalyst combination consisting of nickel-moly on alumina and palladium on silica alumina was tested to provide the additional hydrogenation function of the palladium. Typical results were: gases 54%, liquids 27% and char 19%. While the gaseous yield and the liquid yields were comparable to the two-stage gasification system, again the yield of ethane was slightly higher than the yield of methane. These typical results are contained in Table 2.

Inasmuch as the hydrogen for conversion of coal to high-BTU gas must ultimately come from water, it is of value to know the equilibrium values for the production of CH_4 , CO_2 , CO and H_2 as a function of percent steam in the gas phase as well as a function of temperature and pressure. It is of value, also, to know the heating value of the dry gas in these equilibrium mixtures. A computer analysis of various systems was undertaken to determine these equilibrium values. This information has been published in the literature.¹ Figure 5 gives the heating value of the dry gas at equilibrium for various values of hydrogen/steam ratio, temperature and pressure. Figure 6 presents the equilibrium values in the dry gas for CH_4 , CO_2 , H_2 and CO .

Reference

1. W.H. Wiser and S.S. Kithany, Fuel, 57, 485 (1978).

Heating Value: 1202 BTU/cu ft

Table 1. Product Distribution of Overall Process

TABLE 2
COMPARISON OF THE TWO-STAGE GASIFICATION PROCESS
WITH THE ONE-STAGE PROCESS

	<u>Two-Stage Gasification</u>	<u>One-Stage Gasification</u>	<u>One Stage Gasification</u>
Catalyst	Ni-Mo/Al ₂ O ₃	Ni-Mo/Al ₂ O ₃	Ni-Mo/Al ₂ O ₃ : Pd/SiO ₂ -Al ₂ O ₃
Reactor Temp. (°C)	480 - 525	500	500
H ₂ -Pressure (psig)	2000 - 1750	1000	1000
Residence Time (min.)	60	21	13
Wt. % Char	18.60	19.33	19.40
Wt. % CONversion	81.40	80.67	80.60
Yield (Wt. %)			
CH ₄	39.65	14.09	24.88
C ₂ H ₄	0.00	0.13	0.35
C ₂ H ₆	8.12	17.49	28.60
C ₃ H ₆	0.00	0.13	0.23
C ₃ H ₈	4.94	4.08	0.00
I-C ₄ H ₁₀	0.10	0.00	0.00
1-C ₄ H ₈	0.10	0.00	0.00
n-C ₄ H ₁₀	1.98	4.86	0.00
2-C ₄ H ₈	0.30	0.00	0.00
Totals:			
Gases	55.09	41.31	54.06
Liquids	26.31	39.36	26.54
Char	18.60	19.33	19.40

Figure 1. Effects of Temperature on Conversion and Product Distribution in 1st Stage (Ni-Mo Catalyst)

Figure 2. Effects of Pressure on Conversion and Product Distribution in 1st Stage (Ni-W Catalyst)

Figure 3. Effects of Temperature on Conversion and Product Distribution in 2nd Stage (Ni-Mo Catalyst)

Figure 4 Effect of Temperature on Gas Yield in 2nd Stage (Ni-Mo Catalyst)

FIGURE 5

FIGURE 6

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

Faculty Advisor: L.L. Anderson

Introduction

As part of the evaluation of the effectiveness of production of liquids from coal by catalytic processes and extraction, some characterization was completed on the liquids. In the process of this work a new characterization scheme was developed. The purpose of the scheme was to determine, so far as possible, the characteristics of the liquids and also to relate these to structural entities and characteristics of the solid coal. Three coal-derived liquids (CDL) were prepared from the same coal representing different severities of attack on the coal material. These were compared as to their molecular weight, aromaticity and molecular character as revealed by nuclear magnetic resonance and infra red spectral analysis.

Characteristics of the liquid product led to the following general conclusions about the high volatile bituminous coal (Clear Creek, Utah) used in the study: 1) Aromatic clusters of essentially the same size were present in all of the CDL products. 2) As severity of processing increased, the number average molecular weight for the liquid products decreased but this was primarily due to a decrease in the number of aromatic clusters per molecule. 3) The types of molecular species obtained as products were predictable provided that high temperature (over 500°C at long residence times) severe cracking conditions were avoided.

During the work performed on this project, measurement of molecular weight was important but difficult for the complex liquids being studied. Some criteria were established for obtaining satisfactory results and a paper outlining the method was published.¹

The purpose of the work reported in this report was to elucidate some of the chemical nature of bituminous coal. Considering the difficulties and complexity in the investigation of coal, a scheme has been devised to acquire primary information on structural features of coal governing potential products, their distribution and the liquefaction process producing them. One high volatile bituminous coal has been examined in detail through two liquefaction processes. Although the liquefaction products have not been completely analyzed (i.e., every component has not been identified),

molecular level information has been obtained by means of average molecular structural parameters.

Coal is such a mixture that direct examination in the solid state does not result in much specific information, and numerous investigators have studied coal-derived liquids for the elucidation of coal structure and chemistry. Some of the approaches used in the preparation and characterization of CDL are reviewed here and comparison is made with the new scheme.

Coal can be transformed into liquid or soluble products by several means such as oxidation, hydrogenation, solubilization and depolymerization. In the oxidation of coal, various oxidants have been used in different media, acidic, basic or neutral. Oxidation often causes drastic destruction of coal molecules, but recently controlled oxidations have been reported wherein only certain bonds or structures are attacked.

Hydrogenolysis is a good way of converting coal into identifiable products of low molecular weight, still maintaining some original structural features of the coal. Hydrogenolysis of coal has been performed with or without catalyst, using hydrogen-donor agents and/or hydrogen, at temperatures of 300 to 500°C. Some variations in the hydrogenation procedure have been adapted by several investigators to minimize the degradation of the chemical units of coal.

Depolymerization and solubilization of coal are usually conducted at lower temperatures, less than 100°C. Alkylation, reductive alkylation and acylation have been employed in these processes.

Once coal has been converted to liquid (or soluble) products, these have been examined chemically or physically to acquire information about their precursor, coal or on the liquefaction behavior of coal. Even though CDL are more accessible than coal, they are still complex in terms of number of different structural components, their molecular size and functionalities. Thus a complete analysis of CDL is impractical, if not impossible, and instead some type of "characterization" is performed to obtain selective information such as quantitative distribution of compound types or functional groups.

Due to the complexity of CDL, major emphasis has been given to the separation of CDL into different fractions. Distillation, solvent extraction and chromatography have been employed for separation into fractions. Typical characterization schemes are the following:

1) Solvent extraction using benzene and hexane or heptane or pentane has been a traditional method to characterize CDL. In this method, the benzene soluble-hexane insoluble portion of CDL is called "asphaltenes," and the alkane soluble portion is called "oil". Weller and co-worker related this scheme to coal liquefaction in the following reaction scheme:

Since their work was done, CDL have been frequently characterized in terms of asphaltenes and oil, and the nature of asphaltenes has been investigated further. Later this scheme was modified to include preasphaltenes, a pyridine soluble-benzene insoluble fraction.

Although the solvent extraction scheme is widely used, the nature of preasphaltenes and asphaltenes is not well understood, and not well related to the chemical properties of coal. Recently in his liquefaction study of coal, Neavel questioned the validity of the mechanism, "coal→asphaltenes→oil" on the basis of complexity involved in coal liquefaction. However, Lieberberg and Potgieter and Yoshida et al. related asphaltenes and oil to coal liquefaction in more complicated ways. The usefulness of the solvent extraction scheme is in providing information that can be related to a complex phenomenon like coal liquefaction in the absence of more suitable methods.

2) A characterization scheme combining solvent extraction and chromatography has been used. In this procedure CDL is fractionated into five groups: (a) benzene insoluble, (b) asphaltenes, (c) saturates, (d) aromatics and (e) resins. The chromatographic separation is added to the above solvent extraction scheme to fractionate oil into the last three fractions. Farcasiu pointed out that this scheme is not applicable to whole coal-liquids because of irreversible adsorption of some CDL components and some intrinsic disadvantages of ion-exchange resins used in the scheme.

3) Farcasiu proposed the fractionation of the whole CDL by liquid chromatography in a method called sequential elution by solvents chromatography (SESC). The separation gives nine fractions of different chemical functionalities, resulting from sequential elution with specific solvents on silica gel columns. Her comparison with the solvent extraction scheme revealed that this chromatographic scheme separates oil, asphaltenes and preasphaltenes further into sub-fractions. This scheme has been employed for an extensive study of coal liquefaction, but the contribution of this scheme to the elucidation of coal structure and coal liquefaction behavior is not yet clear.

Results and Discussion

The limited information obtainable from the direct examination of coal in the solid state suggests that investigation of coal-derived liquids may be practical way for obtaining additional information on coal as recognized and attempted by many investigators. However, significant structural information gained from CDL is minimal compared to its potential. A new characterization scheme is described here which was developed for defining structural features of coal. The development of a new procedure for molecular weight determination, which is of fundamental importance to the new scheme was also developed.

Due to the complexity of CDL, only its characterization can be done within a reasonable time and effort. Characterization has long been practiced in petroleum research. Nevertheless, the nature of characterization could be different between petro-

leum research and coal research. The nature of characterization needs to be carefully examined in terms of its purpose, the material to be characterized, the chemical characteristics to be determined and the procedure.

The purpose of characterization in petroleum research has been mainly to obtain necessary information for further processing of petroleum or its fractions. In coal research, elucidation of the chemical structure of the CDL precursor (coal) and its chemistry is of much interest. In addition, CDL is much different from petroleum. For example, unlike petroleum a CDL can be prepared in many different ways. The nature of CDL will vary significantly depending on the method of preparation.

The particular purpose and the nature of CDL suggest that it is essential to improve our understanding of coal structure and its relationship to CDL to devise a better characterization scheme for CDL. In turn, a better scheme will provide us with more information on coal.

The previous characterization schemes reviewed were designed apparently with little understanding of the implications of the particular characterization purpose, or with a limited understanding of available information on coal and CDL. A proper understanding of both the particular purpose of characterization and the nature of coal and CDL is expected to provide basic guidelines on how the characterization should proceed. Even with a well-defined purpose, it seems a challenging task to have a proper perception of coal structure and its chemistry due to vast and fragmentary information on the subject. The formulation of the new characterization scheme was started with a comprehensive study of available information on coal structure and its liquefaction behavior. Based on this study, each necessary step in the scheme was identified, and possible ways of carrying out each step were evaluated.

Much information on coal structure has been accumulated, but most of it is not directly interpretable or is mutually contradictory because different investigators used different reaction conditions, different coals or different methods of analysis. Hence a careful generalization was made to obtain as simple and yet comprehensive chemical picture of coal as can be ascertained with the limited information available.

Coal is a complicated mixture of polymer-like constituents. The constituents could belong to different types or groups of chemical species. Molecular weights of most of the constituents are larger than 2000. Each constituent appears to consist of stable structural units like aromatic and/or hydroaromatic rings connected by linkages.

CDL, especially those obtained by hydrogenation, are basically products from depolymerization of coal. Molecular weights of CDL constituents are substantially smaller than those of coal constituents. Other structural features of coal except for the

molecular weight, would be either conserved or absent in CDL depending on the nature of structural features and condition of the depolymerization process. Hence a CDL needs to be carefully prepared in accordance with the selected structural information on coal that is of interest.

In this case the purpose was to elucidate chemical structure and liquefaction behavior of coal. It is necessary to express the purpose in specific terms, since other steps of characterization can be directed sufficiently toward achieving that specific purpose. According to evaluation of currently available information, clarifying fundamental aspects of coal structure and liquefaction appeared most desirable. The fundamental aspects include heterogeneity, polymeric nature, and aromaticity of coal. Accordingly the specific purpose of the new scheme was to confirm the current qualitative understanding of these properties of coal and to express them in a quantitative manner.

To extract information on coal from CDL, it is essential to prepare CDL in a controlled manner. The nature of coal and its relationship to CDL suggest the following needs to be considered in the preparation of CDL:

- 1) A CDL should represent the coal under investigation in quality and quantity. Coal being a heterogeneous mixture, it is necessary or preferable to examine a whole CDL obtained from a major portion of coal. A CDL should retain some structural features of coal or contain some information which can be related to the structure of coal.
- 2) Controlling the degree of depolymerization will provide interesting information. Since depolymerization is supposed to involve large changes in molecular weight, but little alteration in other structural features, a careful control of depolymerization is useful for understanding the polymeric nature, aromaticity and heterogeneity of coal.
- 3) A CDL must be amenable to analysis as close as possible to the molecular level. Although almost all modern analytical methods have been used, little information on CDL has been obtained due to the complexity in the composition of such materials. Some of the complexity could be alleviated through the proper choice of depolymerization conditions.

Based upon these considerations, CDL were prepared in high conversion processes with a high degree of depolymerization. The fractionation was included to alleviate the complexity in composition, and to determine the heterogeneity and polymeric nature of coal. Molecular size was chosen as a first separation criterion. This criterion was indicated by the characteristics of the depolymerization process.

Vacuum distillation among other methods was used first; for nondistillable CDL fractions solvent extraction was used for separation. The choice of separation method (distillation or extraction) was based on experimental observations.

Fractions from the separation were analyzed for elemental composition, molecular weight, and NMR spectra. These raw data were used to calculate average structural parameters of each fraction such as aromaticity, number of aromatic rings, number of naphthenic rings, number of aromatic clusters, etc. With these parameters, each fraction was treated as an average molecule.

The new scheme is different in major aspects from the other schemes mentioned earlier. In the other schemes much attention has been paid to the fractionation of CDL, and apparently little consideration has been given to their preparation.

In the other schemes, the fractionation of CDL has been based on functionalities instead of molecular size.

In the new characterization scheme, the correct determination of molecular weight was considered to be indispensable because of the nature of the depolymerization process and the need for molecular level information. Several investigators, however, reported divergent data in the technical literature differing 20 to 200% for the same samples. The results were obtained with vapor phase osmometry. Since this method is one of the most widely used in coal research and other methods are considered to be undependable, it was examined in detail to develop a new procedure. The new procedure has been published.¹

Structural parameters. The structural parameters of a sample were calculated from the elemental composition, molecular weight, and proton NMR spectrum. Their definitions and formulae are:

NUMBER OF AROMATIC CARBONS

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

FRACTION OF AROMATIC CARBONS (=AROMATICITY)

$$f_A = \frac{C_A}{C} \quad (2)$$

TOTAL NUMBER OF RINGS

$$R_T = \frac{2C - H + 2}{2} - \frac{1}{2} C_A \quad (3)$$

NUMBER OF AROMATIC CLUSTERS

$$C_{AP} = H_A + \frac{1}{2} H_{2\alpha} + \frac{1}{3} H_{3\alpha} \quad (4)$$

$$\#cl = \frac{1}{3} (C_{AP} - \frac{1}{2} C_A) \quad (5)$$

NUMBER OF AROMATIC RINGS

$$R_A = \frac{C_A - 2 \#cl}{4} \quad (6)$$

NUMBER OF NAPHTHENIC AND SATURATED RINGS

$$R_N = R_T - R_A \quad (7)$$

$$\text{MOLECULAR WEIGHT} = \text{MW} \quad (8)$$

$$\text{CLUSTER SIZE} = R_A / \#cl \quad (9)$$

$$\text{CLUSTER WEIGHT} = \text{MW} / \#cl \quad (10)$$

In the formulae, C and H are the numbers of carbon atoms and hydrogen atoms, respectively, in the empirical formula of a sample. The formula was obtained from elemental composition and molecular weight. The elemental compositions of SP-300 and SP-320 fractions, revealed substantial amounts, ~10%, of an unknown component. In the calculation of empirical formula, the unknown was assumed to be Na or Cl incorporated to the fractions during the solubilization, since more than 85% of original ash in coal was recovered in the pyridine insolubles of SP-300 and SP-320. The incorporation means that the molecular weight of each fraction includes the contribution of Na or Cl in the fraction. In the empirical formula, Na or Cl was not included because the contribution of either one was minor. The number of hydrogen, H, was divided into those of five types, H_{AP} , $H_{2\alpha}$, $H_{3\alpha}$, H_β and H_γ based on the assignments of NMR Spectra. This division was done in HVL-P fractions. In SP-300 and SP-320 fractions, however, $H_{3\alpha}$ and H_γ were included in $H_{2\alpha}$ and H_β , respectively, because their spectra showed that (1) $H_{3\alpha}$ and H_γ were much smaller than $H_{2\alpha}$ and H_β , respectively, and (2) the resolution was poor.

Parameters, R_A , R_N , R_T , MW and #cl are for the average molecule of a sample; they will be called molecular parameters. Parameters, $R_A / \#cl$ and $\text{MW} / \#cl$, are for the average cluster; these will be called cluster parameters. Carbon aromaticity, f_A , is for either the average molecule or the average cluster; f_A of the molecule is the same as that of the cluster. The first one, I, has a single component, and the second is a mixture of two components. The calculations of the parameters are self-explanatory except for #cl. An aromatic cluster is defined as an aromatic ring not fused to another one, or a group of aromatic rings fused together. For example, in system I two aromatic rings on the left side are fused together and make one aromatic cluster, while one ring in the right side is separated from the cluster in the left by non-aromatic bonds and makes one cluster by itself.

The components of System II are hypothetical decomposition products from System I. In the decomposition process, the molecular parameters decreased to one half, while the cluster parameters and f_A remained the same. Thus the structural parameters can be used to understand the relation between a certain chemical system and its decomposition process.

There are some limitations and approximations adopted in the formulae, (1) to (7). They are of analytical, theoretical or practical in nature. Among several, a few of the more important

ones deserve a careful examination. First, in formulae (1) and (4) it is assumed that two hydrogens of type, $H_{2\alpha}^1$ or H_{β}^1 are attached to one carbon atom. There have been a few reports related to this assumption. According to the results, the ratio of $H_{2\alpha}$ or H_{β} to respective carbon appears to be close to two within a possible error of 10%.

Second, formula (3) holds for all hydrocarbons without olefinic (double) or triple bonds. There has been little indication of such bonds in CDL. Existence of such bonds does not affect the values of other parameters except for R_N . The presence of oxygen does not affect the calculation of the formula. Other heteroatoms, S and N, are to be taken into consideration. In our use of the formula, the effect of the heteroatoms was neglected because of their low content in our samples.

Third, formulae (5) and (6) are exact expressions for cata-condensed aromatic clusters. Fortunately there are only cata-condensed clusters with three or less aromatic rings. With four or more aromatic rings, there are a few other configurations of the clusters in between the two extremes, cata- or peri-condensed clusters as shown in Figure 1. Thus formulae (5) and (6) are approximate expressions for samples containing large aromatic clusters in the absence of information on the types of ring condensation.

In brief, the structural parameters and their formulae were chose to express quantitatively the structural features of the complex mixture, CDL, in average terms based on available analytical data. The soundness and usefulness of the formulae are to be judged from the information obtainable to describe chemical characteristics of CDL.

Paraffinic material. The paraffins removed were approximately 7% of the heavy liquid, HVL. Mass spectra obtained by chemical ionization revealed that the material consisted of long chain paraffins of 16 to 32 carbon atoms. Other investigators have observed the occurrence of substantial amounts of paraffins in coal products. Considering the nature of reaction mechanisms in coal liquefaction processes, the paraffinic material has been assumed to exist in bituminous coals and lignites.

The removal of paraffins is necessary for better information on the nonaliphatic portion of HVL (HVL-P). Otherwise this paraffinic material would be interpreted as aliphatic side chains on aromatic rings.

Fractionation of HVL-P. In preliminary experiments, solvent extraction was compared with distillation for the fractionation of HVL-P. Table 1 shows yields and analytical data on solvent extraction products with ethanol and distillation products of the ethanol soluble, ES.

Although solvent extraction was performed on HVL, ES and EI-AS (ethanol-insoluble acetone-soluble) practically represent HVL-P

because EI-AI (ethanol-insoluble acetone-insoluble) was mostly paraffinic material. Yields reveal that ES is a major portion of HVL-P. There are slight differences between ES and EI-AS in molecular weight, empirical formula, and the content of phenolic hydroxyl groups (ϕ -OH).

On the other hand, distillation of ES disclosed that there are large differences between the distillable, ES-dist, and the non-distillable, ES-resid. The two fractions have similar yields, but the molecular weight of ES-dist is only one-half of that of ES-resid. Oxygen and ϕ -OH content are much higher in ES-dist. Empirical formulae and physical appearance clearly reveal that the two fractions are chemically as well as physically different.

Comparison of the separation results by the two means indicates that solvent extraction using ethanol is not as effective as distillation. Distillation is very effective in fractionating ES according to molecular size and ϕ -OH content. The large differences in the content of oxygen and ϕ -OH between ES-dist and ES-resid seem to indicate a trend in the distribution of oxygen or ϕ -OH in coal. Since ES comprised 60% of HVL, distillation was expected to fractionate HVL-P in a similar fashion.

Results from the distillation of HVL-P are shown in Table 2. The table also includes distillation data of CyS (cyclohexane soluble of HVL-P). Elemental compositions and empirical formulae of HVL-P and CyS fractions are listed in Tables 3 and 4. CyS was examined to compare distillation with the traditional solvent extraction separating a CDL into asphaltenes and oil, which is CyS.

HVL-P fractions have substantially different molecular weights ranging from 183 to 390 as expected from the distillation of ES. Distillable fractions, light, middle and heavy, are a major portion of HVL-P, with the non-distillable, Resid, being 40% by weight. In terms of number of molecules, Resid is 30% of HVL-P. The loss during the distillation was not further reduced, because it seemed unnecessary at this stage.

The difference in molecular weight among the fractions are noticeable. They are 122 between Heavy and Resid, 62 between Middle and Heavy, and 29 between Light and Middle. Considering the yields, the differences suggest that there is a unique distribution of molecular weights in HVL-P constituents. The distribution is shown in Figure 2. This kind of distribution has not been reported in the literature, and will be further discussed shortly after examining the distillation data of CyS.

As shown in Table 1, cyclohexane dissolved more than 70 wt.% of HVL-P. CyS fractions from the distillation show a wide spread in molecular weight, which ranges from 181 to 401. The spread is practically the same as that of HVL-P. The yields and molecular weights reveal that cyclohexane dissolved all of light and middle, and about 50% of Heavy and Resid in HVL-P. It is interesting to note that the portion of Heavy and Resid dissolved in cyclohexane

have similar molecular weights, respectively, to those of Heavy and Resid in HVL-P. This suggests that Heavy and Resid have a narrow molecular-weight range, supporting the distribution sketched in Figure 2.

These results on CyS fractions indicate that the traditional solvent extraction method and distillation are different. Distillation separated HVL-P according to molecular size while the solvent extraction was much less effective in this regard. The solvent extraction or cyclohexane separated a CDL according to some structural features in addition to molecular weight. The extraction classified a major portion of HVL-P as Oil (i.e., CyS), which consists of quite different fractions in molecular weight as revealed by distillation.

The two sets of results from the solvent extractions by ethanol and cyclohexane disclose that it would be difficult to observe the distribution shown in Figure 2 through solvent extraction. Most fractionations (or characterization) by CDL by others has been done by solvent extraction. Even where distillation was employed, the distribution was usually not reported. Possible reasons are (1) molecular weight was not determined, (2) molecular weight was determined incorrectly, or (3) the nature of a sample was different from HVL-P. In summary, the distillation separated HVL-P into fractions of different molecular weight much more effectively than the solvent extractions. The fractionation through distillation suggested a unique distribution for HVL-P constituents in molecular weights. The combination of distillation and solvent extraction indicated that a fraction from distillation has a narrow range in molecular weight. Thus our distillation method appeared to be suitable as a separation means for the new characterization scheme.

Conclusions

The purpose of this investigation was to elucidate fundamental structural features of coal by means of chemical characterization of coal-derived liquids (CDL). A new characterization scheme was devised based on available information on coal and CDL. Three CDL from a high volatile bituminous (hvb) coal were prepared in two high-conversion processes, and characterized according to the new scheme.

Major findings from the three CDL are as follows:

- 1) A CDL (HVL-P) produced by hydrogenation at 500°C with several seconds of residence time and zinc chloride as catalyst was almost completely depolymerized, that is, the number of ring systems per molecule was reduced essentially to one. This material apparently were derived from three or four different structural units in coal.
- 2) A solubilization product (SP-300) obtained in a reaction with NaOH/ethanol at 300°C, was much less depolymerized than HVL-P, but the average size of its aromatic clusters was almost the same,

2.2 aromatic rings per cluster, as that of HVL-P. This agreement indicated that the average size of aromatic clusters in the hvb coal was about 2.2.

3) The SP-300 consisted of three molecular groups. Each molecular group was made up of aromatic clusters containing 1.4, 1.9 or 4.0 aromatic rings per cluster. Each molecular group had, on the average, almost three aromatic clusters. The agreement in the average cluster size stated in (2) indicated that the different sizes of aromatic clusters must be in the coal.

4) The distribution of the aromatic clusters identified in (3) was estimated by examining another solubilization product (SP-320) prepared at 320°C. Analytical data revealed that the clusters of 1.3 and 1.9 would be convertible quantitatively to smaller species like lighter fractions of HVL-P, while the larger clusters of 4.0 would become large molecular-weight species similar to the heavy fractions contained in HVL-P.

5) With the quantitative convertibility in (4) and the conservation of the aromatic clusters in (3), the aromatic clusters in the particular coal were identified in average structural terms and their distribution was estimated.

6) The IR spectra of coal, SP-320 and HVL-P fractions showed large differences in absorption at 1200-920 cm^{-1} and 700-400 cm^{-1} .

7) Oxygen content in the three CDL decreased as the severity of the liquefaction processes or the degree of depolymerization increased. Complete depolymerization of the hvb coal in the hydrogenation process (using ZnCl_2) was accomplished by a 73% reduction in oxygen content.

The above findings support the current qualitative understanding that coal is a heterogeneous, polymer-like material consisting of aromatic clusters. The present results revealed the heterogeneity, polymeric nature and aromatic clusters of coal more quantitatively. Considering the complexity of coal, the new characterization scheme and the procedure for determining structural parameters seem to be a practical way of improving our understanding of some of the structural features of coal.

References

1. K.E. Chung, L.L. Anderson and W.H. Wiser, Fuel, 58, 847 (1979)

TABLE 1

Yields and Analytical Data on Ethanol-
Extraction Products from HVL-P and
Distillation Products from the
Ethanol Soluble

Separation Process	Solvent Extraction of CDL ^a		Distillation of ES	
Products	ES	EI-AS	ES-dist.	ES-resid
Yield				
Wt %	60.3	25.4	56.0	44.0
Mole %	--	--	71.7	28.3
Average Molecular Formula				
C	17.9	19.3	12.9	27.7
H	20.2	21.7	16.7	27.6
N	0.2	0.2	0.1	0.3
O	1.2	1.1	1.1	1.1
Molecular Wt	257	273	192	383
Atomic H/C	1.13	1.13	1.29	1.00
Total O (% W/W) ^b	7.38	6.17	9.41	4.69
Phenolic O (% of Total oxygen) ^c	58.2	52.7	70.0	26.4
Physcial Appearance at room temperature	Black Liquids, Very Viscous.		Yellowish- Brown Liq, Much Less Viscous Than ES.	Black Solid, Brittle and Shiny.

^aThe third fraction (EI-AI) is mostly paraffinic material.

^bDetermined by difference from C-H-N analysis.

^cDetermined from NMR spectra, elemental composition and molecular weight.

TABLE 2
Comparison of Distillation Products
from HVL-P and its Cyclohexane
Soluble Fraction

Sample	Operation	Product	Molecular Weight	Yield	
				Weight %	Mole %
HVL-P	---	---	258	100	(100)
	Distillation	Light	183	19.2	30.4
		Middle	210	15.7	21.6
		Heavy	272	17.6	18.7
		Resid	390	40.0	29.2
		Loss	-	7.5	--
HVL-P	Cyclohexane	CyS		72.1	--
		CyP		29.7	--
CyS	---	---	267 (254)	72.1(100)	(100)
	Distillation	Light	181	19.6(27.2)	40.4
		Middle	229	16.7(23.2)	27.2
		Heavy	290	7.9(11.0)	10.2
		Resid	401	23.8(33.0)	22.2
		Loss	---	4.1(5.6)	--

TABLE 3.
Elemental Compositions* of
HVL-P and CyS Fractions

	C%	H%	N%	O%	$\Delta\%^{**}$
<u>HVL-P</u>	85.64	8.11	1.23	4.81	0.21
Light	81.63	8.90	1.00	5.46	3.01
Middle	84.27	8.77	1.21	5.12	0.63
Heavy	86.17	8.14	1.30	5.00	-0.61
Resid	87.37	7.31	1.26	4.25	-0.19
<u>CyS</u>	87.37	7.99	0.76	3.59	0.29
Light	81.72	8.94	0.80	4.53	4.01
Middle	87.67	9.11	0.92	3.86	-1.56
Heavy	87.84	8.55	0.89	3.71	-0.99
Resid	88.36	7.81	0.85	3.12	-0.14

*Weight % of each sample

** $\Delta\% = 100 - C\% - H\% - N\% - O\%$

TABLE 4.
Empirical Formula of HVL-P
and CyS Fractions

Sample	M.W.	C	H	N	O
HVL-P	258	18.4	20.9	0.23	0.78
CyS	267	19.4	21.3	0.15	0.60
Light	183	12.4	16.3	0.13	0.62
CyS-Light	181	12.3	16.2	0.10	0.51
Middle	210	14.7	18.4	0.18	0.67
CyS-Middle	229	16.7	20.9	0.15	0.55
Heavy	272	19.5	22.1	0.25	0.85
CyS-Heavy	290	21.2	24.8	0.18	0.67
Resid	396	28.8	28.9	0.36	1.05
CyS-Resid	401	29.5	31.3	0.24	0.78

IDEAL CATA-CONDENSED SYSTEMS

IDEAL PERI-CONDENSED SYSTEMS

NON-IDEAL SYSTEMS

Figure 1. Forms of Condensed Aromatic Rings

Figure 2. Molecular Weight Distribution in HVL-P

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

Faculty Advisor: L.L. Anderson

Introduction

Extensive characterization, separation and analyses have been performed on many coal-derived liquid (CDL) fuels obtained by solvent extraction, hydrogenation, pyrolysis, catalytic processing and combinations of these methods. In previous work at the University of Utah, the application of ultrasonic energy resulted in increased yields of extract at a given temperature. The feasibility of using this energy source to effect extraction of coal with a donor solvent was therefore proposed. Other energized conditions were also applied.

The objective of this project was to determine the kinetics of the extraction reactions as well as the yield of products and the optimum conditions for extraction of bituminous coals using ultrasonic energy and/or catalysts as well as strictly thermal extraction of such coals. Hydrogen donor solvents and hydrogen gas were also used to promote the reactions. A system was designed to carry out the experiments for controlling temperature, residence time, pressure and intensity of any auxiliary energy into the system. The characteristics of the coal-derived extraction products were determined. Several coals of different characteristics were studied.

The work of this project was divided into three main parts. One part (I) consisted of design and operation of a batch-recycle system using tetralin as a hydrogen donor solvent and hydrogen gas at 1500 psi. Ultrasonic energy and short residence time experiments were conducted to obtain coal extraction products. The kinetics of the reactions were studied and the products were separated, characterized and analyzed.

In a second part of this work (II), dry coal was hydrogenated in the presence of a catalyst (ZnCl_2 at 5% by weight of the coal feed) at short residence time (50 to 100 sec) and 1800 psi (hydrogen pressure). The liquid products from this processing were characterized and analyzed after being separated into fractions based on volatility (by vacuum distillation). Structural parameters for the liquid products were calculated from the elemental composition, molecular weight and proton nuclear magnetic resonance spectra. These structural parameters gave possible chemical structures leading to the products obtained. Also, the same high volatile bituminous coal was solubilized by reaction with sodium hydroxide and ethanol at

320°C. The resulting liquid products were separated and analyzed in a way similar to that used for the hydrogenation liquids, and implications of the common characteristics were investigated.

The final part (III) of this project included solvent extraction of coals under mild conditions (below 300°C) and the characterization and identification of the chemical species of such extractions. A variety of solvent was used, and the extraction yields were low. This led to a more comprehensive understanding of the chemical structure of the coals for each of the coals as seen from the gas chromatograms of the extracts. Some proton and carbon-13 magnetic resonance studies were also done on some of the coal extracts.

Experimental

Ultrasonic energy raised the instantaneous temperatures and pressures in the liquid to higher values than those measured by static methods. However, this method of heating and pressurizing was not as efficient as other methods. Furthermore, the application of intense ultrasonic fields was extremely difficult where the liquid had to be contained in pressurized lines and vessels. Other methods of attaining energized conditions were eventually used for most of the experiments performed.

The kinetics of the extraction process were measured at 350°, 375° and 400°C. The product liquids and gases were analyzed in detail by solvent separation, molecular weight determination, elemental analysis, gas chromatography, proton magnetic resonance, infrared, ultraviolet and mass spectroscopy. Blank runs were also made to observe the stability of the solvent, tetralin, at the reaction conditions. These conditions were optimized at short residence times of about 6 sec per pass through the dissolver. Figure 1 is a schematic diagram showing the essential parts of the extraction system. The system maintained uniform distribution of the coal particles and temperature in the dissolver when turbulent conditions were achieved in the transport lines. At these conditions the flow velocity of coal-solvent slurry was about 7 feet per sec.

The actual reaction zone occupied a portion of the total charge of reactants in the middle of the recycle loop of the reactor system. The reactants rapidly heated when entering the reaction zone and then were quenched. Because of the short contact time, the conversion of coal to soluble products per pass was small, and consequently mass and heat transfer effects were minimized. The quenching of the reactants and products immediately after the reactor may have preserved intermediate species which were labile at reaction conditions but still survived due to short thermal contact times. Expanded time for the sample acquisition also facilitated observation of any rapid initial reactions.

To calculate the reaction time (T) and its relationship to the actual run time (t), the following relationship was

applied. (This relationship is valid for conditions of rapid recycle rate and homogeneous mixing of products.)

$$wr = W \, dC/dt \quad (1)$$

where r = rate of reaction, C = conversion, w = reactor hold (mass), W = total mass charge less reactor hold, and t = clock time or run time. Reaction time, T , for the conversion can be obtained by rearranging Eq (1)

$$r = dC/d(w/Wt) = dC/dT \quad (2)$$

$$T = (w/W)t \quad (3)$$

As shown in Figure 1, the apparatus was composed of a slurry storage and suspension system, recycle loop, and charge and discharge systems. The recycle loop was composed of pumps, a preheater, a reactor or dissolver, and a quench heat exchanger. All the materials under severe temperature and pressure conditions were made of stainless steel type 316. The slurry storage and suspension system was a 200 ml high pressure autoclave manufactured by Autoclave Engineering, Erie, Pennsylvania with a MagneDrive turbine stirrer.

Two high volatile bituminous coals were used in this study, Hiawatha, hvbb, Utah coal and Kentucky #14, hvbb, coal. These coals were chosen from different geographic locations to observe any differences in their reactivity and products. Kentucky #14 coal has been extensively studied by others. Table 1 shows representative proximate and ultimate analyses, and heating values of these coals.

As an example of preparation, Hiawatha coal (lump) was pulverized, separated into discrete size ranges and stored in sealed cans until needed. However, the mineral matter (and probably heavier petrographic portions of the coal) were disproportionated densimetrically during sieve separation. Some experiments were conducted using proper amounts of lump coal where the total lump samples were pulverized to pass a 270 mesh screen and used as the coal charge. Fresh samples were pulverized before each run with a Mini-Grinder manufactured by the Chemical Rubber Company, Cleveland, Ohio while cooling water was circulated. This modified procedure allowed minimal air exposure of the coal between grinding and conversion and prevented disproportionation of the lump coal properties. The minimum time required for processing lump coal through the entire process of drying, grinding, sizing and conversion was no longer than 1 day. Prior to the preparation of the coal slurry for experiments, the coal was kept with P_2O_5 in dessicators blanketed by an inert gas.

Results and Discussion

Figures 2 and 3 are plots of conversion vs. time for Hiawatha, Utah and Kentucky #14 coals run at 400°C and 1500 psig H₂. Both coals were rapidly converted to a spectrum of products during the initial 5 to 7 min. The conversion rate gradually decreased as reaction time increased. Comparison of kinetic data showed different reactivity for the two coals. Hiawatha coal appears to be more reactive (in its rate of reactions and extent of conversion), although both coals had similar elemental constitutions, except for sulfur (Utah = 0.7%, Kentucky #14 = 3.5%). The nature of the difference in the rate for the process of conversion was better understood after the yield data were investigated as a function of reaction time.

Figure 4 shows two or more consecutive maxima of the product fraction (asphaltols, asphaltenes and cyclohexane fractions), indicating substantial portions of asphaltols and asphaltenes may be intermediates during the conversion to oils (hexane solubles). The formation of light fixed and hydrocarbon gases may be related to the products of the extraction. Figure 5 shows the composition of gases from the reaction of Hiawatha coal with tetralin and hydrogen as a function of residence time. Water, carbon monoxide (CO) and methane constituted most of the product gases initially, but CO decreased rapidly with reaction time.

Kinetic models for the coal dissolution process as proposed by several other investigators were evaluated but were inadequate to explain the data obtained. A hybrid model, where both first order and second order rates were involved in coal dissolution based on the views of previous investigators, was developed to fit the kinetic data which was obtained by the batch recycle system. The differential rate expression is

$$dx/dt = k_1(x_{\max} - x) + k_2(x_{\max} - x)^2 \quad (1)$$

or

$$dx^*/dt = k_1(1 - x^*) + k_2(1 - x^*)^2 \quad (2)$$

where x is the fraction conversion at time t , $x_{\max}$ is the potential maximum conversion, $x^* = x/x_{\max}$ which is a fraction conversion normalized to the potential maximum conversion, and k_1 , k_2 are apparent rate constants for first and second order rate terms.

Integration of Eq (2) with boundary conditions of $x^*=0$ and $x^*=1$ at $t=\infty$ yields

$$1 - x^* = 1 - x/x_{\max} = \frac{k_1 \exp(-k_1 t)}{k_1 + k_2 (1 - \exp(-k_1 t))} \quad (3)$$

Figure 6 shows typical conversion-time data obtained at 350, 375 and 400°C for conversion of Hiawatha coal. Conversion data were based on the benzene solubility of the products. The curves of the solid lines in the figure represent the data calculated by the model after a least square evaluation of rate constants. The $x_{\max}$ was also evaluated by a least square approximation, considering the experimental errors involved.

The rate constants evaluated were

<u>Temperature °C</u>	<u>Rate Constant (min⁻¹)</u>	
	k_1	k_2^*
350	-0.00016558	0.30946654
375	-0.0004548	0.31559708
400	-0.00126438	1.0467179

* Dimension of k_2 is same as k_1 , since conversion unit is fractional, i.e., non-dimensional.

The $\ln(k/T)$ of $\ln k$ versus $1/T$ for both first and second order rate constants are correlated in Figures and . The enthalpy and entropy of activation, and the Arrhenius activation energy and frequency factor were as follows:

	<u>1st Order</u>	<u>2nd Order</u>
Activation enthalpy ($\Delta H^\ddagger$, kcal/mole)	-32.8	-18.9
Activation entropy ($\Delta S^\ddagger$, cal/mole °K)	-17.0	-24.6
Arrhenius activation energy, (kcal/mole)	-34.1	-20.2
Frequency factor (in units of 10^4 sec^{-1})	45750	206.4

The model represented the data quite well as shown in Figure 6, although there are deviations in the data obtained at 375°C. This model was as good or better than the others found in the literature. Since this model is mathematical, no theoretical significance, as far as the mechanism is concerned, has been placed on the chemistry of reactions based on the numerical constants. However, the enthalpies of activation for the first order reaction or part are approximately equivalent to those previously reported for pyrolysis, hydrogenation

and higher temperature dissolution. The second order values of activation enthalpy (or Arrhenius activation energy) are rather low for chemical processes.

An example of the infrared spectra obtained for the products of the extraction process is given in Figure 7. The spectra of asphaltenes were obtained from Hiawatha coal at various reaction times at 400°C. Band assignments for the infrared spectra were made based on information obtained from the literature. An important difference between the spectra of the two coals studied was noted in the frequency range of 1300-1000 cm^{-1} . Hiawatha coal spectra showed higher absorption intensity, especially in the region of 1200-1000 cm^{-1} . The assignment of this absorption region may be due to the various types of C-O stretching such as phenols, ethers (aromatic, aliphatic and cyclic), alcohols, etc. Also it may include the strong absorptions of mineral matter such as kaolinite and quartz which commonly occur in coals. For this particular spectra, Hiawatha coal contained 10.03 wt% (HTA) and Kentucky coal contained 7.96% mineral matter. Without the precise correction for mineral matter absorption, quantitative comparison may not be possible; nevertheless, the coal spectra indicated some differences in the oxygen structures in the region of 1200-1000 cm^{-1} between the two coals.

Conclusions

These conclusions are based on the study of Hiawatha, Utah and Kentucky #14 coals. However, some of these conclusions may be applicable to other coals of similar rank and origin.

- 1) The average basic skeletal unit in the bituminous coal structure is composed of 3 to 4 ring clusters.
- 2) Ether bonds and short hydrocarbon chains ($\text{C}_1\text{-C}_3$) are labile linkages in the dissolution process, but ethers constitute the major species.
- 3) Ether, phenol and carbonyl may have some interaction during the dissolution process, and the hydrogenolysis of phenol is the limiting step for the removal of oxygen atoms.
- 4) Even similar bituminous coals show significant differences in reactivity and product distribution under the same dissolution treatment.
- 5) Some carbonyls in the primary extracts and probably in the coals are aldehyde type.
- 6) During the initial reaction period, hydrogen supplied to the extraction products comes preferentially from coal (intra H-transfer at the expense of aliphatic (alkyl and naphthenic). During this reaction period, significant changes also take place in the functionality of the soluble products.

7] Long-term reaction results in net loss of extract due to the formation of light end products (oil and gas). Significant H-transfer takes place from the solvent to the total extraction products.

8) Higher conversion temperatures promote utilization of the coal-derived hydrogen which is accompanied by increased aromaticity of the extraction products.

The results of this part of the project have been published in a dissertation by Dr. Doohee Kang. Results are also being submitted for publication in the technical literature.

TABLE 1

	Hiawatha, Utah	Kentucky #14
Proximate Analysis (Dry Basis)		
Volatile Matter, w%	49.18	38.00
Fixed Carbon, w%	44.27	54.04
Ash, w%	6.55	7.96
Ultimate Analysis		
Carbon, w%	81.3	77.73
Hydrogen, w%	5.7	5.61
Nitrogen, w%	2.0	1.72
Sulfur, w%	0.7	3.48
Oxygen (by difference), w%	10.3	11.47
H/C Ratio	0.841	0.866
Calorific Value, Moisture Ash Free base, Btu/lb	13,500	13,280

Figure 1. Batch Recycle System for Dissolution of Coal in a Hydrogen Donor Solvent

Figure 2 % CONVERSION VS RESIDENCE TIME

Figure 3 % Conversion vs. residence time

Figure 4 Yields (wt % per MMF ccal) vs. residence time

Hiawatha coal, 400 °C, 1500 psig H₂

Figure 5 Formation of light gases vs. residence time

Hiawatha coal, 400 °C, 1500 psig H₂

Figure 6. Kinetic Data and Fitness to the Hybrid Model.
Coal: Hiawatha

Figure 7. Infra-red spectra for asphaltenes

Hiawatha, 400 °C, 1500 psig H_2 .

	<u>Res. time, min.</u>	<u>% Conversion, benzene sol.</u>
1.	0.1	5.6
2.	0.19	28.6
3.	1.8	50.4
4.	34.2	87.6

4* = sample 4 in dichloromethane solution.

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

Extraction Under Mild Conditions

Faculty Advisor: L.L. Anderson

Introduction

This part of the project was concerned with extractive coal liquefaction under mild conditions (low temperature) using a variety of solvents. The objective of such extractions was to identify chemical species present in coal at low conversions and use this information to assess the contribution to the composition of extracts and other liquid products obtained from coal at higher conversions.

A review of the literature of the extraction of coal at mild conditions of less than 100°C revealed that little had been done in a systematic way to qualitatively and quantitatively identify the extracts. This is understandable since much of the material involved at such temperatures is highly dependent on the nature of the coal, and correlation between coals is often therefore not possible. For example, some coals contain occluded resins, waxes or other materials that may not be part of the major portion of the coal. The approach used in this study was to examine in detail one coal by extraction with a series of solvents. After several coals are studied, the results can be analyzed to determine similarities that may be significant.

Experimental

Samples of Coalville (Utah), Hiawatha (Utah), Clear Creek (Utah) and Kentucky #14, all high volatile bituminous coals except Coalville which is subbituminous, were used for the extractions. The coals were crushed and the 60 - 100 mesh fraction was dried and stored until used for extraction. The solvents included benzene, chlorobenzene, toluene, aniline, benzaldehyde, anisole and benzyl alcohol. Extractions were conducted either in soxhlet units or in magnetically stirred glass vessels for 24 hour. Five to fifty grams of coal were used for each individual experiment and the solvent was removed from the extracts by vacuum or steam distillation.

Results and Discussion

Extracts produced from the coals under mild conditions were markedly different in physical appearance depending on the coal and the solvent used. Benzene extracts were different both in amount and character from the different coals. High volatile

bituminous Utah coal extracts in general contained more paraffinic material (alkanes) and a diversity of carbonyl-type compounds.

As representative information on coal extracts, Figure 1 gives results of a series displacement index for spectra of liquids produced from Hiawatha (Utah) coal. Although the points (+) are not definitive, they do show a probable presence of the various types of compounds. Figure shows the strong presence of alkanes and carbonyls (but not whether these are separately contained) and a lack of aromatic compounds.

Similar information from Clear Creek (Utah) coal and CMR and PMR data gave aromaticity = $f_a = 0.21$ and indicated the presence of long chain alkyl groups, with an average chain length of 30-35 carbon atoms, in benzene extracts.

Pyridine was also used to extract the coals treated previously with benzene. While pyridine could extract a larger portion of the coal and the benzene soluble portion of the pyridine extract was larger than the benzene extract, the composition of the benzene soluble portions in both cases were essentially identical. This indicates that benzene could not extract all of the benzene soluble material in the coal. Pyridine "swells" the coal and allow the removal of "trapped" material in the coal.

Conclusions

Examination of the extracts from coal at mild conditions by infrared spectroscopy was made and results confirmed the observations made in Parts I and II of this report. More work needs to be done in this area. Work is continuing, using a variety of solvents and homogeneous catalysts. Coal slurries will also be processed in integral reactors at short residence time under mild temperature conditions ($T < 300^\circ\text{C}$). Low conversions will be obtained in each step of the reaction as conditions increase in severity. Repeated, progressive extractions, coupled with the application of selective catalysts will, hopefully, yield relatively simple primary products. In the end information obtained will be useful in ascertaining the structural components and interconnecting functional groups in coal as well as providing clues to more efficient liquefaction methods.

Figure 1. Series Desplacement Index.

Steam Reforming of Aromatic Compounds

Faculty Advisor: A. G. Oblad

Graduate Student: S. K. Goyal

Introduction

Because of the importance of synthesis gas for the production of ammonia, methanol, hydrogen, and the coming importance for synthetic fuels, it was thought to be important to extend steam reforming to heavier petroleum materials and even to coal liquids. Up to the present time the principal feedstocks for steam reforming are methane and naphtha. Processes using these same materials are used worldwide but ever-expanding uses of synthesis gas will advance the need for heavier feedstock. At present processes utilizing these heavier feedstocks involve partial oxidation which requires oxygen production facilities and special particulate-removing equipment. These two requirements involve large investment and operating costs. On the contrary, steam reforming is relatively simple and employs only the reaction of steam with hydrocarbons at the right conditions.

Since heavier petroleum liquids and liquids produced from coal contain aromatic substances, it is necessary to know under what condition aromatics will react with steam. With methane and light naphtha aromatics are not present as such. Very little information is available on the steam reforming of aromatic feedstocks.

Considering the above background, we carried out an extensive program on steam reforming of aromatic compounds such as benzene, substituted benzenes, naphthalene, and other aromatics likely to be found in heavy petroleum coal derived liquids and coal itself.

The general reactions of interest are:

Our objectives were:

- 1) examine the thermodynamics of the reactions of steam with aromatics to outline reaction temperatures and the equilibria possible.
- 2) develop catalysts of suitable activity and sulfur resistance and sufficient life for aromatic steam reforming.
- 3) determine the conversion and approach to equilibrium as a function of the main variables of the reaction such as temperature, pressure, contact time and steam/carbon ratio (methane equivalent).
- 4) determine reaction mechanisms.
- 5) determine the kinetics of the reaction.

This report contains a brief description of the experimental procedures and programs carried out to achieve the above objectives.

Experimental

The reaction system is shown schematically in Figure 1. The main parts of the system are reservoirs (burettes) for hydrocarbon and water, preheaters including steam generator, a flanged electrically heated reactor 1" i.d., 30" long of 316 ss capable of temperatures to 750°C and up to 400 psig. (commercial reactors operate to 850°C and 500 psig), condensers and product accumulators, pressure control valve and gas metering equipment. Product gas was sampled and analyzed using a Packard Gas Chromatograph (TCD). Liquid products were measured after phase separation and drying. The hydrocarbon product was analyzed on a HP 5730A Gas Chromatograph using a Dexsels column and (FID). This analysis was confirmed by mass spectrometric analysis of key products. Material balances were very good, generally 100%±2% (Table 1).

In this work nickel was used as the catalyst. It was selected as it is the most effective metal in steam reforming and is used in all commercial catalysts. We could thus draw on all the experience and extensive literature available on nickel catalyzed steam reforming of methane and light naphtha. Nickel is known to be sensitive to sulfur poisoning in this use.

Commercial catalysts are prepared by impregnation of $\text{Ni}(\text{NO}_3)_2$ on $\alpha\text{Al}_2\text{O}_3$, and $\alpha\text{Al}_2\text{O}_3$ together with other refractory materials containing CaO and MgO . These catalysts have nickel metal areas of less than $\frac{\text{M}^2}{\text{gm}}$. Even with this low area, nickel

catalysts are adequate to do the job required in reforming methane and naphtha. Higher areas if sustainable at reaction

conditions (800°C and high partial pressures of steam, CO and H₂) would lower catalyst requirement for a given capacity but ordinary support materials including Al₂O₃, Ca (AlO₂)₂, cements, etc. collapse rapidly at the reaction conditions.

Since aromatics are more difficult to reform than paraffins, we made an effort to find more active catalysts than the present commercial catalysts. Accordingly, a number of support materials and available catalysts were tested for stability at temperatures up to 900°C in air and in the presence of steam to 800°C. After considerable effort, Alcoa H-1 was chosen as the most stable material tested. Figure 2 shows a comparison of Alcoa H-I and F-I, two of the better materials tested. Alcoa H-I can be seen to be quite stable and approaches a stable area of about 150M²/gm. This stability was adequate for our purposes. However, run times in excess of those studied may show further collapse of area on the part of H-I. This is a subject for our future research on steam reforming of aromatics.

Alcoa H-I was sintered at 900°C for 96 hours, impregnated using Ni(NO₃)₂ solution, drying at 110°C and calcining at 500°C with a repeat of impregnation, etc. Resulting catalysts had 21-23 wt % Ni metal content. Samples of these catalysts were treated in steam at 700°C for various times. The effect of this treatment on metal surface area as determined by X-ray line broadening is shown in Figure 3. The nickel metal area stabilized above 4M²/gm cat.

Results and Discussion.

Thermodynamic equilibria of reactions between steam and aromatic hydrocarbons as a function of temperature, pressure, steam ratio (moles of steam per gm atom carbon in the hydrocarbon feed) and hydrogen/carbon atom ratio in the hydrocarbon feed were calculated. The thermodynamic minimum steam ratio below which coking is inevitable was also calculated. The compounds studied were benzene, toluene, naphthalene, and anthracene.

These calculations were accomplished by development of a computer program (for details see Ph.D. thesis of S. K. Goyal, March 1979, University of Utah). Free energies of formation of most species were taken from NBC circular 6461. Those energies and thermodynamic constants not thus obtained were taken from other sources such as Perry's Handbook (and other literature). The calculation methods were checked by comparing values obtained with methane and naphtha with those in the literature. The agreements were within graphical readout errors and were considered excellent.

The equilibrium calculations showed that 100% conversions of aromatic compounds with steam to CO₂, CO, H₂, CH₄ were possible under the same conditions used in steam reforming of CH₄ and naphtha; some of the results of these calculations are shown in Figures 4, 5, 6, 7 where equilibrium concentrations of CH₄, CO₂, CO, and H₂ (the only stable products) are given in the

form of monographs. These figures are only representative of those calculated. Representative heating values of product gases at equilibrium are shown in Figures 8 and 9. Minimum steam ratios (for benzene to avoid carbon formation) are shown in Figure 10. Minimum steam ratios are determined by consideration of the reactions 5 and 6:

In methane and naphtha reforming and presumably aromatics carbon formation is fairly certain to come from reaction (5). Thus, by controlling the water gas shift reaction (which is always near equilibrium in steam reforming) by steam partial pressure, carbon formation can be controlled. Minimum steam/carbon ratio is that ratio at which the steam partial pressure just avoids carbon formation.

Reforming of benzene was studied with catalysts Ni-3 (above). The catalyst was mixed with $\alpha\text{Al}_2\text{O}_3$ pellets (.33 Ni-3, .67 $\alpha\text{Al}_2\text{O}_3$) for heat transfer since the reaction is highly endothermic when conversion occurs. At temperatures up to 750°C with no catalyst, no reforming of benzene occurred at atmospheric pressure and usual methane equivalent space velocities of 5000-10000/hour.

Testing of catalyst Ni-3 with benzene showed coking occurred rapidly at any condition where reforming took place. This is similar to the performance of nickel catalysts with naphtha as feed. It was therefore necessary to develop a catalyst which would resist carbon formation. M. W. Kellogg Co. and Imp. Chem. Industries had developed catalysts which were resistant to carbon formation by adding alkali metal carbonates or hydroxides to the catalyst base. We therefore began a series of experiments adding alkali from Na_2CO_3 solution to Ni-3 to produce catalysts having up to 12% Na_2O content. These catalysts were tested for reforming benzene at 550°C and for minimum steam carbon ratio at 700°C all at 1A. Onset of carbon formation was observed by pressure drop across the catalyst bed. These results are shown in Figure 11. Conversion was observed to be a maximum at 6.7 wt.% promoter (Na_2O). Conversion of Ni-3 (0% Na_2O) is initial only as this catalyst coked rapidly. As a result of these tests, catalyst Ni-3-3 having a composition of 71.4 wt% Al_2O_3 , 21.9% Ni and 6.7% Na_2O was used for extensive testing in these studies.

Results for steam reforming of benzene as a function of steam ratio are shown in Figure 12. The points on the extreme left are not significant since coking occurred in each case. Conversion remained approximately constant at each of several temperatures. This can be interpreted, when the reaction is non-coking, that the contact time is essentially constant for these runs (mol% steam is high in all cases). Product distributions for these runs are shown in Figures 13 and 14. The main products in benzene reforming are H_2 , CO and CO_2 . Methane does not seem to be a primary product. The effect of temperature on conversion

and product distribution with W/F (gm. cat/gm feed/hour) as a parameter are shown in Figures 15, 16, and 17. The approach to equilibrium (dotted lines) is better at the higher temperatures.

The effect of pressure on steam reforming of benzene is shown in Figures 18, 19, 20 and 21. The conversion increased with pressure due to the increased residence time. As pressure increased H₂ and CO decreased while CH₄ and CO₂ increased. These trends are expected considering equilibrium calculations. The increase of methane with concomitant decrease in H₂ and CO further indicates that CH₄ is not a primary product but a secondary product from the reaction (3).

The effect of residence time (varying W/F) is shown in Figures 22 and 23. (W/F is not the true residence time but is related to it.) Conversion increased and the product composition approached equilibrium values with increase of residence time (larger W/F).

Analysis of the data including calculation of the true residence times led to the conclusion that the steam reforming of benzene can best be represented by a first order irreversible plug flow reaction:

$$kt = -(1 + \epsilon_A) \ln (1 - X_A) - \epsilon_A X_A$$

where t is true residence time; X_A, fractional conversion; A, 0.187; and k is reaction rate constant.

Plot of the right hand side of equation (5) versus time t, is shown in Figure 24. All the plots are linear within experimental error. From the slope of the lines at different temperatures values of k were obtained. These were used to determine the activation energy from the plot of lnk vs. 1/T shown in Figure 25. The value was found to be 38.3 K cal/mol.

The effects of the various parameters on the conversion, approach to equilibrium and product gas composition are summarized in the following table.

	Steam Ratio↑	Temperature↑	Pressure↑	(W/F)↑
Conversion	→	↑	↑	↑
Approach to Equilibrium*		+	+	+
% H ₂	↑	↓	↓	↓
% CO	↓	↑	↑	↑
%CH ₄	↓	↓	↑	↓
%CO ₂	↑	↓	↑	↓

*approach to equilibrium is + when T decreases

These data indicate that the catalyst Ni-3-3 readily catalyzes the reaction of steam with benzene without coke formation at steam ratios of 3 or higher. To determine the effectiveness of the catalyst at conditions approaching those in commercial steam reformers, a run was made at 750°C, 400 psig (max. safe conditions for the lab reactor). (Commercial steam reforming of naphtha operates above 850°C, 500 psig, 3-4 steam/carbon ratio using promoted nickel catalysts of the same compositions studied herein.) The results of this run are presented in Table 2. Conversion was in excess of 99%. It was concluded that catalysts can be developed with sufficient activity to reform aromatics completely at equivalent conditions to those in commercial operation with naphtha. Yet to be shown in future studies are operations over longer periods of time with coal liquids and heavy petroleum feedstocks and the development of a sulfur resistant catalyst. Based on the results obtained so far and from recent reports of the development of a sulfur resistant catalyst, the prospects look bright.

Other work carried out in this program involved brief studies of the steam reforming of toluene, ethyl benzene, cumene, and methyl naphthalene. All these materials reformed readily; although, because of the alkyl groups, the reactions were more complicated than with benzene. Dealkylation and dehydrogenation were found to occur while isomerization and polymerization do not appear to take place. Conversions as a function of the main variables were studied and reaction networks to explain the hydrocarbon products observed were developed. For detail of these studies and more detail than that presented for benzene, the reader is referred to the thesis of Dr. S. K. Goyal (March 1979, University of Utah).

Conclusions

The results obtained from this study of the steam reforming of aromatic compounds indicate the following:

1. Thermodynamic results suggest that the steam reforming of aromatic compounds can be carried out with slightly higher minimum steam ratios compared with that for methane and naphtha.

2. The most active catalyst which requires a minimum steam ratio for the steam reforming of aromatic compounds is the sodium promoted nickel catalyst having a composition of 71.4% Al_2O_3 , 21.9% Ni and 6.70% Na (as Na_2O) on a wt basis.

3. The rate of reaction of benzene and steam over the above-mentioned catalyst is first order with respect to benzene and zero order with respect to steam, with an activation energy of 38.35 Kcal/mole, and the frequency factor is temperature dependent ($k_0 = aT^{3.5}$).

4. The primary products from the aromatic compounds steam reaction are hydrogen and carbon dioxide.

5. The rate of dealkylation of alkyl-benzenes is faster than the rate of ring breakdown.

6. In the steam reforming of aromatic compounds, isomerization and polymerization do not take place.

7. The rate of dealkylation decreases with increased temperature and pressure.

8. The dehydrogenation of higher alkyl benzenes increases with increased temperature and decreases with the increased pressure,

9. The reaction rate of alkyl benzenes decreases with the number of carbons in the side chain.

10. The reactivity of aromatic ring compounds decreases as the number of rings in the compound increases.

11. A fuel gas of medium heating value (up to 650 BTU/SCF) gas can be produced directly by steam reforming of aromatics.

Table 1
EFFECT OF STEAM RATIO AT 650°C ON
STEAM REFORMING OF BENZENE ON Ni-3-3

Run No.	8082	8083	8084
Feed Rate, cc/min.	2.22	2.22	2.22
Water Feed Rate, cc/min.	8.54	7.23	5.95
Steam Ratio	3.16	2.58	2.21
Methane Equivalent Space Velocity, hr ⁻¹	10087	10087	10087
W/F ($\frac{\text{gm. cat. min.}}{\text{gm. C}_6\text{H}_6}$)	10.249	10.249	10.249
LHSV ($\frac{\text{c.c. C}_6\text{H}_6}{\text{hr. gm. cat.}}$)	6.66	6.56	6.66
Catalyst Temp., °C	650	650	650
Conversion %	37.9	39.6	40.4
Product Gases, (c.c./ min. at S.T.P.)	4073	4297	4250
Vol. % H ₂	69.6	69.1	68.5
Vol. % CO	6.7	7.8	9.7
Vol. % CH ₄	0.1	0.1	0.2
Vol. % CO ₂	21.4	21.1	21.6
Product Liquid (c.c./min.)	8.10	6.60	5.40
Vol. % H ₂ O	83.0	80.0	75.7
Vol. % C ₆ H ₆	17.0	20.0	29.3
Carbon Balance	98.9	98.9	98.9
Coking	No	No	No
KWGS	1.190	1.309	1.254
KM/S	1.216	1.457	1.771

Table 2
RESULTS AT 750°C, 400 psi, OF
STEAM REFORMING OF BENZENE ON Ni-3-3

Run No.	E034
Feed Rate, c.c./min.	1.928
Water Feed Rate, c.c./min.	7.333
Steam Ratio	3.13
Methane Equivalent Space Velocity, hr ⁻¹	8760
W/F ($\frac{\text{gm. cat. min.}}{\text{gm. C}_6\text{H}_6}$)	11.80
LHSV ($\frac{\text{c.c. C}_6\text{H}_6}{\text{hr. gm. cat.}}$)	5.72
Catalyst Temp. °C	750
Pressure (psig)	400
Conversion %	99.7
Product Gas (c.c./min. at S.T.P.)	5907
Vol. % H ₂	51.3
Vol. % CO	8.2
Vol. % CH ₄	15.7
Vol. % CO ₂	25.1
Product Liquid (c.c./min.)	4.56
Vol. % H ₂ O	99.9
Vol. % C ₆ H ₆	0.1
Carbon Balance	98.8
Coking	No
KWGS	1.604
KM/S	2.89

Figure 1. Apparatus

Figure 2. Sintering of F-1 and H-151 (ALCOA) at 900°C.

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

Figure 4. Equilibrium Concentration of Methane as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 5. Equilibrium Concentration of Carbon Monoxide as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 6. Equilibrium Concentration of Carbon Dioxide as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 7. Equilibrium Concentration of Hydrogen as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 8. Heating Value of Dry Gas as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 9. Heating Value of CO₂ Free Dry Gas as a Function of Temperature, Pressure and Steam Ratio for Benzene.

Figure 10. Thermodynamic Minimum Steam Ratio as a Function of Temperature and Pressure for Benzene.

Figure 11. % conversion (550°C) and minimum steam ratio (700°C) for different amounts of sodium on Ni-3 (23% Ni) for benzene.

Figure 12. Effect of steam ratio on conversion of benzene.

Figure 13. Effect of steam ratio on conversion and product distribution for benzene-steam reaction (475°C).

Figure 14. Effect of steam ratio on conversion and product distribution for benzene-steam reaction (700°C).

Figure 15. Effect of temperature on conversion of benzene.

Figure 16. Effect of temperature on conversion and product distribution for benzene-steam reaction (W/F = 5, — Experimental and ---- Theoretical).

Figure 17. Effect of temperature on conversion and product distribution for benzene-steam reaction (W/F = 40, — Experimental and ---- Theoretical).

Figure 18. Effect of pressure on conversion of benzene.

Figure 19. Effect of pressure on conversion and product distribution for benzene-steam reaction ($W/F = 20$, 475°C - Experimental and ----- Theoretical).

Figure 20. Effect of pressure on conversion and product distribution for benzene-steam reaction ($W/F = 10$, 600°C - Experimental and ----- Theoretical).

Figure 21. Effect of pressure on conversion and product distribution for benzene-steam reaction ($W/F = 10$, 700°C - Experimental and ----- Theoretical).

Figure 22. Effect of residence time on conversion of benzene at different temperatures.

Figure 23. Effect of residence time on conversion and product distribution for benzene-steam reaction (700°C, — Experimental and ---- Theoretical).

Figure 24. First-order integral rate vs time factor.

Figure 25. The Arrhenius Plot for the rate constant (k) vs reciprocal of absolute temperature.

Study of Thermal and Vapor Phase Catalytic Upgrading
of Coal Liquids

Faculty Advisor: J. Shabtai

Introduction

Project A-7 comprised parallel systematic investigations of the 1) hydrogenation of coal-derived liquids (CDL) and related polycyclic arenes and heterocyclics in the presence of sulfided catalyst systems, 2) catalytic cracking of hydrotreated CDL and related polycyclic naphthenes and naphthenoaromatics, 3) hydropyrolysis of CDL and related model compounds, and 4) catalytic hydrodeoxygenation of CDL and related oxygen-containing compounds.

The main objective of research Project (1) was to develop a versatile process for controllable hydrotreating of highly aromatic coal liquids, viz., a process permitting production of feedstocks containing variable relative concentrations of hydroaromatic vs. aromatic ring structures. Such feedstocks, including the extreme case of a fully hydrogenated coal liquid, were examined (research Project 2) as starting materials for catalytic cracking, oriented toward preferential production of light liquid fuels. The overall objective of projects (1) and (2) was, therefore, to provide fundamental data needed for development and optimization of a hydrotreating-catalytic cracking process sequence for upgrading of coal-derived liquids into conventional fuels.

The objective of Project (3) was to develop and optimize a hydropyrolysis process as a novel, alternative approach to the upgrading of heavy coal liquids into light liquid products and/or C₂-C₄ gases.

Project (4) was undertaken to achieve a molecular-level understanding of the mechanism of hydrodeoxygenation of oxygen-containing components present in CDL feedstocks. This work was done to clarify the role of such compounds in sulfide-catalyzed upgrading reactions.

Results and Discussion

Project (1) was subdivided into three subjects. The first was a study of metal sulfide-catalyzed hydrogenation of model polycyclic arenes present in coal liquids, e.g., phenanthrene, pyrene, anthracene and triphenylene, as a function of catalyst type and experimental variables. This study provided basic information on the kinetics, mechanism and stereochemistry of hydrogenation of structurally distinct aromatic systems in the presence of sulfided catalysts.¹⁻⁵

Hydrogenation of phenanthrene (P) to perhydrophenanthrene (1) in the presence of sulfided Ni-W/Al₂O₃, Ni-Mo/Al₂O₃ and Co-Mo/Al₂O₃ proceeds via a series of partially hydrogenated intermediates, i.e., 9,10-dihydroP (2), 1,2,3,4-tetrahydroP (3), 1,2,3,4,5,6,7,8-octahydroP (4), 1,2,3,4,9,10,11,12-octahydroP (5) and isomeric mixtures of decahydroP (6) and dodecahydroP (7). Compound 3, which contains a strainless hydroaromatic ring derived from an end benzene ring, is the strongly preferred first step intermediate. Competing hydrogenation at C₉-C₁₀ to yield 2, which has a somewhat strained inner hydroaromatic ring, occurs to a lower extent. Subsequent hydrogenation of 3 is a fast step, yielding 4, which contains a residual inner aromatic ring. Flatwise adsorption of the latter on the sulfide catalyst surface is sterically hindered, and, consequently, hydrogenation of 4 to the final product 1 is a slow step, apparently involving edgewise adsorption of 4. As a result of this and other possible factors, the stereochemistry of hydrogenation of phenanthrene to 1 is fundamentally different from that found in the presence of metal catalysts belonging to the platinum group. With platinum catalysts the predominant perhydrophenanthrene stereoisomer formed has a cis-syn-cis configuration, while the main products obtained with sulfided catalysts are the trans-anti-trans and trans-anti-cis stereoisomers (essentially no cis-syn-cis isomer is observed). The dependence of the reaction stereochemistry upon the inherent steric characteristics of the reactant (and/or reaction intermediates) as well as upon the geometric-topographical constraints imposed by the sulfide catalyst surface is being elucidated and surface-reactant models at the molecular level are being developed.

The kinetics of sulfide-catalyzed hydrogenation of other polycyclic arenes shows similar dependence upon steric-geometric factors. For example, hydrogenation of pyrene (8) to yield 4,5-dihydropyrene (9), 1,2,3,3a,4,5-hexahydropyrene (10) and 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene (11) proceeds at a high rate, since steric interference with flatwise adsorption of intermediates 9 and 10 on the catalyst surface is minor. In contrast, the last-step hydrogenation of the residual tetrasubstituted ring in 11 to give perhydropyrene (12) proceeds at a low rate due to considerable steric hindrance for flatwise adsorption of this ring. Another example is the reaction of triphenylene (13), which contains a fully blocked, hexasubstituted aromatic ring. Hydrogenation of the peripheral rings in 13 to give dodecahydrotriphenylene (14) is fast, but subsequent hydrogenation of the residual central aromatic ring in 14 does not produce significant amounts of perhydrotriphenylene (15). This is in agreement with surface-reactant models which indicate that hydrogenation of 14 on a conventional sulfided surface is sterically and geometrically excluded.

Anthracene (16), which is a suitable representative compound of the class of condensed linear arenes, was also systematically investigated. Results on product composition changes in the range of 200-380°C (at 2900 psi) are given in Figures 1A and 1B.

As seen from Figure 1A, the main hydrogenation product from 1 at low temperature is 9,10-dihydroanthracene (17). This primary product is accompanied by smaller amounts of 1,2,3,4-tetrahydroanthracene (18), the anticipated alternative first-step product. With an increase in temperature from 200° to 350°C, there is a sharp decrease in the concentration of 17, while the concentration of compound 18 first slightly increases, and after passing through a maximum around 300°C, quickly decreases at a higher temperature. Simultaneously there is a rapid build up in the concentration of 1,2,3,4,5,6,7,8-octahydroanthracene (19). After reaching a maximum around 325°C, the concentration of compound 19 slowly decreases at higher temperatures, while the concentration of the final hydrogenation product, perhydroanthracene, slowly increases (Figure 1B). The change in concentration of 1,2,3,4,9,10,11,12-octahydroanthracene (20), which is formed in markedly lower amounts than the symmetric isomer 19, indicates that this intermediate compound also participates somewhat in the overall hydrogenation process.

To examine the possibility that the first-step intermediate 17 serves as a precursor of 1,2,3,4-tetrahydroanthracene (18), a comparative series of experiments were also carried out using 17 as a feedstock. The results obtained show that 17 is hydrogenated at a higher rate than anthracene (16) under identical experimental conditions. Further, the rapid increase in the concentration of the sym-octahydro derivative 19 with temperature is consistent with a fast hydrogenation-rearrangement step of 17 into 18, which precedes the hydrogenation of 18 to 19. The results obtained further provide evidence that the rate at which the 9,10-dihydroanthracene converts to 1,2,3,4-tetrahydroanthracene (18) is faster than the rate at which compound 18 converts to the sym-octahydroanthracene (19). Between 300°C and 325°C, compound 19 increases sharply while 1,2,3,4-tetrahydroanthracene (18) decreases sharply. This suggests that the sym-octahydroanthracene (19) is formed entirely from 18 as an intermediate.

At higher temperatures (Figure 1B), the sym-octahydroanthracene slowly decreases while the perhydroanthracene increases and the unsymmetric octahydroanthracene remains essentially unchanged. This indicates that hydrogenation of the unsymmetric octahydroanthracene to perhydroanthracene is even slower than hydrogenation of sym-octahydroanthracene to perhydroanthracene. Under these same conditions, there is almost a quantitative yield of perhydrophenanthrene from the hydrogenation of phenanthrene. Thus, the hydrogenation of sym-octahydrophenanthrene to perhydrophenanthrene is much faster than the hydrogenation of sym-octahydroanthracene to perhydrophenanthrene over the sulfided Ni-W catalyst used. This information is very important, since it indicates that in linear polycyclic naphthenoaromatic components of coal liquids,

any aromatic ring flanked by two naphthenic rings (as in compound 19) may show considerable resistance to hydrogenation.

The change in product composition from the hydrogenation of anthracene as a function of hydrogen pressure in the range of 250 to 2000 psi (temperature, 341°C) is summarized in Figures 2A and 2B. The patterns are generally consistent with those in the study of the temperature effect, although the above mentioned slow rate of hydrogenation of 19 into perhydroanthracene is more clearly seen (Figure 2B).

The data in Figures 1A and 1B indicate that the sulfided Ni-W/Al₂O₃ catalyst causes some skeletal isomerization of sym-octahydroanthracene or its precursors into hydrogenated phenanthrene derivatives. This was confirmed when sym-octahydroanthracene was reacted at 300°C over the same catalyst under nitrogen pressure, P=600 psig, for 2 hours. The ratio of sym-octahydrophenanthrene to sym-octahydroanthracene in the product was 0.3.

The results obtained in the hydrogenation study of anthracene can be rationalized by a mechanism as outlined in Figure 3. Kinetic studies confirmed this mechanism.

An account of the above mentioned hydrogenation studies, including reaction kinetics and stereochemistry, will be published shortly in the J. Catalysis.

The results obtained provide a plausible explanation for the observed resistance of coal-derived liquids to complete (exhaustive) hydrogenation in the presence of conventional sulfided catalysts, even when the aromatic saturation equilibria are fully displaced in the direction of saturation. To overcome this and other limitations in the application of conventional sulfided catalysts, a systematic structural-activity study of sulfided catalysts at the molecular level was recently initiated in collaboration with Dr. F.E. Massoth. The objective of this new project is to develop the theoretical background for designing and optimizing a new generation of sulfided catalysts for coal-liquid and petroleum upgrading (Project B-1, funded by the Department of Energy under a new contract).

The second subject of Project (1) involved a study of metal sulfide-catalyzed hydrogenation-hydrodenitrogenation of condensed N-heterocyclics as a function of molecular structure and experimental conditions. This study provided basic information on the kinetics, mechanism and stereochemistry of hydrodenitrogenation of structurally distinct multiring (ring number ≥ 3) N-heterocyclics found as typical components of coal-derived liquids.

Marked differences are observed in comparative high pressure (500-2900 psig) hydrogenation of 5,6-benzoquinoline (1) and 7,8-benzoquinoline (2) in the presence of sulfided Ni-W/Al₂O₃. The first reaction step, involving hydrogenation of the pyridine ring, is faster by at least one order of magnitude with 1 than with 2.

This can be attributed to the steric effect of the 7,8-benzo-group, which prevents edgewise adsorption of 2 through the pyridine nitrogen. In contrast, such adsorption, which could polarize the pyridine ring and facilitate hydrogenation, is easily attained with 1. In the subsequent reaction step, the intermediate from 2, viz., 1,2,3,4-tetrahydro-7,8-benzoquinoline (3), undergoes direct hydrodenitrogenation to yield 6-n-propyl-naphthalene (4). However, the intermediate from 1, viz., 1,2,3,4-tetrahydro-5,6-benzoquinoline (5), undergoes essentially complete hydrogenation of the end benzene ring to form 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline (6) prior to the hydrogenolysis step. The latter ultimately yields 5-n-propyl-1,2,3,4-tetrahydronaphthalene (7). The direct hydrogenolysis of 3 is apparently due to the destabilizing steric effect exercised by the peri H-atom at C-14 upon the C-N bonds in the hydrogenated pyridine ring. The strong influence of steric effects, mode of adsorption and catalyst surface structure upon the rate and direction of hydrodenitrogenation was clearly evident also in studies with other model compounds, e.g., 1,10-phenanthroline and phenanthridine.

The third subject of Project (1) involved a study of the metal sulfide catalyzed hydrogenation of coal-derived liquids (CDL). The hydrogenation of Synthoil and fractions derived from Synthoil was systematically investigated (in a specially designed fixed bed flow reactor) as a function of experimental variables, e.g., process time, temperature, pressure, hydrogen/substrate ratio and space velocity. The indicated optimal conditions for hydrogenation of Synthoil, as reflected in the depth and selectivity of the process, are 340°C, 2900 psig and LHSV=0.5 hr⁻¹ (catalyst, sulfided Ni-Mo/Al₂O₃). At temperatures >350°C the hydrogenation selectivity is lower due to side reactions, in particular cracking. It is found by C¹³NMR analysis that even under the above indicated optimal conditions the hydrotreated product contains 15-20% of residual aromatic rings. Since under such conditions the aromatic saturation equilibria of polycyclic arenes are displaced in the direction of saturation, it was concluded, in line with results obtained with the model compounds, that the resistance of CDL to exhaustive hydrogenation is due to steric and surface geometry factors. Further, results of the HDN studies of CDL and model compounds indicate that commercial sulfided catalysts possess insufficient C-N hydrogenolysis activity. This latter observation points to the necessity of research on a new generation of improved sulfided catalysts.

In the framework of Project (2), the feasibility of a hydro-treating catalytic cracking process sequence for upgrading of coal liquids was examined by performing a detailed catalytic cracking study of hydrogenated coal-derived liquids (hydro-CDL) and related polycyclic naphthenes and naphthenoaromatics.⁶ In spite of the major industrial importance of catalytic cracking processes, there are relatively scarce molecular-level data on the variation of product composition as a function of catalyst type, nature of feed-stock and operating conditions. This is particularly true for catalytic cracking of polycyclic naphthenes,

as essentially no data have been reported previously on the exact molecular structure of product components even from simple bicyclic naphthenes, e.g., decalin. Since hydrogenated coal liquids consist mostly of polycyclic naphthenes and naphthenoaromatics, a systematic cracking study of representative model compounds, e.g., decalin, perhydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydrophenanthrene and 9,10-dihydroanthracene, was first carried out. This was followed by a catalytic cracking study of hydro-CDL samples, in particular a hydro-treated SRC middle-heavy distillate.

Catalysts applied in the study included both conventional zeolite-containing systems, e.g., Mobil Durabead, as well as newly developed large-pore molecular sieves. The latter are prepared by cross-linking of layer silicates and are designated as CLS catalysts. Strongly acidic forms of CLS were tested as cracking catalysts. Such CLS 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.⁷

The following are some typical results obtained with decalin (1) and perhydrophenanthrene (2) as feedstocks, using a conventional zeolite-containing catalyst (Mobil Durabead-8): In the mild temperature range of 300-450°C and at LHSV=0.65 hr⁻¹, the conversion of 1 increases from ca. 45% to ca. 95% by wt. The selectivity for formation of liquid products is very high (> 90%), while formation of gases and coke is very low. The C₁₀ alkylcyclohexenes, which are indicated as primary cracking products, represent the major fraction of 300°C. These compounds steadily decrease in concentration with an increase in temperature, while the concentration of C₁₀ alkylbenzenes, which are derived from the C₁₀ alkylcyclohexenes by hydrogen transfer, passes through a maximum at about 325°C and then decreases, due to dealkylation reactions at higher temperature. The C₆-C₉ benzenes, formed by complete or partial dealkylation of the C₁₀ alkylbenzenes and by aromatization of dealkylated C₁₀ alkylcyclohexenes, increase steadily in concentration with temperature. The C₆-C₈ cyclanes, which consist mainly of methylcyclopentane, dimethylcyclopentane and methylcyclohexane, are also formed. Such products pass through a maximum around 425°C and then decrease due to secondary cracking. In addition to the above mentioned C₆-C₉ alkylbenzenes, the most important cracking products at temperatures above 400°C are C₅-C₈ paraffins and olefins. Changes in product composition as a function of contact time follow the same patterns.

Results from cracking of perhydrophenanthrene (2) show that in the mild temperature range of 325-425°C and a LHSV=0.75 hr⁻¹ the conversion of compound 2 increases from 43 to 96% with preservation of high selectivity for production of liquid products. The change in liquid product composition as a function of reaction temperature was investigated in detail. The C₁₄ octahydroanthracenes, which are indicated as the primary cracking products, decrease steadily with increasing temperature. Further,

lower cyclenes and cyclanes derived from these primary products, e.g., C₁₁ tetrahydronaphthalenes, decalin, tetrahydronaphthalene, methylindan, C₁₀ alkylcyclohexenes, and C₆-C₇ cyclanes and cyclenes, first pass through a maximum and then decrease with a further increase in temperature. At temperatures above 375°C, C₅-C₈ open-chain paraffins and olefins and C₆-C₉ benzenes gradually become main liquid products.

Subsequent to the investigation with polycyclic naphthenes and naphthenoaromatics, a detailed catalytic cracking study of hydro-CDL samples was carried out, using a range of conditions indicated as optimal for conversion of the above mentioned model compounds into light liquid products.

The feedstocks used in this part of the study consisted of (a) a middle-heavy distillate (230-455°C) of the SRC II product; and (b) four liquid products obtained by hydrotreatment of the above fraction to different saturation depths. The analyses, C-aromaticities and densities of these five feedstocks are summarized in Table 1. The changes in product composition as a function of temperature, space velocity (LHSV), and catalyst type, were investigated in detail.⁶ Figure 4 summarizes the yields of gasoline-range products from cracking of the hydrotreated SRC II liquids as a function of reaction temperature and depth of hydrotreatment. As in the case of polycyclic naphthenes and naphthenoaromatics, the selectivity for liquid product formation is very high (>80%).⁶ Figures 5 and 6 show gas chromatograms of the liquid product from cracking of the SRC II D feed. Figure 5 indicates a gradual conversion to lower boiling liquids with increase in cracking temperature, while Figure 6 illustrates the similarity in the bp range of the products with those obtained from perhydrophenanthrene (2).

The following conclusions were reached on the basis of results obtained:

(1) Hydrotreated SRC II liquids and structurally related polycyclic naphthenes and naphthenoaromatics undergo smooth catalytic cracking under mild temperature conditions (325-425°C) to yield predominantly light liquid products, with little concurrent gasification and very low coke formation.

(2) The composition of liquid products from catalytic cracking of hydro-SRC II and related polycyclic naphthenes is easily controllable, and by appropriate coordination of operating variables, gasoline-range products containing high concentrations of iso-paraffins, C₅-C₁₂ naphthenes and C₆-C₁₂ benzenes can be obtained.

The great potential of the newly developed, large-pore cross-linked smectite (CLS) catalysts for cracking of heavy feedstocks was demonstrated in comparative cracking studies with bulky (kinetic diameter ≥ 11 Å) polycyclic naphthenes and naphthenoaromatics, e.g., perhydrophenanthrene and 1,2,3,4,5,6,7,8-octahydrophenanthrene, indicating a sharply higher activity of RE-Al-CLM (rare-earth exchanged hydroxy-aluminum montmorillonite) than

that of conventional REY-type zeolite catalysts, e.g., Mobil Durabead. Results obtained will be presented at the 7th International Congress on Catalysis, Tokyo, 1980.⁸

Project (3) was concerned with the development of a new processing concept for upgrading of coal liquids and other heavy oils into light liquids and/or C₂-C₄ gaseous products. The process involves hydropyrolysis (non-catalytic hydrocracking) in the temperature range of 480-650°C and hydrogen pressures of 120-2250 psig. Three types of starting feeds, including model compounds, were employed in the study: a) normal paraffins, in particular n-hexadecane; b) polycyclic naphthenes, in particular decalin and c) coal liquids and other heavy oils or solids. A special reactor for hydropyrolysis under quantitative conditions was designed and constructed for the purpose of this investigation. The change in product composition as a function of feedstock chemical structure and of experimental conditions was systematically investigated, and mechanistic aspects of the thermal hydrocracking process were elucidated.^{9,10}

Some typical results of hydropyrolysis of C₁₀-C₁₆ n-paraffins, follows: The hydropyrolysis of n-hexadecane (1) was systematically investigated as a function of experimental variables, i.e., temperature, hydrogen pressure and space velocity (LHSV). The study was performed in comparison with a parallel investigation of thermal cracking of 1 under nitrogen pressure, using otherwise identical operating conditions. For the temperature range (480-600°C) and pressure range (500-2250 psig) studied, the rate of hydropyrolysis of 1 is markedly higher than that of thermal cracking of the same compound under nitrogen. Further, unlike thermal cracking, hydropyrolysis is an easily controllable process, which by proper selection of temperature, hydrogen pressure and contact time, can be operated for preferential formation of products of any desired molecular weight range lower than that of the starting material. For example, at 525°C and a hydrogen pressure of 1000 psig, hydropyrolysis of 1 yields mainly (~55% by wt) C₅-C₁₂ liquid products, whereas at 575°C and a pressure of 2250 psig, 1 is converted almost entirely, viz., 92% by wt, into C₁-C₄ gaseous products (C₂-C₃ hydrocarbons comprise 76% of the total gas product, while methane formation is low). Variation in experimental conditions also affects the structural type distribution of the products. For a given pressure, the relative yield of 1-olefins decreases, while that of paraffins and internal olefins increases (and ultimately tends toward a stable level) with an increase in temperature. Further, for a given temperature the concentration of paraffins increases, while that of 1-olefins quickly decreases with an increase in pressure; internal olefins slightly increase and then remain at a stable level with an increase in pressure. The systematic study of 1 provided a basic understanding of the hydropyrolysis process. The results were interpreted by means of a chain mechanism.¹⁰

The initiation step under mild temperature and pressure involves homolytic cleavage of a C-C bond in 1 to produce two lower molecular weight primary radicals. The latter are

preferably saturated by interaction with molecular hydrogen. Hydrogen atoms thus produced propagate the chain by abstraction of hydrogen from other hydrocarbon molecules. Such abstraction preferably yields a secondary radical, which upon splitting gives a lower primary radical and a 1-olefin. Lower radicals formed by such splitting become saturated by interaction with hydrogen or hydrocarbon molecules to give product paraffins with regeneration of the reaction chain. Higher 1-olefins formed as intermediate products undergo secondary reactions such as double bond isomerization, allylic cleavage and non-catalytic hydrogenation (under high hydrogen pressure only), thus contributing to the final composition of the product.

Similar hydropyrolysis patterns were obtained in experiments with C₁₀-C₁₄ n-paraffins as feedstocks. The hydropyrolysis of decalin (2), selected as a representative compound of the important class of polycyclic naphthenes, was systematically investigated as a function of reaction temperature and hydrogen pressure. The product composition from 2 and its change as a function of reaction variables is markedly different compared with that from 1, as illustrated by the following: a) Liquid (C₅-C₁₀) products are strongly predominant (yields 60-95% by wt) between 500-600°C; correspondingly, the relative yield of C₁-C₄ products is much lower than that from 1 under identical conditions; b) At 500-525°C, practically the only products from 2 are C₁₀ alkylcyclohexenes and 1,2,3,4,5,6,7,8-octahydroanthralene; between 525-600°C, these primary products gradually evolve into lower (C₆-C₈) cyclohexenes and C₅-C₈ open-chain (mainly branched) hydrocarbons and to a small extent into C₆-C₈ arenes; the conversion temperature of the initial products into lower (C₅-C₈) liquid products can be reduced by an increase in the operating hydrogen pressure; c) Under any set of identical operating conditions, thermal cracking of 2 under nitrogen pressure proceeds with much lower overall conversion than in hydropyrolysis and with formation of large amounts (10-40% by wt) of high boiling condensation and aromatization products. In comparison, no products higher than the feedstock are formed in hydropyrolysis of 2. The activation energy found for hydropyrolysis of decalin is around 59.0 kcal/mole. This is lower than reported values of 64.3-72.0 kcal/mole for thermal cracking of decalin.

Results obtained can be explained by the following mechanism: The reaction is initiated by preferential abstraction of a tertiary hydrogen in 2 by means of an initiator such as R· or H· (alternative abstraction at secondary carbon positions also occurs but to a lower extent). The resulting tertiary radical undergoes β-splitting to form unsaturated C₁₀ radicals, which by hydrogen abstraction yield 1-butylcyclohexene and 1-methyl-3-propylcyclohexene. Alternatively, the intermediate C₁₀ radicals can undergo additional β-scission steps to yield C₆-C₈ cyclohexenes. Additional β-splitting reactions of alkylcyclohexene products result in cleavage of the second ring (in the original bicyclic starting compound) to yield C₅-C₈ open-chain paraffins and olefins.

A reaction competing with the above is removal of the second tertiary hydrogen in 2 to form 1,2,3,4,5,6,7,8-octahydronaphthalene, which upon splitting yields cyclic dienes serving as precursors of C₆-C₁₀ alkylbenzenes. Alternatively, the octahydronaphthalene may undergo dehydrogenation to tetrahydronaphthalene which upon splitting yields C₆-C₁₀ arenes.

Hydropyrolytic experiments with higher polycyclic naphthenes, e.g., perhydrophenanthrene, show similar, easily controllable decomposition patterns.

Hydropyrolysis studies were carried out using the following types of feedstocks: a) Synthoil - characterized as a mostly aromatic coal liquid; b) Asphalt Ridge (Utah) tar sands bitumen - a highly naphthenic crude and c) Altamont (Utah) crude - a highly paraffinic crude. All of these feedstocks are highly viscous (semisolid) at room temperature. The results show that hydropyrolysis (in the temperature range of 450-575°C and a hydrogen pressure range of 250-2500 psig) is a very efficient process for conversion of such heavy feedstocks into light liquid products, as illustrated by the following examples:

1. Synthoil, which contains about 45% by wt of components boiling above 500°C (as found by simulated distillation) is hydropyrolyzed at 525°C and a hydrogen pressure of 1500 psig to yield 26% of gaseous products and 74% of light liquid products distilling between 60-380°C.

2. Asphalt Ridge tar sands bitumen, which distills only to the extent of 40% by wt up to 530°C, is hydropyrolyzed at 500°C and a hydrogen pressure of 1500 psig to yield 17% gaseous products and 83% of a light oil distilling between 105-450°C; at 525°C and 1500 psig, the yield of light liquid boiling between 30-400°C is 73% by wt.

3. Altamont crude, which is a solid material distilling to the extent of 90% between 160-450°C (as determined by simulated distillation) is hydropyrolyzed at 550°C and a hydrogen pressure of 1000 psig to yield 75% of a light liquid product distilling between 30-350°C; at 575°C and a pressure of only 250 psig, the yield of light liquid distilling between 50-400°C is 71% by wt.

These and other results demonstrated the high efficiency and versatility of hydropyrolysis as a process for conversion of heavy coal liquids and other heavy oils into light liquid products and C₂-C₄ gases. This newly developed process concept for upgrading and utilization of coal liquids seems to be highly superior to conventional techniques, such as coking.¹⁰

A systematic hydrodeoxygenation (HDO) study of coal liquids and related O-containing compounds was initiated during the last year of the contract. The feedstocks examined included model compounds, e.g., polycyclic ethers, phenols, ketones and esters, as well as coal liquids, e.g., SRC fractions. These studies are exemplified by the following summary of results obtained with a representative cyclic ether, i.e., isochroman (1);

The change in product composition from 1 as a function of experimental conditions, i.e., catalyst type, reaction temperature and contact time, was investigated in detail. In the presence of sulfided Ni-W/Al₂O₃ or Co-Mo/Al₂O₃ as catalysts, the main products from 1 at low temperatures (170-200°C) are the dibenzyl ether 2 and alcohols 3 and 4:

Extrapolation to temperatures below 170°C indicates that the main product under such conditions is ether 2. With a gradual increase in temperature above 170°C, there is a gradual decrease in the concentration of 2, while the concentration of 3 and 4 sharply increases. After reaching a maximum of ca. 70 mole % at a temperature near 230°C, the concentration of alcohols 3 and 4 decreases at a higher temperature, while that of the final deoxygenated product, i.e., methylethylbenzene (5), correspondingly increases. At this higher temperature range (230-290°C), there is also formation of the unsaturated alcohols 6 and 7. Similar trends are also observed with a sulfided Co-Mo/Al₂O₃ catalyst

although there are also some significant differences. In particular a markedly lower rate of hydrodeoxygenation with the Co-Mo catalyst is observed, as reflected in the much lower extent of formation of the final product 5 at temperatures above 230°C. Further, there is only a small extent of formation of 6 and 7, apparently due to the lower acidity of the sulfided Co-Mo/Al₂O₃ catalyst. The lower hydrodeoxygenation activity of the latter catalyst may be due to faster poisoning by polymerization of intermediate unsaturated products (*vide infra*).

The change in product composition from HDO of 1 as a function of reaction time at a temperature of 290°C, keeping a constant pressure of 1550 psig and using the sulfided Ni-W/Al₂O₃ catalyst was also studied. The concentration of 3 and 4 first increases with time and then, after a period of 5 min, gradually decreases. Also the concentration of the final product 5 first decreases and then, after about 5 min, gradually increases. This behavior is obviously due to the instability and apparent over-activity

of the fresh catalyst. After formation of some water by hydrodeoxygenation, the catalyst is quickly stabilized, and at reaction times longer than 5 min, the change in composition follows the anticipated pattern, viz., a gradual decrease in the concentration of the intermediate alcohols 3 and 4, and a corresponding gradual increase in the concentration of the final HDO product 5. At the relatively high temperature employed (290°C), the extent of formation of ether 2 is lower than that of ethers 3 and 4.

The results obtained can be rationalized by considering the mechanism outlined in Figure 7. In the first reaction step, the isochroman (1) could form a surface alkoxide intermediate by chemisorption and associated cleavage of the heterocyclic ring. Subsequent reaction of such alkoxide species would involve either protonation to yield alcohols 3 and 4, or etherification, viz., interaction of two chemisorbed species, to yield compound 2. At low temperatures the protonic acidity of the sulfided catalyst is low and, consequently, protonation of the postulated alkoxide species to yield alcohols 3 and 4 would proceed at a lower rate than the etherification reaction which could easily proceed by a concerted mechanism. However, at higher temperatures protonation of the alkoxide species is fast, which would result in preferential formation of 3 and 4.

The indicated preferred pathway of deoxygenation in the range of 200-290°C involves hydrogenolysis of the intermediate alcohols 3 and 4. However, at temperatures below 200°C hydrogenolysis of the ether intermediate 2 becomes competitive. Formation of methylstyrenes (9) via hydrogenolysis of the unsaturated alcohols 6 and 7 also contributes to the overall HDO process. Indeed, formation of methylstyrenes (9) as indicated above, or by dehydration of 4, may be responsible for the gradual deactivation of the sulfided catalyst, since such reactive monomers can be expected to undergo fast polymerization (coking) under the experimental conditions. The systematic study of 1, therefore, indicates for the first time certain reaction pathways by which oxygen-containing compounds may produce reactive poison precursors leading to coke formation in conventional sulfided catalysts.

Formation of reactive intermediates was also found in HDO of oxygen-containing ketones, esters and phenolic derivatives, as well as of CDL fractions. Thus, contrary to prevailing views, HDO is not a simple and relatively nonsequential reaction in catalytic upgrading of coal liquids, but rather a very complex process leading to major catalyst deactivation problems. Results obtained also point to the strong necessity of systematic work on the synthesis of a new generation of sulfided catalyst systems having higher C-O hydrogenolysis activity as compared to that of conventional commercial catalysts.

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Table 1

Properties of Untreated and Hydrotreated SRC-II Liquid Feedstocks.

Type of feedstock	Untreated middle-heavy distillate fr. ^a	Hydrotreated SRC-II liquids ^{b,c}			
Denotation	SRC-II	SRC-IIA	SRC-IIB	SRC-IIC	SRC-IID
Elemental Composition, % by wt.					
Carbon	87.29	87.90	88.32	88.03	86.35
Hydrogen	8.34	10.00	10.60	11.45	13.54
Oxygen	2.90	1.00	0.80	< 0.5	< 0.1
Nitrogen	1.20	1.09	0.28	< 0.014	< 0.01
Sulfur	0.27	< 0.01	< 0.01	0	0
C-Aromaticity, %	64	52	46	40	12
Density, g/cc	1.28	1.16	1.15	1.15	1.01

^aB. p. range, 230 - 455°C; ^bObtained by hydrotreatment of SRC-II middle-heavy distillate fraction (hydrogenation depth increases gradually from SRC-IIA to SRC-IID); ^cCatalyst: sulfided Ni-W/Al₂O₃ (Nalco Sphercat 550).

(A)

(B)

Figure 7. Change in product composition from hydrogenation of anthracene as a function of temperature. Pressure: 2900 psig.

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

FIG. 3 INDICATED MECHANISM OF ANTHRACENE HYDROGENATION
(CATALYST: Ni-W-S/Al₂O₃) *

* Accurate kinetic measurements (to be reported in J. Catalysis) indicate that Steps 1 and 2 (as reflected in k_1 and k_2) are very fast; Steps 5 and 6 (k_5 and k_6) are fast; Step 4 (k_4) is slow; Steps 7 and 8 (k_7 and k_8) are very slow; and Step 3 essentially does not occur (k_3 value close to zero).

Figure 4. Total Liquids Yield and Gasoline Liquids (C₅ - 230°C) Yield from Cracking of Hydrotreated SRC-II as a Function of Reaction Temperature and Depth of Hydrotreatment (catalyst, Durabead-8; LHSV, 0.38 hr⁻¹; C-aromaticity (%): SRC-II, 64; IIA, 52; IIB, 46; IIC, 40; IID, 12).

Figure 5. Chromatograms of SRC middle-heavy distillate and the liquid product from catalytic cracking (Catalyst, Mobil-Durabead-8).

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LIQUID PRODUCT FROM HYDROGENATION
FOLLOWED BY CAT. CRACKING OF SRC II
AT 375° C AND LHSV = 0.48 Hr⁻¹

GAS CHROMATOGRAPH PEAK INTENSITY

LIQUID PRODUCT FROM CAT. CRACKING OF
PERHYDROPHENANTHRENE AT 375° C &
LHSV = 0.44 Hr⁻¹

RETENTION TIME, MINUTES

Figure 6. Chromatograms of liquid product from catalytic cracking of perhydrophenanthrene and hydrogenated SRC II (Catalyst, Mobil-Durabead-8).

Fig 7 Suggested Mechanism of Isochroman Hydrodeoxygenation

Synthesis of Light Hydrocarbons from H_2 and CO

Faculty Advisors: F.V. Hanson
A.G. Oblad

Introduction

The increasing dependence of the United States upon imported petroleum to meet its liquid fuel requirements has focused considerable attention on the development of alternative energy resources. In general, these efforts have been directed toward the production of liquids derived from coal, shale kerogen or bitumen-impregnated sandstones and the production of synthesis gas from coal for the indirect liquefaction via Fischer-Tropsch related technology. A process strategy which has not received as much support from the Department of Energy as it deserves is the production of low molecular weight olefins and BTX (benzene, toluene and xylenes) from hydrogen and carbon monoxide rather than from petroleum feedstocks. If a substantial fraction of these commodity chemicals could be produced via the hydrogenation of carbon monoxide, a significant amount of our domestic petroleum resource could be diverted to the production of liquid fuels.

The primary focus of past carbon monoxide hydrogenation studies has been either directed to the production of synthetic natural gas or to the production of liquid fuels. The reported process variables were 1-25 atmospheres pressure, 473-573 K reactor temperature, 1-2 hydrogen to carbon monoxide ratio and gas hourly space velocities of approximately 3000-5000. Unfortunately, there is a paucity of reported work on specific investigations aimed at the development of catalytic materials selective for the production of low molecular weight olefins. In addition, very few process variables and reactor studies have been reported for the production of low molecular weight olefins from hydrogen and carbon monoxide.

The objectives of this project were to screen a significant number of promoted and unpromoted mono- and multimetallic catalysts containing iron, cobalt and nickel for the hydrogenation of carbon monoxide to produce low molecular weight olefins. The more active and/or selective catalysts would later be subjected to extended process variable studies. The catalyst evaluation parameters, temperature, pressure and H_2/CO ratio were determined by the activity and selectivity exhibited by the catalysts whereas the space velocity, 3000-5000 GHSV, was limited to the range of values typical of commercial operations of similar or related conversion processes.

Extensive literature surveys of the carbon monoxide literature have been reported^{1,2} and are beyond the scope of this report.

Experimental

1. Catalyst Preparation

The catalysts used in these investigations were prepared by conventional coprecipitation and impregnation techniques.^{3,4} All catalysts investigated were prepared in the laboratory due to the lack of commercially prepared catalysts. The details of the preparation procedures are described below.

Coprecipitation Technique

Individual solutions of the metal nitrate salts were prepared and combined in the appropriate proportions to give the atomic ratios of the metals desired in the final catalyst (i.e., copper-nickel, copper-cobalt, iron-manganese, etc). The precipitated catalyst was formed by adding the mixture of nitrate salts slowly to an alkali solution (sodium carbonate) or to an hydroxide solution (ammonium hydroxide) at a specified temperature. In some instances the alkali solution was added to the mixture of metal salts. The solution was continuously stirred during the precipitation and the pH was maintained above 9 at all times to insure complete precipitation of the metals.

When the precipitation was complete, the catalyst was collected by filtration. The wet coke was then washed with hot distilled water until the coke was nitrate or carbonate free. The nitrate or carbonate free wet coke was dried overnight at 373K.

Impregnation Technique

The appropriate amount of metal salts were dissolved in the minimum amount of distilled water (defined to be that amount of water required to just fill the pore volume of the support material). The metal salt solution was added to the support material and the water was evaporated. The support-metal support mixture was dried overnight at 373K. The catalysts used in the screening tests are presented in Table 1, whereas the copper-cobalt catalysts and the iron-manganese catalysts used in the extended process variable studies are listed in Tables 2 and 3, respectively.

2. Catalyst Evaluation Apparatus

A schematic of the bench-scale fixed bed reactor system used to evaluate the catalysts in both the screening and process variable phases of the project is presented in Figure 1. The catalysts were evaluated at nearly isothermal conditions. The details of the experimental apparatus and the operating and analytical procedures have been reported previously.^{1,2} The standard catalyst test conditions were 500 psig reactor pressure, a hydrogen/carbon monoxide ratio of two, a space velocity of $1.06 \text{ cm}^3 (\text{g catalyst})^{-1} \text{s}^{-1}$ and reactor temperatures in the range 473-523K depending upon the desired conversion level in the screening studies. The exothermic nature of the carbon monoxide hydrogenation makes it imperative that the conversion level be maintained at reasonably low levels. Therefore, in all experiments the conversion of carbon monoxide was kept below 10% which corresponded to an observed reactor temperature rise of less than 2°C.

The process variables studied in these investigations were reactor temperature at constant pressure, space velocity and

hydrogen/carbon monoxide ratio; space velocity at constant pressure, hydrogen/carbon monoxide ratio and carbon monoxide conversion; hydrogen/carbon monoxide ratio at constant pressure, space velocity and carbon monoxide conversion; and reactor pressure at constant space velocity, hydrogen/carbon monoxide ratio and carbon monoxide conversion. The process variable investigation for the manganese-iron system was conducted with four of the catalysts, that is, Mn/100Fe = 2.2, Mn/100Fe = 8.4, Mn/100Fe = 63 and Mn/100Fe = 278 and for the copper-cobalt system with a single catalyst having a copper to cobalt ratio of about 0.8. The catalysts were activated in-situ in flowing hydrogen at 773K and 15 psig hydrogen pressure for 20 hours.

The reproducibility of the catalyst evaluation technique was determined and the data were found to be reproducible to within 5-10 percent.

Results and Discussion

The data developed in the course of these investigations will be discussed under three headings; that is, the catalysts screening experiments, the copper-cobalt catalyst system investigation and the iron-manganese catalyst process variable investigation.

Catalyst Screening Experiments

The catalyst screening program was initiated by investigating the activity and selectivity of a series of Fischer-Tropsch type metal catalysts which included iron, cobalt, nickel, copper and cobalt-thorin. The results of these initial screening tests are presented in Table 4. The iron catalysts tested were olefin selective relative to the other metals, rejected oxygen in the form of carbon monoxide as expected, and did not produce excessive amounts of methane. The olefin selectivity revealed in these preliminary tests led to the selection of iron as a candidate for expanded study.

The cobalt catalyst exhibited approximately equal selectivities for the three primary "lumps" in the product slate, that is, methane, low molecular weight hydrocarbons (C_2-C_4) and higher boiling hydrocarbons (C_5^+). The olefin selectivity was somewhat lower than that of the iron catalysts; however, approximately 40% of the low molecular weight hydrocarbons were olefinic. As expected, the oxygen was rejected in the form of water and no alcohols were detected in the product. The reasonable olefin/paraffin ratio and yield of low molecular weight hydrocarbon led to the inclusion of cobalt for expanded study. The copper, nickel and copper-nickel catalysts were not included in the expanded screening tests because they failed to produce any but expected results; that is, copper was highly selective for alcohol and the nickel catalyst was selective for methane.

The expanded catalyst screening program was initiated by investigating the activity and selectivity of a series of iron and promoted iron catalysts for the hydrogenation of carbon monoxide. The focus was on singly promoted catalysts as the

addition of two or more promoters simultaneously made it virtually impossible to interpret the effects of individual promoters. The basic for comparison of catalysts prepared in the laboratory was Imperial Chemical Industries' (ICI) ammonia synthesis catalyst. A precipitated iron catalyst was prepared in the laboratory as a basis for comparison and this same technique was used to prepare all promoted iron catalysts. The promoters selected for use in this investigation were zinc, copper, chromium, magnesium, manganese, calcium and potassium. The iron catalysts screened included both singly and doubly promoted catalysts. The results of the screening tests with these iron catalysts are presented in Table 5. The precipitated iron catalysts were more stable than the ICI catalyst; however, they were less active. The rapid deactivation of the ICI catalyst was probably related to the high conversion of carbon monoxide which is speculated to have been accompanied by rapid deposition of a carbonaceous residue on the catalyst which would have accompanied the high catalyst surface temperature that would be expected at such high conversion levels (75-80%). A series of promoted, precipitated iron catalysts was prepared for each promoter and evaluated to determine which promoter was the most selective for low molecular weight hydrocarbons and to determine the preferred promoter concentration. Manganese was found to be the most effective promoter for low molecular weight hydrocarbon selectivity (Figure 2) and was found to have little effect upon the water gas shift activity of the iron. The suppression of methane selectivity by the addition of potassium to the precipitated iron catalyst (Figure 3) leads to the suggestion that a precipitated iron catalyst doubly promoted with potassium and manganese might be a highly selective catalyst for the production of low molecular weight olefins.

Process Variable Investigation: Iron Manganese Catalyst System

The results of the evaluation of the iron-manganese catalyst system for the production of low molecular weight olefins are summarized in Figure 4. The temperature required to maintain the carbon monoxide conversion constant at 7.0 to 7.5 percent is plotted against the catalyst composition in Figure 5.

The yield of low molecular weight hydrocarbons was independent of the composition of the catalyst; that is, it was approximately 50 percent for all catalysts tested ($\text{Mn}/100\text{Fe} = 0$ to $\text{Mn}/100\text{Fe} = 607$). The selectivity exhibited two distinct transitions; that is, the olefin/paraffin ratio increased from a value of 1 for the pure iron to a value of 2.5 to 3 for the manganese-iron catalysts having a composition in the range $\text{Mn}/100\text{Fe} = 2.2$ to 63. The olefin-paraffin ratio then decreased significantly for catalysts containing more than 100 parts of Mn per 100 parts of Fe. Concomitant with this loss of olefin selectivity was an increase in methane production.

The investigation of the effect of catalyst composition upon selectivity can be conducted in either of two operational modes; that is, at constant catalyst temperature where the conversion is allowed to vary as the other process variables or catalyst composition are changed or at constant reactant conversion where the catalyst temperature is adjusted to maintain constant

conversion as the process variables or catalyst composition are changed. The majority of the work reported here was obtained in the constant conversion mode; however, one of the catalysts (Mn/100Fe = 2.2) was also studied at constant temperature.

The yield and selectivity data for the 2.2 Mn/100Fe catalyst (FM-3) as a function of temperature are presented in Figure 6. The effect of space velocity, hydrogen/carbon ratio and reactor pressure on yield and selectivity for this catalyst at constant carbon monoxide conversion are presented in Figures 7 through 9 and at constant temperature (493K) are presented in Figures 10 through 12. The hydrocarbon (C_2-C_4) yield was insensitive to variations in space velocity, H_2/CO ratio and reactor pressure at constant carbon monoxide conversion and at constant temperature for the range of process variables studied in this investigation. The catalyst was more olefin selective as the reactor temperature was raised, the olefin/paraffin ratio increased from one at 473K to 3.5 at 508K. Concomitant with this shift in olefin selectivity, the yield of methane decreased from around 30% to around 12%. At constant carbon monoxide conversion, the olefin selectivity improved with increasing space velocity or decreasing residence time and decreased with increasing hydrogen partial pressure or H_2/CO ratio. The influence of reactor pressure on selectivity was not clearly defined in these experiments; however, the trends for olefin selectivity do not reproduce the trends reported in the literature, and these experiments are currently being repeated. At constant reactor temperature (493K) the catalyst was more olefin selective with increasing space velocity and was less olefin selective with increasing H_2/CO ratio. Again the influence of pressure was not clearly defined and the experiments are being repeated.

The yield and selectivity data for the Mn/100Fe = 8.4(FM-7), Mn/100Fe = 63(FM-11) and Mn/100Fe = 278(FM-13) are summarized in Figures 13 through 21. The hydrocarbon (C_2-C_4) yield was insensitive to variations in process variables irrespective of the catalyst composition. The olefin selectivity decreased with increasing hydrogen partial pressure (H_2/CO ratio) for all three catalysts; however, the trend was more pronounced for the lower Mn/Fe ratio FM-7 catalyst. The olefin selectivity appeared to increase with increasing space velocity up to the standard value ($1.06 \text{ cm}^3\text{g}^{-1}\text{s}^{-1}$); however, the olefin/paraffin ratio remained constant above a space velocity of one for the lower Mn/Fe ratios. The influence of reactor pressure on the olefin selectivity for the Mn/100Fe = 63 catalyst was contrary to predictions in the literature, that is, the olefin/paraffin ratio increased with reactor pressure. The iron-manganese catalysts system studied in this investigation unfortunately did not include a catalyst of composition 900 Mn/100Fe; however, from the trends observed, we speculate a catalyst of this composition would not have reproduced the selectivity reported by Kolbel and Tillmetz (5)

The interpretation of the trends observed in this investigation will require a detailed characterization of the nature of the catalyst surface as a function of the composition and the development of an appropriate technique for the determination of the extent of catalyst coking during the course of an experiment. These

characterization studies are currently underway in our laboratory and the development of a method for coke determination is being actively pursued.

Extended Investigation of Copper-Cobalt Catalyst System

Effect of Catalyst Pretreatment on Activity and Yield

A series of different catalyst pretreatment procedures were investigated for the same batch of catalyst. Catalyst 8 (Table 2) was evaluated after two different pretreatment procedures. The first aliquot of catalyst was heated in air at 520°C for four hours followed by reduction in hydrogen at 275°C and five psig for two hours. The second aliquot of catalyst was reduced in hydrogen at 275°C for four hours. The catalyst pretreated by the first procedure was almost twice as active for carbon monoxide conversion than the catalyst prepared by the second procedure. Selectivity for the C₂-C₄ product fraction was higher in the first pretreatment than in the second pretreatment (Table 6). These results were probably due to the conversion of hydrated-alumina to γ -alumina which increased the acidity of the catalyst carrier.

Catalyst 7 was subjected to two different pretreatments: (a) the catalyst was reduced in hydrogen at 520°C and five psig for four hours, and (b) the catalyst was calcined in air at 520°C for four hours, followed by a reduction in hydrogen at 275°C and five psig for two hours. The activity for carbon monoxide conversion was almost two times greater for catalyst reduced only in hydrogen than for the catalyst calcined in air. There was no difference in the product selectivity. This was probably due to the incomplete reduction of metal compounds in the second pretreatment procedure. The effect of different pretreatments on Catalyst 7 are presented in Table 7.

Catalyst 38 was evaluated after three different pretreatments: (a) the catalyst was reduced in hydrogen at 225°C and five psig for four hours, then at 520°C and five psig for four hours, (b) the catalyst was reduced in hydrogen at 520°C and five psig for four hours, and (c) the catalyst was reduced in hydrogen at 60 psig at 225°C for four hours, then at 520°C for four hours. The data for this catalyst are presented in Table 8.

The catalyst reduced in hydrogen at five psig with two-stage heating gave the best activity for carbon monoxide conversion. The catalyst with two-stage heating in 60 psig hydrogen gave the same carbon monoxide conversion activity and product selectivity as the catalyst heated in hydrogen at 520°C and five psig for four hours. High hydrogen pressure probably caused a high reduction rate of metals, and the catalyst metal structure was sintered. Two-stage heating of the catalyst at five psig in hydrogen would promote dispersion of the metals on the carrier. Slow reduction of cobalt-copper metal catalysts decreases agglomerations of metal clusters. Therefore, metal clusters were more dispersed, and the catalysts contained more active sites for reaction.

Effect of the Nature of Copper Salts on Activity and Selectivity

Cupric nitrate and cupric chloride were used to prepare catalysts, Catalysts 38 and 43, and 10 and 16, respectively, of the same metal content. The effect of copper salt on the conversions and product selectivities are presented in Table 9. Catalysts 10 and 38 were prepared by coprecipitation with ammonium carbonate, whereas

16 and 38 were prepared with sodium carbonate. In both cases, the catalyst containing chloride has low activity for carbon monoxide conversion, a low concentration of carbon dioxide in the product, and a low C_5^+ and oxygenated hydrocarbon fraction selectivity. However, these catalysts had high CH_4 , C_2-C_4 fraction selectivities. These effects resulted from residual chlorine on the catalysts which was not removed during the preparation.

Effect of Sodium

The effects of sodium content on the catalysts were evaluated. Catalyst 43 was prepared without sodium by coprecipitation of cobalt, copper, and aluminum nitrates with ammonium nitrate. Catalysts 44 and 51 were prepared with five percent and three percent weight of sodium, respectively, by impregnation on oven-dried Catalyst 43. As sodium content increased on the catalyst, carbon monoxide conversion decreased, while product selectivity remained unchanged. Catalysts prepared by coprecipitation had the same estimated activity for carbon monoxide conversion as catalysts with oxygen and three percent sodium. However, Catalyst 44 with five percent sodium had lower activity for carbon monoxide conversion than the catalyst prepared by coprecipitation. These results are presented in Table 10.

Effect of Different Carriers

Catalyst 35 was prepared by impregnation of cobalt, copper nitrate and sodium carbonate on γ -alumina. The activity of this catalyst, as measured by carbon monoxide conversion, was very low compared with the estimated carbon monoxide conversion for the catalyst of similar composition prepared by coprecipitation.

Catalyst 32 had a metal composition similar to Catalyst 35 except that metal salts were impregnated on a Linde molecular sieve Na-Y. The activity for carbon monoxide conversion of catalyst 32 was low compared to the catalyst of similar composition supported on γ -alumina (Table 11). Catalyst 31 was prepared by impregnating Co-Cu nitrates on Attapulugus clay. Its composition was similar to Catalyst 38, however, the activity of Catalyst 31 was lower than that of Catalyst 38.

Effect of Process Variables

The effects of process variables on conversion are presented in Table 12. Larger conversions were obtained at a higher temperature and H_2/CO ratio, while pressure had little effect. The following selectivity trends were observed: (a) increased temperature, a higher production of C_2-C_4 and C_5^+ with a lower production of CH_4 and a lower olefin/paraffin ration, (b) increased H_2/CO ratio, lower olefin/paraffin ratio, and (c) increased pressure, no effect on product distribution.

Effect of Total Metal Loading

The effect of catalyst composition was studied in some detail. Several catalysts with different cobalt/copper ratios and different total metal loadings were prepared by coprecipitation on alumina. The activities of the catalysts were compared using carbon monoxide conversion as an index. At the standard reaction conditions of $275^\circ C$, 750 psig, 0.77 cc/gm/sec and $H_2/CO = 2/1$, the carbon monoxide conversions increased sharply from 20% to 80%, as the total metal loading was increased from eight percent to 18%. The conversions of carbon monoxide remained fairly constant as total metal loading was increased from 18% to 24%. The variations in conversion and

selectivity at the standard condition as a function of loading are presented in Figure 22. Other run conditions gave similar trends.

The selectivities of the hydrocarbon products are plotted against Cu/(Cu + Co) percentages in Figure 23. The carbon dioxide fraction selectivity was closely related to the carbon monoxide conversion. Hydrocarbon selectivities correlated best with metal ratios. At one extreme, the carbon monoxide catalyst produced a high percentage of CH₄ and no R-OH. As the fraction of Cu increased, CH₄ decreased and R-OH increased. Of significance, C₂-C₄ was higher over a wide range of catalyst compositions. The C₅⁺ fraction showed a similar trend. At the other extreme, the Cu catalyst gave high R-OH with only a small percentage of CH₄ and C₂-C₄.

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Table 1

Compositions of Catalysts Screened for
Carbon Monoxide Hydrogenation¹

Catalyst Number	Identification/Composition	Catalyst Number	Identification/Composition
#1	ICI 35-4	#56	Fe:K=100:0.187
#2	Co:Tho ₂ :Kieselghur=49.2:7.7: 43.1	#57	Fe:K=100:0.187
#3	Co:Cu:Al ₂ O ₃ =4.6:12.7:42.0	#58	Fe:K=100:0.489
#4	Co:Cu:Al ₂ O ₃ =4.2:22.2:51.6	#59	Fe:Cu:K=100:35.08:0.175
#5	Co:Cu:Al ₂ O ₃ =4.6:8.2:41.9	#60	Fe:Cu:K=100:28.05:0.1213
#6	Co:Cu:Al ₂ O ₃ =6.2:9.5:47.4	#61	Fe:Cr:K=100:16.28:0.272
#7	Co:Cu:Al ₂ O ₃ =6.9:8.8:41.9	#62	Fe:Cr:K=100:2.68:0.031872
#8	Co:Cu:Al ₂ O ₃ =8.7:8.2:46.4	#63	Fe:Zn:K=100:13.0:0.228
#9	Ni:Cu:Al ₂ O ₃ =8.2:10.0:40.3	#64	Fe:Zn:K=100:9.22:0.09791
#10	Co:Cu:Al ₂ O ₃ =5.1:4.0:43.7	#65	Fe:Zn:K=100:2.13:0.7089
#11	Co:Cu:Al ₂ O ₃ =2.1:8.6:43.7	#66	Fe:Zn:K=100:4.52:0.8057
#17	Co:Cu:Al ₂ O ₃ =7.5:4.9:45.5	#67	Fe:Zn:K=100:4.34:0.9178
#18	Co:Cu:Al ₂ O ₃ =8.13:16.1:41.0	#68	Fe:Zn:K=100:0.406:0.4929
#19	Co:Cu:Al ₂ O ₃ =7.4:1.3:46.5	#69	Fe:Zn:K=100:0.749:0.8386
#22	Fe:Cu:K ₂ O=16:83:3	#70	Fe:Zn:K=100:8.24:0.8650
#23	Fe:Co:Kieselghur=45:10:45	#71	Fe:Zn=100:2.64
#24	Co:Cr:Al ₂ O ₃ =6.1:7.35:43.6	#72	Fe:Zn=100:2.3
#25	Co:Cu:Al ₂ O ₃ =8.9:21.4:36.5	#73	Fe:Zn:K=100:2.3:0.1689
#26	CaO:MgO:Cu:Fe ₂ O ₃ :Al ₂ O ₃ :K ₂ O 2.0:0.3:10.84:2.5:0.8	#74	Fe:Zn:K=100:2.3:0.3905
#27	Co:Cu:Al ₂ O ₃ =5.9:6.5:87	#75	Fe:Zn:K=100:2.3:0.539
#29	Fe:Cu:Houdry S1-Al=12:6:82	#76	Fe:Zn:K=100:2.3:1.2253
#30	Fe:K ₂ O=100:3	#77	Fe:Zn:K=100:2.3:0.1203
#31	Co:Cu:Al ₂ O ₃ =4.3:6.2:43.6	#78	Fe:Zn:K=100:2.3:0.2777
#32	Co:Cu:Y-Sieve=6.1:7.4:86	#79	Fe:Zn:Cu:K=100:13.49:10.70: 0.15
#33	Co:Al ₂ O ₃ =7.3:47.0	#80	Fe:Zn:Cu:K=100:5.40:6.00: 0.29
#34	Cu:Al ₂ O ₃ =12.3:46.3	#81	Fe:Zn:Cu:K=100:4.32:7.31: 0.1727
#35	Co:Cu:Al ₂ O ₃ =5.1:5.2:86.6	#82	Fe:Mg=100:0.12
#36	Co:Cu:Al ₂ O ₃ =4.8:1.1:46.2	#83	Fe:Mg=100:2.67
#37	Co:Cu:Al ₂ O ₃ =9.8:8.1:41.4	#84	Fe:Mg=100:3.17
#38	Co:Cu:Al ₂ O ₃ =6.4:8.8:43.4	#85	Fe:Ca=100:1.07
#42	Co:Cu:Al ₂ O ₃ =5.5:15.5:40.0	#86	Fe:Ca=100:8.44
#43	Co:Cu:Al ₂ O ₃ =4.9:3.4:46.8	#87	Fe:Ca=100:12.46
#44	Co:Cu:Al ₂ O ₃ =4.8:3.6:42.3	#88	Fe:Mn=100:1.14
#51	Co:Cu:Al ₂ O ₃ =5.6:4.5:45.0	#89	Fe:Mn=100:2.84
#52	Fe:K=100:0	#90	Fe:Mn=100:12.18
#53	Fe:K=100:0.027	#91	Fe:Mn=100:12.18
#54	Fe:K=100:0.0339	#92	Fe:Mn=100:28.09
#55	Fe:K=100:0.1252	#93	Fe:Mn=100:33.89
		#94	Fe:Mn=100:43.59

Table 2

Compositions of Co-Cu Catalysts¹

<u>Catalyst Number</u>	<u>Co:Cu:Al₂O₃Ratio</u>
CC-# 3	4.6/12.7/42.0
CC-# 4	4.2/22.2/51.6
CC-# 5	4.6/8.2/41.9
CC-# 6	6.2/9.5/47.4
CC-# 7	6.9/8.8/41.9
CC-# 8	8.7/8.2/46.4
CC-#10	5.1/4.0/43.7
CC-#11	2.1/8.6/43.7
CC-#17	7.5/4.9/45.5
CC-#18	8.13/16.1/41.0
CC-#19	7.4/1.3/46.5
CC-#35	5.1/5.2/86.6
CC-#36	4.8/1.1/46.2
CC-#37	9.8/8.1/41.4
CC-#38	6.4/8.8/43.4
CC-#42	5.5/15.5/40.0
CC-#43	4.9/3.4/46.8
CC-#44	4.8/3.6/42.3
CC-#51	5.6/4.5/45.0

Table 3

Compositions of Mn/Fe Catalysts²

<u>Catalyst Number</u>	<u>Mn/Fe Ratio*</u>
MF-1	Pure Fe
MF-2	1.1
MF-3	2.2
MF-4	3.2
MF-5	4.4
MF-6	5.6
MF-7	8.4
MF-8	11.7
MF-9	17.7
MF-10	41.0
MF-11	63.0
MF-12	109.0
MF-13	278.0
MF-14	607.0
MF-16	2.1
MF-15	Pure Mn

*Atomic Ratio: Atoms Mn/100 Atoms Fe

Table 4

Screening Test Results

Catalyst	Fe 23	Fe 22	Fe 26	Fe ICI	Co 33	Cu 34	CoThO ₂ K1 ²	CuNi K5
Pretreatment*	a	a	a	a	b	b	c	c
Temp, °C	225	225	260	225	250	275	225	275
Pressure, psig	750	750	750	750	750	750	120	750
Space velocity, cc/gm/sec	1.54	1.54	1.54	1.54	0.77	0.77	0.6	0.77
H ₂ /CO	1/1	1/1	1/1	2/1	2/1	2/1	7/3	7/3
CO conversion, %	57.6	0.9	94.7	89.4	16.95	11.57	84.0	18.3
Product selectivity, %								
CO ₂	51.6	0.0	64.7	39.4	5.3	0.0	7.0	63.1
CH ₄	15.8	25.9	8.3	11.7	34.0	11.6	32.0	24.4
C ₂ -C ₄	18.7	51.6	17.5	24.8	27.4	5.3	12.0	9.7
C ₅ +	10.3	22.5	8.7	22.0	33.3	1.2	49.0	2.8
R-OH	3.5	0.0	0.8	2.1	0.0	81.9	--	0.0
O/P	2.0	2.2	1.3	2.9	0.77	0.44	0.14	0.06

Pretreatment*

- a Reduced in H₂ at 550°C for 20 hr nitrided in NH₃, 325°C for 6 hr
b Reduced in H₂ at 520°C for 4 hr
c Calcined in air 520°C for 2 hr reduced in H₂ at 275°C for 4 hr

Table 5

Summary of Iron Catalyst Screening Tests

Catalyst	ICI 35-4	29 Fe-Cu-K	15 Fe-K	Hematite ore	Magnetite ore	4 Fe	8 Fe+Cu+K	35 Fe+Zn	36 Fe+Zn+K
Pretreatment*	a	b,c	b,c	b	b	b	b	b	b
Temperature °C	250	250	250	250	250	250	250	230	235
Pressure Psig	750	750	500	500	500	500	500	500	500
Space velocity cc/gm/sec	1.54	0.77	1.06	1.06	1.06	1.06	1.06	1.06	1.06
H ₂ /CO	1/1	1/1	2/1	6/4	6/4	6/4	6/4	2/1	2/1
CO% conversion	79.91	13.23	1.88	17.65	7.61	20.01	24.32	13.44	19.17
Products % selectivity									
CO ₂	57.85	5.07	7.12	11.84	8.26	14.85	62.24	9.80	42.51
C ₁	2.50	23.37	37.32	14.68	18.96	13.07	3.59	18.03	6.23
C ₂ -C ₄	21.50	34.50	43.67	48.00	50.23	45.01	20.15	47.01	26.07
C ₅ ⁺	18.15	25.28	11.32	21.86	17.55	24.23	9.94	17.21	14.33
ROH	0.0	11.76	0.58	7.75	4.99	2.85	4.08	7.94	10.88
O/P	4.65	1.15	0.75	0.90	0.28	0.73	2.29	1.09	1.98

Pretreatment*

- a Reduced in hydrogen at 400°C for 20 hrs
- b Reduced in hydrogen at 500°C for 20 hrs
- c Impregnated on Houdry Si-Al

TABLE 6
COMPARISON OF TWO DIFFERENT PRETREATMENTS
FOR Co-Cu CATALYST 8

CATALYST:	8 Co-Cu-Al ₂ O ₃			
PRETREATMENT:	a		b	
TEMPERATURE, °C	250	275	250	275
PRESSURE, psig:	750	750	750	750
Sp Vel, cc/gm/sec	0.77	0.77	0.77	0.77
H ₂ /CO	7/3	7/3	7/3	7/3
CO % CONVERSION:	5.65	21.35	9.93	39.40
PRODUCT SELECTIVITY:				
CO ₂ %	0.0	9.77	0.14	20.77
CH ₄ %	49.46	33.08	37.47	28.14
C ₂ -C ₄ %	28.46	32.67	44.10	34.45
C ₅ [±] %	22.08	24.48	18.29	16.63
ROH %	---	---	---	---
O/P in C ₂ -C ₄	0.58	0.70	1.29	0.85

a reduced in H₂ at 275°C for 4 hours

b calcined in air at 520°C for 4 hours, then reduced in H₂ at 275°C for 2 hours

TABLE 7
COMPARISON OF TWO DIFFERENT PRETREATMENTS
FOR CO-Cu CATALYST 7

CATALYST:	7 Co-Cu-Al ₂ O ₃			
PRETREATMENT:	a		b	
TEMPERATURE, °C:	275	275	275	250
PRESSURE, psig:	750	500	750	750
Sp Vel, cc/gm/sec	0.77	0.77	0.77	0.77
H ₂ /CO	7/3	7/3	7/3	6/4
CO % CONVERSION:	58.14	20.72	34.29	6.37
PRODUCT SELECTIVITY:				
CO ₂ %	17.43	2.05	10.83	11.66
CH ₄	33.24	38.92	38.35	38.08
C ₂ -C ₄ %	34.17	36.50	33.77	47.08
C ₅ ⁺ %	15.16	22.52	17.05	13.01
ROH %	---	---	---	---
O/P in C ₂ -C ₄	0.03	0.22	0.18	0.42

a reduced in H₂ at 520°C for 4 hours

b calcined in air at 520°C for 4 hours, then reduced in H₂ at 275°C for 2 hours

Table 8

Effect of Pretreatment on Conversion

Pretreatment ^a : Catalyst	Co Conversion, %			
	A	B	C	D
7 ^b	37	58		
38 ^c		17	38	16

^aPretreatments:A - (1) air, 520°, 4 hr. (2) H₂, 275°, 2 hr., 5 psigB - (1) H₂, 520°, 4 hr., 5 psigC - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr., 5 psigD - (1) H₂, 225°, 4 hr. (2) H₂, 520°, 4 hr., 60 psig^bReaction conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec.^cReaction conditions: 250°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

Table 9

Effect of Copper Salt on Catalyst Activity

Pair	1		2	
Catalyst #	10	43	16	38
Cu salt ^a	Cl	NO ₃	Cl	NO ₃
Co. Conv., % ^b	9	39	59	90
<u>Selectivity</u>				
C ₁	42	35	40	26
C ₂ -C ₄	45	38	41	42
C ₅ +	13	19	18	26
ROH	0.2	8	2	6

^aUsed in catalyst preparation^bReaction Conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/g sec.

Table 10

Effect of Sodium on Catalyst
Properties and Activities

Catalyst #	43	51	44
Na, %	0	3.8	5.4
Reduction, %	52	56	66
Dispersion, %	19	19	15
O ₂ Adsorption, mg/g	2.6	3.2	2.5
CO conversion, %	39	30	3

TABLE 11

ACTIVITY TESTING RESULTS OF
IMPREGNATED Co-Cu CATALYSTS

CATALYST:	35 γ -alumina		32 linde Na-Y		31 Attapulugus Clay		38 coprecipited	
PRETREATMENT:	reduced in H ₂ at 520°C for 4 hours							
TEMPERATURE, °C:	250	275	250	275	250	275	250	275
PRESSURE, psig:	750	750	750	750	750	750	750	750
Sp Vel, cc/gm/sec:	0.77	0.77	0.77	0.77	0.77	0.77	0.77	0.77
H ₂ /CO:	2/1	2/1	2/1	2/1	2/1	2/1	2/1	2/1
CO % CONVERSION:	10.79	12.64	8.91	26.26	6.96	9.23	16.75	89.46
PRODUCT SELECTIVITY:								
CO ₂ %	0.0	3.51	0.67	7.47	0.36	1.96	1.10	51.77
CH ₄ %	23.35	43.09	60.69	42.85	23.81	28.76	32.62	12.46
C ₂ -C ₄ %	10.73	14.11	28.12	27.44	12.87	18.51	42.11	20.16
C ₅ ⁺ %	1.91	4.13	10.52	15.86	1.97	2.89	11.48	12.48
ROH %	63.81	35.16	0.0	6.38	60.99	47.87	12.69	3.13
O/P in C ₂ -C ₄	0.74	0.22	0.36	0.18	0.42	0.22	0.91	0.04

TABLE 12
EFFECT OF PROCESS VARIABLES ON CONVERSION

		Values are CO Conv., %			
Temp., °C		235		250	
H ₂ /CO		3/1	1/1	3/1	1/1
Pres. psig	750	34	13	77	37
	1000	41	10	--	29
Catalyst 38, 0.38 cc/g sec

A: CO/H₂ Synthesis Gas
 B: Hydrogen Supply
 C: Helium Supply
 D: High Pressure Flow Meter
 E: Pressure Gauge
 F: Valve
 G: Micro-metering Valve
 H: 4-way Valve

K: Reactor
 L: Embedded High Temperature Heating Wire
 M: Heating Tape
 N: Cyclone Separator & Liquid Collector
 P: Gas Sampling Point
 R: Flask
 S: Wet-test Meter
 T: Bubble Flow Meter

Figure 1. The Reactor System Flowchart

FIGURE 2b. H.C. PRODUCTS SELECTIVITY OF Fe-K CATALYST

FIGURE 3a. CARBON PRODUCT SELECTIVITY OF (Fe-Mn) CATALYSTS

Figure 3b Hydrocarbon Product Selectivity of (Fe-Mn) Catalysts

Figure 4. Hydrocarbon Yield and Selectivity Versus Catalyst Composition
 $H_2/CO = 2/1$; $SV = 1.06 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$; $P = 500 \text{ psig}$; CO conversion: 7.0-7.5%

Figure 5. Reactor Temperature for Constant Conversion Versus Catalyst Composition
 $H_2/CO = 2/1$; $SV = 1.06 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$; $P = 500 \text{ psig}$; CO conversion: 7.0-7.5%

Figure 6. Effect of temperatures.
 FM #3, Atomic 2.2 Mn/100 Fe, 500 psig, 1.06 cc/g/sec, $H_2/CO=2/1$

Figure 7. Effect of space velocity (based on constant CO conversion).
 7.0-7.5% CO conversion, Atomic 2.2 Mn/100 Fe, 500 psig, $H_2/CO=2/1$

Figure 8. Effect of H_2/CO ratios (based on constant CO conversion).
5.5~7.0% CO conversion, Atomic 2.2 Mn/100 Fe, 1.06 cc/g/sec, 500 psig

Figure 9. Effect of Pressure (based on constant CO conversion)

Figure 10. Effect of space velocity (based on constant temperature).
220°C, Atomic 2.2 Mn/100 Fe, 500 psig, $H_2/CO=2/1$

Figure 11. Effect of H_2/CO ratios (based on constant temperature).
220°C, Atomic 2.2 Mn/100 Fe, 1.06 cc/g/sec, 500 psig

Figure 12. Effect of pressures (based on constant temperature) 220°C, Atomic 2.2 Mn/100 Fe, 1.06 cc/g/sec, $H_2/CO=2/1$

Figure 13. Effect of Space Velocity over 8.4 Mn/100 Fe Catalyst.

Figure 14. Effect of H_2/CO Ratio over 8.4 Mn/100 Fe Catalyst.

Figure 15. Effect of Pressure over 8.4 Mn/100 Fe Catalyst.

5.7~7.0% CO Conversion, Atomic 63.0 Mn/100 Fe, 500 psig, $H_2/CO=2/1$

Figure 16 Effect of Space Velocity over 63.0 Mn/100 Fe Catalyst.

5.4~6.1% CO Conversion, Atomic 63.0 Mn/100 Fe, 1.06 cc/g/sec, 500 psig

Figure 17 Effect of H_2/CO Ratio over 63.0 Mn/100 Fe Catalyst.

5.8~7.6% CO Conversion, Atomic 63.0 Mn/100 Fe, 1.06 cc/g/sec, $H_2/CO=2/1$

Figure 18 Effect of Pressure over 63.0 Mn/100 Fe Catalyst.

7.7~9.0% CO Conversion, Atomic 278.0 Mn/100 Fe, 500 psig, $H_2/CO=2/1$

Figure 19 Effect of Space Velocity over 278.0 Mn/100 Fe Catalyst.

5.5~8.0% CO Conversion, Atomic 278.0 Mn/100 Fe, 1.06 cc/g/sec, 500 psig

Figure 20. Effect of H_2/CO Ratio over 278.0 Mn/100 Fe Catalyst.

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

Figure 21. Effect of Pressure over 278.0 Mn/100 Fe Catalyst.

Figure 22. The Effect of Total Metal Loading on Co-Cu Catalysts Activity.

Cu/(Co + Cu)
 Conditions: 275°, 750 psig, 2H₂/CO, 0.77 cc/gs

Figure 23. The Effect of Cu/(Co + Cu) ratio on Hydrocarbon Selectivity of Co-Cu Catalysts.

Synthesis of Light Hydrocarbons From CO
and H₂ (Continued)

Catalyst Characterization Studies

Faculty Advisor: F.E. Massoth

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 high pressure reactor. Of particular interest are metal areas, evidence of alloy formation, phase structures and catalyst stability. Also, variables in catalyst preparation and pretreatment are examined to establish effects on catalyst properties. Finally, characterization results are compared with catalyst activities to obtain correlating relationships.

The basis of this report is taken from the M.S. Thesis of Bailey.¹ For further information, the reader is referred to this report.

Experimental

The CoCu/Al₂O₃ catalysts studied in the present work were prepared for the catalyst evaluation tests on another phase of this project. The catalysts were made by a coprecipitation technique. A hot solution of nitrates of Co, Cu and Al was added to a hot solution of Na₂CO₃ which effected precipitation leaving 1/2-1% sodium content on the catalysts. To test the effect of sodium as a possible promoter, several catalysts were prepared with NH₄OH as the precipitating agent. These catalysts were then impregnated with various amounts of NaNO₃. One catalyst was prepared for comparison purposes by co-impregnating the two metal nitrates on an attapulgus clay support.

Analyses of the catalysts for copper and cobalt were performed by means of a spectrophotometric method similar to one developed by Lindley.² Sodium was determined by atomic adsorption. The quantitative results of the copper, cobalt and sodium analyses are given in Tables 1 and 2. These pertain to an oven dried basis.

Surface area analyses (BET) were performed on three catalysts which had been reduced in H₂ at 500°C. Catalysts 19, 38 and 42

had surface areas of 202, 186 and 202 m²/g, respectively.

Catalyst oxidation-reduction studies and oxygen chemisorption were carried out in a flow microbalance system similar to that described by Massoth.³ A standard treatment consisted of heating about 300 mg of catalyst, contained in a quartz bucket, to 500°C in a H₂ flow and holding for four hours. An average weight loss in this step corresponded to about a 30% reduction in the charge weight of the oven dried catalyst. The gas flow in the reactor was then switched to nitrogen and the catalyst cooled to room temperature and subsequently to 0°C with an ice bath placed around the reactor. Next, air was admitted and the weight of oxygen chemisorbed was measured. The catalyst was then heated up in H₂ to 500°C until the weight had stabilized. The H₂ was replaced by N₂ for several minutes, then air, recording the net weight gain.

The above procedure gives two important pieces of data: (1) weight of O₂ chemisorbed, which is related to the total metal area; and (2) weight change in oxidation, which is related to reducible metal present. Oxidation states at 500°C are assumed to be CuO and Co₃O₄. From this information, together with the metal contents, an average percent reduction can be calculated, and assuming all the copper is reducible, the percent Co reduction and the reduced copper mole fraction, $[Cu/(Cu + Co)]_{red}$ can also be calculated. Because the stoichiometry of O₂ adsorption on Cu and Co are not known, a percent dispersion is defined as the O₂ weight pickup divided by the high temperature oxidation weight gain.

A special infrared cell was built and used in conjunction with a dual-beam Perkin Elmer IR Spectrophotometer. This permitted samples to be pretreated and exposed to CO in-situ. Details are given by Bailey.¹ The reference window allowed cancellation of gaseous CO present in the cell. The catalyst sample was pressed into a wafer of about 15 mg/cm². The wafers made from the reduced catalysts with high copper content were black and had a mirror-like finish. The wafers made from high cobalt content catalysts were lighter in color and had a duller texture.

With the catalysts of high copper content, the response of the IR spectrophotometer was highly increased, the scale was expanded and the reference beam was manually attenuated to enhance transmission. Under these conditions, especially due to the attenuation of the reference beam, absorption bands of CO gas appeared because they were not effectively cancelled out of the spectra by the reference beam.

A temperature programmed desorption (TPD) apparatus was constructed for this project similar to that reported in the literature.⁴ This consisted of a fixed-bed reactor with a thermocouple located in the catalyst bed, a tubular furnace and a differential thermal conductivity cell. Linear heating

rates were achieved with a Fischer Temperature Programmer. Further details are given by Bailey.¹

The catalyst was charged to the reactor and pretreated in H₂ at 500°C for several hours. After cooling to room temperature, a 2% CO/He mixture was passed over the catalyst for 8 min, followed by a He flush until base line was achieved. Then temperature programming was started at 20°C/min, and the desorption chromatogram recorded as a function of temperature. The lag time at the flows used was about one minute between the reactor and the thermal conductivity cell.

X-Ray diffraction analysis, performed on a Phillips Norelco unit with Cu-K_α radiation, was used for phase identification and estimation of metal particle sizes by line-broadening.⁵ A Hitachi Scanning Electron Microscope was employed to assess distribution of metal components in the catalyst. Valence states were determined using a Hewlett Packard ESCA instrument. Diffuse reflectance spectra were obtained on a Perkin-Elmer UV-visible spectrophotometer, equipped with a Hitachi integrating sphere attachment.

Results and Discussion

A number of preliminary studies were done to develop techniques for characterizing catalysts and determining proper pretreatment conditions.⁶ These employed the gravimetric method to measure O₂ chemisorption and catalyst reducibility, and X-ray diffraction (XRD) for phase identification and estimation of metal crystallite sizes. Several catalysts were prepared separately for this purpose.

Table 1 presents the results of these studies. All tests were carried out starting with oven-dried catalysts. Heating to 450°C in H₂ sufficiently reduced the Cu and the CoCu catalyst to the metals; but the Co catalyst was only about one-half reduced under these conditions. Under comparable reduction conditions, the CoCu catalyst showed about a ten-fold larger O₂ chemisorption compared with either the Co or Cu catalyst. On a per gram reduced metal basis, these results translate into a three-fold increase over the Co catalyst and a five-fold increase over the Cu catalyst in surface metal area. A two-stage heating schedule gave larger metal areas (greater O₂ adsorptions) compared to a direct heat up to maximum temperature. This was especially marked at 500°C.

Reoxidation of the reduced samples caused changes in metal dispersion. Thus, reduction of the reoxidized CoCu catalyst gave a five-fold loss in metal dispersion. A lesser loss was obtained for the Cu catalyst and no loss was observed for the Co catalyst. Evidently, reoxidation of the reduced catalyst caused sintering of the highly dispersed metal phase.

Pretreatment with N_2 in place of H_2 at $450^\circ C$, followed by reduction resulted in a much lower metal dispersion, being only slightly greater than the reoxidized sample. Also, total reduction was somewhat lower (79%). If all the Cu reduced, then about 50% of the Co also reduced, which is what was obtained with the Co catalyst. Evidently, N_2 pretreatment is equivalent to air oxidation in causing metal sintering and Co interaction with the support.

X-Ray analyses of reduced samples exposed to air showed Cu metal is the major component, with Cu_2O as a minor component. The amount of Cu_2O relative to Cu was greater for those catalysts which had high O_2 adsorptions and negligible for low uptake catalysts. This indicates some surface oxidation of Cu occurred during exposure to air. The Co catalyst contained appreciable amounts of $CoAl_2O_4$ in addition to Co metal, accounting for its incomplete reduction. On the CoCu catalysts, a separate Co metal phase was not detected by X-ray analysis.

Estimates of average particle size from X-ray line broadening generally agreed with the O_2 adsorption results. Although average particle sizes based on adsorption did not give good quantitative agreement with the X-ray values, the trends are nevertheless in the same direction. Uncertainties in the exact stoichiometry of adsorption and possible oxidation beyond the monolayer probably account for these differences.

Cobalt and Cu interact during the prereduction step. The presence of Cu engendered reduction of the Co. The two together resulted in a much greater metal dispersion than each one separately. Reoxidation caused appreciable sintering of the highly dispersed metals. Hence, air regeneration of aged catalysts would most likely cause a severe deactivation of the original catalyst activity.

The degree of dispersion was greatly affected by the pretreatment used. Oxidized and N_2 treated catalysts gave low metal dispersions after high temperature reduction, whereas direct treatment of the oven-dried catalysts with H_2 during heating have much better dispersions. In the latter case, the heating schedule was important, viz., holding at $250^\circ C$ before subsequent high temperature heat-up resulted in even higher dispersions. Similar improvement in metal dispersion was found for Ni catalysts. Evidently, slow heating results in formation of small metal crystallites which are then stable at the higher temperatures.

Following the above studies, a number of catalysts which had been evaluated in the reactor activity testing portion of this project for $CO + H_2$ reaction were characterized in detail.

Table 2 gives the catalysts studied and results of reduction and adsorption measurements. Catalyst reducibility increased

with an increase in the copper fraction in the sample, as shown in Figure 1a. The dotted line represented the expected increase in total reduction with increasing copper content if both metals existed as separate phases. All catalysts except Catalyst 18 lie above this line indicating an enhanced reducibility. Figure 1b shows the increase in cobalt reducibility as the fraction of copper was increased in the catalysts. This assumes copper was completely reduced in these samples. These results confirm the influence of copper on the cobalt reducibility. Sinfelt reported a similar effect for RuCu and OsCu catalysts.⁸

Adsorption of O_2 was used as a measure of total metal area as it strongly chemisorbs on both cobalt and copper. As noted previously, the composite catalyst exhibited appreciably higher adsorptions than the end members, and adsorption increased with an increase in total metal loading. Dispersion also increased in the mixed-metal catalysts as compared to that predicted from additions of the individual metals. This can be easily seen in the impregnated clay Catalyst 31, which gave 13% dispersion (16% predicted) versus the mixed catalyst of similar mole fraction (37) which gave 34% dispersion. These results indicate that coprecipitation of copper-cobalt with alumina results in a synergistic effect in the reduced catalysts, giving highly dispersed metal phases, whereas, simple impregnation on a performed support results in separate metal phases of low dispersion. Other characterization techniques discussed below confirm this viewpoint.

The presence of sodium appeared not to affect catalyst reducibility or dispersion in these catalysts.

X-Ray diffraction patterns of the reduced CoCu/ Al_2O_3 catalyst system are summarized in the following: (a) cobalt metal phase was undetectable; (b) copper metal was identified; (c) Cu_2O peaks were detected (very broad); and (d) $CoAl_2O_4$ and/or Co_3O_4 peaks were present. In the X-ray diffraction patterns, the reduced Co/ Al_2O_3 catalyst failed to show cobalt metal. From the O_2 chemisorption and redox studies, a particle size of 30 Å can be calculated. This is the lower limit for detection by X-ray diffraction.⁵

In the thin metal alloy form, copper and cobalt form f.c.c. phases.⁹ Diffraction patterns of this phase should be similar to the copper phase which is f.c.c. If such phases were present in the alloy catalyst, slight shifting of the copper peak might be noticeable. In the X-ray diffraction done to check for alloy in the bulk, the peaks were very broad. In the Cu/ Al_2O_3 catalyst, the Cu peak was sufficiently narrow to be readily observed, but in the CoCu/ Al_2O_3 catalysts, the peaks were so broad that detection of slight shifts due to alloying were virtually impossible. Therefore, in this well dispersed catalyst system, X-ray diffraction was an impractical method for detection of alloy formation in the bulk.

Scanning electron microprobe analysis of Catalyst 42 at 9000 X and 12000 X showed a heterogeneity of metal particle dispersion. On the surface there were areas of high concentration of metal while some areas were rather low in metal concentration. However, copper and cobalt appeared together in the areas of high concentration and low concentration. Even though copper and cobalt appeared to be dispersed in a similar arrangement on the surface of the catalyst, this is not proof of homogeneous alloying, because of the relatively large areas scanned by this technique. Therefore, although large areas of separate Co and Cu phases do not appear to exist on this catalyst, intimate contact of Co and Cu at the molecular level cannot be assessed by this technique. The results, however, are not contradictory to the possibility of alloy formation.

The reduction results showed some cobalt to be unreducible in the catalysts, especially when copper was absent or low. ESCA was used to examine the oxidized form of the Co/Al₂O₃ catalyst. Samples of CoAl₂O₄, Co₃O₄ and CoO were run as standards. These patterns were compared to the oxidized cobalt catalyst. Note that CoO and CoAl₂O₄ both have Co²⁺ valence states and give the same ESCA patterns. The patterns of Co₃O₄ and CoO are quite different in the position of the satellite peaks. The cobalt catalyst more nearly matched the pattern of CoO (or CoAl₂O₄). Since CoO is easily reducible under our reduction conditions and CoAl₂O₄ is not reducible (established from pure compound studies), the dominant phase present must be CoAl₂O₄. X-Ray diffraction showed the presence of Co₃O₄ and/or CoAl₂O₄ (indistinguishable) but not CoO.

Diffuse reflectance spectra in the visible region showed clear evidence of both octahedral and tetrahedral coordination of cobalt. Cobalt in Co₃O₄ and CoO is octahedral, in CoAl₂O₄ it is tetrahedral. Therefore, these results definitely show at least two phases are present in the catalyst. Considering the results of these tests, the components of the Co/Al₂O₃ catalyst are probably CoAl₂O₄ (non-reducible) and Co₃O₄ (reducible), with a possibility of a small amount of CoO (reducible), although the latter is not the expected stable phase.

Cobalt has been reported to be present in two phases on alumina: in one, cobalt complexes with alumina as cobalt aluminate and is resistant to reduction in hydrogen; in the other, as Co₃O₄, the cobalt is reducible to the free metallic state.¹⁰ Our results are in agreement with these findings. The addition of copper to the system apparently adds another possibility which can compete with or otherwise hinder the formation of the unreducible cobalt phase during reduction. The easily reduced copper may allow cobalt a place in its lattice in the formation of alloy crystallites, or it may act as a hindrance to the formation of the unreducible cobalt alumina phase.

The spectra of CO gas shows a doublet, with peak frequencies of 2110 cm⁻¹ and 2165 cm⁻¹, the latter peak being stronger than the former. This is illustrated in Spectra 2 of Figure 2a. In

Spectra 1 of the same figure, the spectra of CO adsorbed on 12.3% Cu/Al₂O₃ is given. The characteristic frequency for CO adsorbed on copper is 2110 cm⁻¹. The CO gas phase masks the possibility of seeing the adsorbed specie clearly. However, the peaks of the doublet in Spectra 1 are more even in length compared with the doublet of the CO gas phase in Spectra 2. This could be an indication of the presence of the CO adsorbed specie on copper.

Figure 2b illustrates another spectra of a high copper content catalyst with a composition of 5.5% Co 15.5% Cu/Al₂O₃. Interference of the CO gas phase is again observable. However, a new peak at 2050 cm⁻¹ is present. This is an intermediate peak. The peaks which might be expected are due to CO adsorbed on copper at 2110 cm⁻¹ and CO adsorbed on cobalt at 2000 cm⁻¹ and 1880 cm⁻¹. This intermediate peak gives evidence of possible alloying in this mixed catalyst.

Figure 2c shows the spectra of Catalyst 17 with a composition of 7.5% Co 4.9% Cu/Al₂O₃. This spectra was run at normal response and on a normal scale with minimal attenuation of the reference beam, so gas phase adsorption was effectively eliminated. The single peak at 2090 cm⁻¹ is close to the frequency of CO adsorbed on Cu at 2110 cm⁻¹. However, it appears to be shifted slightly towards the lower frequencies associated with CO adsorbed on Co at 2000 cm⁻¹ and 1880 cm⁻¹ as shown in Figure 2d for a 20% Co/SiO₂ catalyst. Blyholder reports that the characteristic peak for CO adsorbed on Cu is much sharper than those for CO adsorbed on other metals, including Co.¹¹ The peak in Figure 2c is broader than expected and more closely comparable to the major peak in Figure 2d. These factors indicate an interaction of the two metals in this catalyst which could be attributable to an alloy phase.

The spectra of Catalyst 37 (9.8% Co 8.1% Cu/Al₂O₃) gave peaks of interest at 2100 cm⁻¹ and at 2030 cm⁻¹ (not shown). Both peaks showed a sharpness characteristic of CO adsorbed on copper. The minor peak at 2030 cm⁻¹ is probably due to an alloy but may be due to a shift of the linear adsorbed specie of cobalt normally found at 2000 cm⁻¹. The major peak at 2100 cm⁻¹ is very close to the linear adsorbed specie of copper. Although the two peaks could be representative of different phases, the fact that CO adsorbs in a linear one to one fashion, could indicate a single surface phase with both copper and cobalt present as surface constituents. The relative sizes of the peaks give evidence of the surface phase (or phases) being copper rich.

Copper appeared to be a dominant phase in the mixed metal catalysts studied. Although, this may be an alloy phase with a copper rich surface, similar to that observed in the CuNi system.¹² In fact, this would account for the failure to observe any characteristic cobalt phase on the mixed catalysts.

Desorption of CO was observable in all catalysts tested. Figure 3 presents results obtained for the various catalysts of interest. Desorption from the Co/Al₂O₃ Catalyst 33 began at about 170°C, possibly due to desorption from cobalt metal, with a peak at 300°C. Desorption from the Cu/Al₂O₃ Catalyst 34 resulted in a peak at 110°C. As copper was added to the cobalt catalyst, the cobalt on alumina peak began to shift towards a newly formed copper peak. As the copper fraction was increased, the two peaks began to blend together as the cobalt appeared to take on the desorptive character of copper. When the weight fraction of copper was increased further, the desorption peaks began to separate again. Finally, with further increase in the copper fraction, the desorption peaks were entirely distinguishable.

These results are similar to those found by Yu and co-workers in their study of CO desorption from the CuNi system.¹³ They observed no shift in the desorption peak of the copper phase with changing composition; however, the Ni phase showed a variable desorption character, its peak position shifting towards the copper peak. They attributed the latter to a mixed ensemble or cluster effect, whereby neighboring copper atoms change the CO bonding strength of the nickel atoms. From the data, they deduced the presence of four surface ensembles in the CuNi system, which in order of increasing desorption temperature were: (1) copper, (2) copper with alloy, (3) nickel with alloy and (4) nickel ensembles. In our CoCu/Al₂O₃ catalyst, as the copper content increased, the bond strength of the cobalt appeared to decrease, indicating formation of similar alloy surface ensembles. However, all four phases were not clearly resolved in our plots due to overlap of desorption peaks.

A summary of catalyst characterization results is given in Table 3. These findings will be correlated to catalytic activity data previously obtained on the same catalysts.⁶ Data for CO conversion are given in Table 2 and for hydrocarbon selectivities in Table 3.

Adsorption of O₂ on the reduced mixed catalysts is considered a measure of the active metal surface present. It increased with total metal loading and may be independent of catalyst composition. Catalytic activity correlated directly with O₂ adsorption, as shown in Figure 4. Here an activity parameter, Y, developed by Yang et al., is plotted at two temperature versus O₂ adsorption.¹⁴ At a reaction temperature of 275°C, activity reached a plateau, due to an essentially complete reaction, after a metal area represented by about 6 mg/g O₂ adsorbed was reached. At this reaction, the plateau corresponds to a total metal loading of about 13%. This has important economic implications, since loadings over 13% result in no further activity and are therefore unnecessary. At a reaction temperature of 250°C, however, activity constantly increased with increasing metal area. Therefore, in reaction at 250°C, higher metal area is necessary for greater activity.

A relationship between hydrocarbon selectivities and reduced copper mole fraction is given in Figure 5. The reduced basis is used here because not all of the Co reduced completely in the catalysts, and the reduced mole fraction basis should give a better estimation of the active metal composition in the bulk. From the plot of Figure 5, the following observations can be made: (a) methane formation decreased continuously with increase in Cu, (b) the C₂-C₄ light hydrocarbon fraction showed a maximum around $[\text{Cu}/\text{Cu}+\text{Co}]_{(\text{red})}=0.8$, (c) the C₅⁺ fraction showed a maximum around $[\text{Cu}/\text{Cu}+\text{Co}]_{(\text{red})}=0.3$ and (d) methanol decreased sharply with addition of Co to Cu.

The parameter $[\text{Cu}/\text{Cu}+\text{Co}]_{(\text{red})}$ does not necessarily correspond to a surface of the same composition.¹⁵ However, an overall reduced metal composition of 0.8 has a corresponding surface which is optimum for the production of C₂-C₄ hydrocarbons. The selectivity plot of Figure 5 does reveal certain surface characteristics. These catalysts have a variety of selectivities. This suggests different types of active surface sites may be present. The Co/Al₂O₃ catalyst is selective towards methane, while the Cu/Al₂O₃ catalyst primarily produces methanol. As the two are combined, a different variety of products, C₂-C₄ and C₅⁺ hydrocarbons, are produced. This by itself is strong evidence of alloying in the mixed catalysts, because separate phases would show only their respective selectivities. In fact, this was observed in the impregnated Catalyst 31, which showed high selectivities toward methane and alcohol. The change in selectivity means new active sites are being formed in the mixed catalysts. The continuous curving nature of the selectivity plot probably indicates the surface composition is changing with changing bulk composition.

From the characterization studies, the following surface CoCu alloy phases (ensembles) are deduced to be present in the various catalysts: (1) A₁:Cu-rich; (2) A₂:similar to A₁ but with less Cu; (3) A₃:intermediate composition and (4) Co-rich. These may not all be different phases, but rather represent difference surface compositions of a continuous alloy phase. As copper is added to the Co/Al₂O₃ catalyst, phase A₁ appears, increasing with increase in Cu. At low Cu mole fractions, phase A₃ also appears, whereas at moderate to high Cu fractions, phase A₄ is present. From comparisons with selectivity, it appears that phase A₄ is responsible for enhanced selectivity of products to C₂-C₄, and A₃ for C₅⁺.

Conclusions

1. Catalyst activity for CO conversion depends upon total metal surface area as determined by O₂ adsorption.

2. Catalyst selectivity for C₂-C₄ products appears to be related to a Co-rich, CoCu alloy surface phase, which is maximum at a reduced Cu mole fraction of about 0.8.

3. Catalyst selectivity for C₅⁺ products appears to be related to a CoCu alloy surface phase of intermediate composition, showing a maximum around 0.3 reduced Cu mole fraction.

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TABLE 1. EFFECT OF PRETREATMENT ON METAL DISPERSIONS

Catalyst ^a	Pretreatment ^b °C	Metal Reduced, %	Weight O ₂ Chemisorbed, mg/g	Av. Metal Particle Size, Adsorption ^c	Size, XRD ^d Å
2	-/450	0	0		
3	250/450	46	1.5(1.5) ^e		
4	250/450	94	2.5(1.5) ^e	130(220) ^e	90(150) ^e
5	250/450	96	19.0(3.5) ^e	25(140) ^e	50(100) ^e
5	250/400	-	22.0	20	30
5	-/400	-	16.5	30	40
5	250/500	-	24.0	20	40
5	-/500	92	10.8		
5	450 ^f /450	79	4.5	90	130

^aCompositions: (2) Al₂O₃; (3) 8.5% Co; (4) 13.0% Cu; (5) 7.8% Co, 11.0% Cu.

^bH₂ used; 2h hold at each temperature.

^cbased on ratio of weights of O₂ chemisorbed to redox change assuming one O per metal site.

^dby x-ray diffraction line broadening.

^eafter high temperature oxidation-reduction cycle.

^fN₂ used.

TABLE 2. CATALYST EVALUATIONS

No.	Catalyst		[$\frac{\text{Cu}}{\text{Co+Cu}}$] ^b _{non} Wt. Fract.	Metal Redn. ^b %	Co Redn. ^c %	O ₂ ads mg/g	Disp. ^d %	[$\frac{\text{Cu}}{\text{Co+Cu}}$] ^e _{red} Mole Frac.	CO Conv. ^f %
	Method ^a	Co, %	Cu, %						
17	Na ₂ CO ₃	7.5	4.9	0.40	73	61	6.8	24	43
18	Na ₂ CO ₃	8.1	16.1	0.67	65	16	9.3	21	96
19	Na ₂ CO ₃	7.4	1.3	0.15	43	39	3.4	27	19
31 ^g	---	4.3	6.2	0.57	97	94	3.9	13	9
33	Na ₂ CO ₃	7.3	0	0	30	30	2.0	25	100
34	Na ₂ CO ₃	0	12.3	1	109	--	3.3	10	12
37	Na ₂ CO ₃	9.8	8.1	0.45	77	63	14.6	34	87
38	Na ₂ CO ₃	6.4	8.8	0.58	88	76	7.6	19	89
42	Na ₂ CO ₃	5.5	15.5	0.74	88	64	16.6	33	92
43	NH ₄ OH	5.0	3.4	0.40	52	29	2.6	19	39
44 ^h	NH ₄ OH+Na	4.8	3.6	0.43	65	47	2.5	15	3
51 ⁱ	NH ₄ OH+Na	5.6	3.9	0.41	56	35	3.2	19	30

^aPrecipating agent used.^bBased on total metals present.^cBased on 100% Cu reduction.^dDispersion.^eBased on reducible metals present.^fData of reference 6.^gImpregnated on Attapulas Clay.^hSubsequently impregnated with NaNO₃; contains 5.4% Na.ⁱDitto; contains 3.8% Na.

TABLE 3. CATALYST CHARACTERIZATION AND ACTIVITY DATA

Catalyst No.	$\left(\frac{\text{Cu}}{\text{Cu+Co}}\right)_{\text{red}}$	IR Peaks cm^{-1}	TPD Peaks $^{\circ}\text{C}$	Metal Phases Deduced ^a	Hydrocarbon Selectivities ^b , %			
					C ₁	C ₂ -C ₄	C ₅	ROH
33	0	--	300	Co	70	18	12	0
19	0.31	--	100, 210	A ₁ + A ₃	38	33	29	0
17	0.50	2090	160	A ₂	38	37	23	2
37	0.55	2100, 2030	---	A ₁ + A ₄	25	47	23	5
42	0.81	2110, 2050	110, 270	A ₁ + A ₄	24	51	22	4
18	0.92	---	110, 280	Cu + A ₄	25	36	16	23
34	1	2100	110	Cu	8	4	2	86

^aA represents possible alloy phase.

^bData of reference 6.

Figure 1. Effect of Catalyst Composition on Reducibility

Figure 2. IR Spectra of CO Adsorbed on Several Catalysts.

Figure 3.
 Temperature Programed Desorption of CO from the Alloy Catalysts.
 $\left[\frac{\text{Cu}}{\text{Cu}+\text{Co}}\right]_{\text{(wt)}}$ for 33=0, 19=.15, 17=.40, 18=.67, 42=.74, 34=1.00

Figure 4. Catalyst Activity vs O₂ Adsorption.

Figure 5. Hydrocarbon Selectivity vs Reduced Composition.

Development of Optimum Catalysts and Supports

Faculty Advisor: F.E. Massoth

Introduction

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

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

This report is based on the MS thesis of M. Moora¹ and C. Kim². Further details are provided therein.

Experimental

Five commercially available aromatic compounds were used in this study. Their properties are presented in Table 1. They have condensed, fused ring aromatic structures and vary from about 7 to 20 Å in critical diameter. Catalyst supports used were γ -aluminas having a range of average pore sizes; properties are given in Table 2. These were gently broken and passed through sieves to obtain various uniform sized batches. Bulk diffusivities were estimated by the Wilke-Chang formula³ since experimental values were not available.

Two nonadsorbing hydrocarbon solvents were used, n-heptane and cyclohexane. These were treated with 13 X zeolite to remove traces of possible adsorbing impurities, including water.

Diffusion runs were carried out in a glass, stirred-tank reactor with removable top. A small stream of the solute-solvent solution was circulated through a flow, UV cell and returned to the reactor. The system is shown in Figure 1.

A filter in the side stream prevented carry over of catalyst particles into the UV cell. A Beckman UV spectrophotometer was used to continuously monitor solution concentration with time. Absorbance was calibrated against concentration by means of standard solutions.

Weighed amounts of catalysts were calcined at various temperatures (mostly 500°C) to remove adsorbed water. They were quickly transferred to a dessicator, and when cool, several ml of solvent was added to prevent adsorption of water during transfer to the reactor. The desired solute-solvent solution was added to the reactor and the side stream monitored until the UV adsorbance was constant. Then the catalyst-solvent was rapidly added to the reactor and the concentration recorded vs. time. As the solute entered the catalyst pores and adsorbed, the solution concentration decreased until adsorption was complete. From the amounts of solute added and left in the solution at equilibrium, the amount of solute adsorbed on the catalyst could be calculated. The nature of the concentration-time decay curve allowed calculation of the effective diffusivity. Although the driving force for movement of solute into the catalyst is due to adsorption, the rate is controlled by diffusion through the catalyst pore structure, since the latter is considerably slower than the rate of adsorption for the systems under study. All runs were made at room temperature.

Equilibrium adsorption measurements were made separately by transferring the calcined catalyst directly into the desired solute-solvent solution and allowing to stand at room temperature. Concentration was checked periodically over a period of days or weeks until equilibrium was established.

Diffusion into catalysts pores, accompanied by adsorption is expressed by Fick's second law given by,

$$\epsilon \frac{\partial C}{\partial t} = D_p \nabla^2 C - \frac{\partial Q}{\partial t} \quad (1)$$

where ϵ = catalyst porosity
 C = solution concentration
 t = time
 ∇^2 = Laplacian operator with respect to r
 r = position along radius of particle
 D_p = pore diffusivity
 Q = amount of solute adsorbed

For porous catalyst structures⁵,

$$D_p = \frac{D_B \epsilon}{\tau} \quad (2)$$

where D_B is the bulk diffusivity of the solute-solvent combination and τ is a tortuosity factor. Solution of Eq (1) depends upon the relationship between Q and C . Two limiting cases were considered:

1. Linear Adsorption Isotherm (Fickian Model)

In this case, a linear equilibrium adsorption is assumed and the rate of adsorption is fast compared to diffusion. Thus,

$$Q = KC \quad (3)$$

where K is an equilibrium adsorption constant. Incorporation of Eq (3) into (1) and solving for the proper boundary conditions yields,⁶

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1) \exp(-D_a q_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (4)$$

where M_t , M_∞ = solute uptake at t and at equilibrium, respectively

D_a = apparent diffusivity

F = solution depletion $(C_o - C_f)/C_o$

C_o = initial solution concentration

C_f = final solution concentration

$\alpha = (1-F)/F$

q_n = non-zero roots of the transcendental equation:
 $\tan q_n = 3q_n/(3 + q_n^2),$

and D_a is given by,

$$D_a = \frac{D_{eff}}{(k+1)\epsilon} \quad (5)$$

where D_{eff} is the measured effective diffusivity to be compared to D_p . The method of Rudloff⁷ was used to determine values of D_a and consequently D_{eff} .

2. Irreversible Adsorption (Shrinking Core Model)

In this case, adsorption is so strong as to be irreversible and Q is given by,

$$Q = M \quad (6)$$

Solution of Eq (1) and (6) with proper boundary conditions yields,²

$$F_D = \frac{D_{eff} C_o t}{a^2 \rho_p M_\infty} = \frac{1}{6Fg} \left[\ln \frac{g^2 - gZ - Z^2}{(g+Z)^2} + 2\sqrt{3} \tan^{-1} \frac{2Z-g}{g\sqrt{3}} \right]_Z - \frac{1}{3F} \left[\ln(1-F+FZ^3) \right]_Z \quad (7)$$

where $Z = r_c/a$

r_c = radius at internal interface between adsorbed and unadsorbed phases

$g = \left(\frac{1-f}{f}\right)^{1/3}$

$f = M_t/M_\infty$

Determination of D_{eff} can be made by plotting the right hand side of Eq (7) against t and measuring the slope.

When surface diffusion contributes to the diffusion flux, the effective diffusivity will be the sum of this and pore diffusion and is given by,⁴

$$D_{eff} = D_p + KD_s \quad (8)$$

where D_p is given by Eq (2) and D_s is the surface diffusivity. Note that the surface diffusion contribution increases with an increase in K .

Restrictive diffusion occurs when the solute molecular size is not negligible compared to the pore diameter. It is of hydrodynamic origin but now well understood from a theoretical point of view. Hence, its effect has been treated empirically through a restrictive factor, K_r , viz:⁶

$$D_{eff} = K_p K_r \quad (9)$$

Thus, K_r is a measure of the lowering of the actual diffusivity from that predicted from pore diffusion. The object is to relate K_r to the ratio of solute size to pore size to develop a fundamental relationship.

Results and Discussion

A number of preliminary runs were made to develop proper techniques for obtaining diffusion data. These included transfer procedures, reactor configurations, stirring, moisture, catalyst particle size and data analysis methods. This was the subject of Moora's thesis¹ and additional details can be found therein.

It was found early that moisture from the air rapidly adsorbed on the catalyst during transfer to the reactor. As little as one minute exposure to laboratory air resulted in 25% loss in solute adsorption, and after five minutes adsorption was 75% less. Similar effects were observed in use of untreated solvent. That water was the cause of these effects was demonstrated in a run in which after solute equilibrium had been reached, several drops of water were added to the reactor solution. The solution concentration immediately increased, signifying that solute was desorbing due to replacement by adsorbed water. Apparently, water is more strongly adsorbed on the alumina than the aromatic solutes, necessitating the precautions mentioned in the Experimental Section of this report.

Several reactor configurations were tested. These included catalyst contained in screen baskets, either located on the bottom of the reactor or attached to the stirrer, and catalyst suspended in the solvent by the stirring action. All give about the same results. Therefore, the latter arrangement was subsequently employed because of easier handling problems and minimum exposure of catalyst to air. However, good stirring was required in all cases, 300-500 RPM being sufficient to achieve good mixing. Higher stirring speeds tended to fracture the catalyst particles.

Smaller sized catalyst particles gave more rapid adsorption than larger ones. Data analysis (see below) showed calculated diffusion coefficients to be inversely proportional to the square of the particle size, demonstrating that diffusion was indeed the rate-limiting step.

Adsorption data for chrysene in n-heptane correlated well with both the Fickian and the Shrinking Core models when solution depletion was small (external solution concentration decreased less than 10% from the original concentration). However, high solution depletion data appeared to fit the Shrinking Core model better. On this basis, diffusivities (diffusion coefficients) were calculated from Eq (7). These diffusivities were appreciably higher than calculated pore diffusivities, yielding unreasonably low tortuosity values (0.2-0.4). The data, if correct, could only be explained by invoking a surface diffusion contribution to the diffusion flux.⁴ Similar results were obtained using cyclohexane as the solvent. A problem now arose in that the Shrinking Core model assumes irreversible adsorption, and consequently surface diffusion should not occur since it entails a rapid adsorption-desorption mechanism.

To confirm the correctness of the preliminary results, a systematic study of several different solute-catalyst systems was undertaken. Questions to be answered were:
(1) Could impurities in the chrysene be responsible for the

high diffusion rates? (2) Is the Fickian or Shrinking Core model the correct one? (3) How general is the surface diffusion phenomenon? and (4) Can restricted diffusion be detected in the larger solutes? This was the subject of Kim's thesis², and additional details are presented therein.

The chrysene used previously was only of 95% purity and contained some 5H-benzo [B] carbozole, which would absorb strongly on the alumina. A higher purity batch (99+%) was obtained and tested. Indeed, lower diffusivities were obtained, as shown in Table 3. However, the lowering was not sufficient to eliminate surface diffusion as a probable cause for high diffusivities in the system.

The nature of the equilibrium adsorption isotherms was investigated to establish the proper diffusion model for the rate studies. Some typical data are shown in Figure 2. The data fit a Langmuir-type isotherm and were reversible. Therefore, irreversible adsorption was not indicated and the Shrinking Core model should not apply. Subsequent data were therefore analyzed with the Fickian diffusion model.

The results of the diffusion runs with five solutes and three catalysts are given in Figure 3. Rate of solute uptake decreased with an increase in molecular size of the adsorbate. Table 4 presents the data analyses. Adsorption uptakes and equilibrium constants (K) increased with increasing molecular size. The effect of catalyst was less marked. Average values of $\log K$ correlated well with the boiling point of the solute. Again, in all cases, the measured effective diffusivities (D_{eff}) were greater than the respective predicted pore diffusivities (D_p). These results indicate that surface diffusion is a general phenomenon in these systems. Estimated surface diffusivities generally decreased with increasing molecular size. However, since the total diffusivity also decreased, the fraction of the surface diffusion contribution was about the same in all cases, viz., 60-80%. This is a surprisingly high fraction of the diffusion flux and signifies that this component must be taken into account in theoretical calculations of diffusivities for these systems.

A further test was made for surface diffusion. This involved calcining the catalyst at different temperatures to obtain different adsorption constants. At lower calcination temperature, more water is retained and solute uptake is decreased. Surface diffusion should increase with an increase in K , as shown by Eq (8). The results for the three catalysts with naphthalene as solute is shown in Figure 4. Although considerable data scatter was obtained in these runs, an increasing trend of D_{eff} with K is evident. Extrapolation to $K=0$ allows calculation of the tortuosity τ , which gave values of 1.6, 2.1 and 1.8 for catalysts C, D and L. These values are reasonable, but are a little lower than might be expected.⁵

Because of the presence of a high surface diffusion contribution, it was not possible to evaluate restrictive diffusion in these systems since analysis now requires combination of Eq (8) and (9), resulting in too many unknown parameters (τ , D_s and K_r). In addition, values of D_B for these systems have not been experimentally determined and estimates based on property correlations are uncertain. However, for the case of the largest molecule in the smaller catalyst size (M in catalyst L), D_{eff} seems appreciably smaller and this is also reflected in a lower % surface flux. Thus, this case may be a possible indication of restrictive diffusion. Further studies are in progress in an attempt to quantify the restrictive diffusion effect by developing better techniques for obtaining more reliable data, separate determination of τ and D_B and making diffusion runs at lower adsorption uptakes to minimize surface diffusion. Also, studies at other temperatures are planned.

Conclusion

Studies of diffusion of condensed, multiring aromatic compounds into porous aluminas showed the following:

- 1) Adsorption increased with molecular size and followed a Langmuir adsorption isotherm.
- 2) Rate of diffusion decreased with molecular size.
- 3) Measured diffusivities were faster than predicted for simple pore diffusion and a surface contribution was postulated.
- 4) Surface diffusivities decreased with molecular size, but the fraction due to surface diffusion remained approximately constant.
- 5) Restricted diffusion was only detected with the largest solute and smallest pore alumina studied.

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TABLE 1. PROPERTIES OF SOLUTES

Property	Solute ^a				
	N	C	P	M	O
Molec. Wt., g/mole	128	228	252	615	793
Boiling Pt., °K	491	721	776	---	605
Critical Diam., Å	6.9	7.5	8.7	20	10
Bulk Diffusivity, ^b cm ² /sec. x 10 ⁶	9.7	7.1	6.6	3.8	---

^aN-Naphthalene, C-Chrysene, P-Perylene, M-Mesotetra-phenylporphine
O-Octaphenylcyclotetrasilane

^bin cyclohexane. Estimated from correlation of Reference 3.

TABLE 2. PROPERTIES OF ALUMINAS

Property	Alumina ^a			
	C	D	L	H
Surface Area, m ² /g	200	245	350	210
Pore Volume, cc/g	0.77	0.60	0.43	0.59
Av. Pore Diameter, Å	154	98	49	113
Particle Density, g/cc	1.01	1.21	1.48	1.17
Void Fraction, cc/cc	0.74	0.68	0.61	0.69
Acidity, Mol/m ² x 10 ⁶	2.4	1.1	0.6	---

^aC, D and L - Kaiser Alumina
H - Harshaw

TABLE 3. EFFECT OF SOLUTE PURITY ON DIFFUSION RATES

Solute ^a	Catalyst	Uptake mg/g	K	$D_{eff} \times 10^6$ cm ² /sec	$D_s \times 10^8$ cm ² /sec
I	C	2.09	120	13.7	9.2
P	C	2.76	157	8.7	3.9
I	D	1.97	146	14.4	8.2
P	D	2.26	167	9.0	3.9
I	L	1.63	164	12.7	6.4
P	L	1.70	171	6.2	2.4

^aChrysene Purity: I > 95%, P > 99%.

TABLE 4. DIFFUSION RUNS WITH CATALYSTS CALCINED AT 500°C

Solute ^a	Catalyst	Uptake mg/g	K	$D_{eff} \times 10^6$ cm ² /sec	$D_p^b \times 10^6$ cm ² /sec	$D_s \times 10^8$ cm ² /sec	Surface Flux %
N	C	0.60	33	11.5	3.6	32.4	69
	D	0.39	29	10.2	3.3	35.0	68
	L	0.68	69	7.8	3.0	11.4	62
C	C	2.33	141	9.4	2.6	6.6	72
	D	2.36	167	9.1	2.4	5.9	74
	L	1.96	171	6.3	2.2	3.8	65
M	C	14.3	583	4.0	1.4	0.6	65
	D	15.4	819	4.0	1.3	0.5	68
	L	12.9	914	2.2	1.2	0.2	48
O	C	13.2	47	2.8	1.2	4.4	55
	D	17.2	80	2.4	1.1	2.4	53
	L	16.7	78	2.5	1.0	3.1	60

^aN-Naphthalene, C-Chrysene, P-Perylene, M-Mesotetraphenylporphine, O-Octaphenylcyclo-tetrasiloxane. Solvent is cyclohexane.

^bEstimated by $D_p = D_b \epsilon/\tau$ (for $\tau = 2$)

Fig. 1 Overall schematic diagram of experimental system.

Legend

A : 500 ml resin flask	B : stirring gland
C : stirring rod with Teflon blade	
D : motor	E : rpm controller
F : peristaltic pump	G : flow rate controller
H : U.V. spectrophotometer with flow type cell	
I : recorder	J : incoming stream
K : outgoing stream	L : filter

Fig. 2 Comparison of diffusion rates of solutes in D alumina.

$\circ$ naphthalene $\triangle$ chrysene $\square$ perylene
 $\bullet$ octaphenylcyclotetrasiloxane $\diamond$ meso-tetraphenylporphine

Fig. 3. Adsorption isotherm of chrysene.

* C, D and L denote the type of adsorbent alumina.

Figure 4. Variation of Effective Diffusivity of Napthalene with Adsorption Constant. Catalysts: C-0, D-Δ, L-□

Project B-2 (Alternate)

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

Faculty Advisor: F.E. Massoth

Introduction

The importance of cobalt-molybdena catalysts for hydro-treating and hydrodesulfurization of petroleum feed stocks is well-known. These catalysts are also being studied for hydro-desulfurization and liquefaction of coal slurries and coal-derived liquids. However, such complex feed stocks result in rapid deactivation of the catalysts. To gain an insight into the deactivation mechanism, the detailed kinetics of benzothiophene hydrodesulfurization are compared before and after addition of various poisons and coke precursors. The studies are carried out using a constant stirred microbalance reactor, which enables simultaneous measurement of catalyst weight change of activity. Supplementary studies are made to gain additional insight into the affect of poisons on the active catalyst sites.

This project was substituted for the original B-2 project in the proposal in accordance with communication with Mr. Paul Scott and Mr. William Wu.

Experimental

Catalysts studied in this project were: 1) 8%-Mo/Al₂O₃, 2) 1%-Co 8%-Mo/Al₂O₃ and 3) 3%-Co 8%-Mo/Al₂O₃. The first two were prepared from a Ketjen γ -Al₂O₃ (CK-300) by impregnation and the last was a commercial Ketjen catalyst. The gases H₂, N₂ and He were passed through special traps to remove oxygen and water impurities. A 9% H₂S/H₂ blend, obtained commercially, was used directly.

Kinetic studies were carried out in a stirred flow microbalance reactor (SF MBR) described previously.¹ Figures 1 and 2 show the microbalance reactor and auxillary apparatus. Description of the various parts are as follows:

- A - wire to suspend catalyst bucket from balance.
- B - quartz fingers to prevent bucket from contacting stirrer (two fingers below and above the plane of the paper not shown).
- C - squirrel cage stirrer.
- D - platinum mesh bucket containing catalyst sample.
- E - thermocouple well.
- F - quartz reactor.
- G - capillary tube for introduction of high boiling liquids.
- GC - gas chromatograph with FID detector.
- H - constant temperature baths.

I - stainless steel saturators.
J - glass saturators.
K - rotameters.
L - septum for injection of liquids via Sage pump.
M - trap for high boiling products.
MB - Cahn microbalance.
FC - flow controller.
FM - flow monitors.
P - pressure gages.

Inlet and outlet lines were heated to prevent condensation of high boiling liquids. Benzothiophene reactant was at first introduced via the saturators I, but the temperatures required to attain reasonable partial pressures in the reactor caused decomposition and polymerization in the saturators. Consequently, the Sage pump was used for the introduction of benzothiophene with heptane as a solvent.

This apparatus permits simultaneous measurement of catalytic reaction rates and weight changes. A series of runs at varying flow rates and compositions allows determination of a rate expression for the kinetics of the reaction.² Consequently, the catalyst can be partially deactivated by introducing specific poisons or coke precursors, the amount added being determined by measuring the increase in catalyst weight. The kinetic series can then be repeated to determine the kinetics over the aged catalyst. Finally, the total amount of poison or coke required to completely deactivate the catalyst can be determined by successive additions of deactivating agents.

Mixing and catalytic activity tests for benzene hydrogenation showed the reactor to respond as a well mixed, stirred tank reactor.¹ However, the introduction of a liquid feed may have caused mixing problems. This was tested using the same benzene hydrogenation reaction but introducing the benzene from the Sage pump instead of the saturators as had been done previously. The results showed that proper mixing of reactants was not achieved. The reactor was subsequently modified as shown in Figure 3. The major modifications were introduction of a premix section below the reactor section and side baffles to help gas mixing in the reactor section. Also, the internals were fabricated of stainless steel instead of glass (the outer envelope remained glass) to improve mechanical strength. This modification gave good results in subsequent tests.

The microbalance reactor was also used to study H_2S adsorption over sulfided and partially deactivated catalysts. Weight changes were monitored as the H_2S/H_2 ratio was changed. Analysis of the data allows calculation of the H_2S adsorption constant and the number of adsorption sites.

Temperature programmed desorption (TPD) was studied in two different apparatuses. In the first, a small tube reactor containing the catalyst, was placed in the GC oven (in place of a normal chromatographic column), and the evolved gases monitored by TC or FI detectors. In the second, a reactor tube with catalyst was placed in a split shell furnace and the evolved gases monitored by a mass spectrometer. In both cases, the procedure involved adsorption of thiophene (TP) from a He carrier by a presulfided catalyst for about one-half hour followed by He purge for two hours, all at 100°C. Then the catalyst was heated in a linear temperature mode to 350°C. Peaks of the evolved gases vs. temperature were recorded. Runs were repeated after partial deactivation of the catalyst. The first apparatus allowed estimation of activation energies of the desorbed species and the second the nature of the desorption products.

Results and Discussion

A summary of the results of coking studies over presulfided Al_2O_3 and $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts are given in Figure 4. Benzothio-
phene (BT) coked over the Al_2O_3 in the presence of either H_2 or N_2 , and none of this coke was removed in a N_2 purge, whereas ethylbenzene (EB) did not coke in either gas. Both BT and EB coked over the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst in N_2 but not in H_2 . It appears necessary to have an olefinic substance such as BT or styrene to initiate coke formation. Ethylbenzene can dehydrogenate over the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst to form styrene, a likely coke precursor.³ The dehydrogenation of ethylbenzene to styrene does not occur over Al_2O_3 . Therefore, no coking is observed. Both Al_2O_3 and $\text{Mo}/\text{Al}_2\text{O}_3$ have sites for the formation of coke. However, only the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst has a hydrogenation function that can prevent coke formation in the presence of a coke precursor and H_2 .

Heterocyclic nitrogen compounds are well-known poisons for hydrodesulfurization reactions over these catalysts.⁴ This effect was tested using pyridine to poison the reaction of BT. Figure 5 shows the results of these tests. Pyridine was added at different partial pressures and conversion determined at steady state. Increasing amounts of pyridine in the feed resulted in increased catalyst weight and lowered conversion. After removal of pyridine from the reactant stream, catalyst weight and conversion did not return to the initial state. These results show that pyridine poisoning affects catalyst activity both reversibly and irreversibly. Further discussion of these results are given elsewhere.⁵ The NH_3 also caused comparable poisoning on a molar basis, but it was completely reversible.

Initial tests were made with the original reactor of Figure 2 for scoping of reaction variables. These were all carried out on presulfided Mo/Al or CoMo/Al catalysts. Increasing the partial

pressures of the various HDS reactants, products and poisons affected the BT conversion as follows: 1) BT-decrease, 2) H₂-increase, 3) H₂S-decrease, 4) EB-no change, 5) water-no change and 6) pyridine-large decrease. In addition, higher temperature resulted in only a small increase in conversion. These results are qualitatively consistent with kinetic rate forms described in the literature,⁴ viz., reactant and H₂S inhibition on the reaction due to competitive adsorption on active sites and positive order in hydrogen. The major product, EB, does not inhibit the reaction, which is most likely due to its relatively weak adsorption on active sites.

A more detailed kinetic run was performed at one temperature by systematically varying partial pressures to develop a kinetic expression for the reaction. Data are presented in Table 1. There was a small but gradual increase in catalyst weight and loss in conversion over the reaction period (compare standard Runs 10, 14 and 19) due to coking of the catalysts. An analysis of material condensed in the exit line trap (M in Figure 2) showed the presence of dimers of BT and/or dihydrobenzothiophene. Apparently some polymerization occurs on the catalysts and contributes to coke formation.

Kinetic analysis of these data was unsuccessful because they did not fit any reasonable rate form. The mixing characteristics of the original reactor used to obtain these data with the Sage pump were re-examined (discussed in the Experimental Section above). Unfortunately, due to the delays in fabrication of the new reactor, time did not permit further kinetic studies on the reaction before the end of the present contract. Nevertheless, the information obtained with the old reactor is valid despite the inability to obtain the precise kinetic data desired.

Adsorption of H₂S over sulfided and pyridine-poisoned Mo/Al₂O₃ catalyst was measured to determine whether partial poisoning of adsorption sites affects H₂S adsorption on remaining unpoisoned sites. Figure 6 shows results in terms of weight adsorbed vs. H₂S pressure at two temperatures. Different compositions of H₂S were achieved by adding excess H₂ or N₂ to the standard 9% H₂S/H₂ mixture. The same adsorption weight was obtained whether H₂ or N₂ was added, indicating that H₂S adsorption was independent of H₂ pressure. Runs were made on fresh sulfided catalyst and after poisoning with pyridine at two levels.

These data were analyzed by a Langmuir adsorption isotherm, viz.,

$$\Delta W_a = \frac{bKp}{1+Kp}$$

where ΔW_a is the weight adsorbed, b the number of adsorption sites, K the equilibrium adsorption constant and p the H₂S partial pressure. A nonlinear least squares technique was used to obtain values of K and b for each data set. The results are given in Table 2. Isotherms reconstructed from these data are

shown as solid curves in Figure 6. Although some scatter in the data is observed, the curves give a good fit to the data, signifying that the assumption of a Langmuir isotherm is a reasonable one. A qualitative consistency is also observed in the decreased amount of H_2S adsorbed with increasing pyridine on the catalyst. The K value of 51 at 400°C is in agreement with a value of 45 obtained in another study.² The higher value at 350°C is consistent with adsorption phenomena, i.e., decrease in adsorption with increasing temperature. An approximate heat of adsorption of 10 kcal/mole is obtained for these two points, which is again consistent with an adsorption process. After addition of pyridine, K values at 400°C increased while those at 350°C were essentially unchanged. The reasons for the increased values are presently not known. The trend in the b values is more consistent, as a decrease in this parameter would be expected if pyridine occupied H_2S adsorption sites. However, the quantitative agreement between the two temperatures is not as good as desired. Also, not all of the pyridine deposited is adsorbed on H_2S adsorption sites as judged by the lower Δb values compared to the amount of pyridine adsorbed. However, the latter values may be high in that some pyridine may have desorbed during the course of the experiment.

Temperature programmed desorption studies were undertaken to determine if adsorption sites for thiophene were affected by poisoning. The catalysts were presulfided at 400°C and the maximum heating temperature used was 350°C . Thiophene was added at 100°C and quinoline at 350°C . The carrier gas was He throughout.

Figure 7 shows some typical data obtained with the 1%-Co 8%-Mo/ Al_2O_3 catalyst. The peaks obtained were very broad and may contain more than one desorption species. By repeating desorption runs at different heating rates, an activation energy of desorption for each peak can be determined according to an analysis given by Cvetanovic and Amenomiya.⁶ The results for the various catalysts are tabulated in Table 3. These values were obtained from the experiments using FID. Over the Al_2O_3 support alone, considerably less thiophene was adsorbed and TPD revealed only a single low temperature peak at about 150°C . The peak decreased in size after poisoning with quinoline. The absence of this peak in the runs with catalysts signifies that either Al_2O_3 -like adsorption sites are not present on the sulfided catalyst or that they are altered by the presence of Mo. The Mo/ Al_2O_3 catalyst showed two characteristic peaks, whereas the CoMo/ Al_2O_3 catalyst showed only the lower temperature peak. After quinoline poisoning, the Mo/ Al_2O_3 catalyst gave a thiophene TPD response similar to the unpoisoned catalyst. For the CoMo/ Al_2O_3 catalyst, however, the original peak shifted to a higher temperature after quinoline poisoning. The latter result indicates that partial site poisoning may affect the adsorption energetics of the remaining sites.

As shown in Figure 7, the TC detector showed additional high temperature peaks not observed by the FI detector. These are inorganic in nature and may be due to H_2S arising from decomposition of the thiophene during desorption. Since the identity of the peaks cannot be established by either TC or FI detection, further experiments were made using a mass spectrometer for detection. This necessitated a different reactor set-up as discussed in the Experimental Section, but the results in both cases should be comparable qualitatively. The objectives of using mass spectrometry are to establish if the major peaks are due to desorption of thiophene and what constitutes the inorganic components.

Figure 8 shows the results of a series of runs with the 3%-Co 8%-Mo/ Al_2O_3 catalyst. Desorption of thiophene from the presulfided catalyst (top plot) showed the presence of thiophene and butene, as well as H_2S and CO_2 . The presence of butene was surprising and signifies that some of the thiophene had undergone decomposition during heating. The presence of H_2S , a decomposition product, confirms this. A composite of the butene and two TP peaks resembles reasonably well the FID peak #1 of Figure 7B. Three separate peaks were resolved by mass spectrometry and analysis suggests the presence of several different adsorption sites for TP on this catalyst. The low temperature TP peak may be due to weak adsorption on Al_2O_3 or Mo- Al_2O_3 sites, since it was also observed on the Al_2O_3 support. The intermediate butene peak may arise from TP which adsorbs on a moderately strong site and decomposes upon heating, or it may be due to readsorption of butene from the decomposition of TP on the first site and subsequent desorption of the butene. The high temperature TP peak evidently involves a strong adsorption site, from which TP desorbs intact. It seems odd that this TP does not decompose to butene in view of the high temperatures involved. However, it may be undergoing some decomposition to coke and H_2S , since the H_2S concentration rises steeply in this region.

The H_2S curve resembles the high temperature portion of the TCD curve of Figure 7, indicating that the latter is mainly due to H_2S from the decomposition of the thiophene. Its evolution at high temperature is probably due to reaction of an adsorbed sulfur atom with surface hydrogen present on the catalyst. The source of hydrogen for formation of H_2S and butene may come from irreversible hydrogen held on the presulfided catalyst.⁷ Since thiophene is H-deficient with respect to butene, some coke must be deposited during decomposition of the thiophene.

A curious finding in this run is the presence of appreciable CO_2 . This was observed in earlier preliminary runs with this catalyst and the Mo/ Al_2O_3 catalyst, but not with the Al_2O_3 support. Therefore, it was indigenous to the Mo present in these catalysts. This might arise from the reaction of butene or condensed hydrocarbons (coke precursors) on the

catalyst with some active oxide phase remaining on the sulfided catalyst. To investigate this possibility, the catalyst was allowed to react with thiophene (in H_2) overnight at $350^\circ C$ to remove all this active oxygen by reaction. A subsequent thiophene TPD run in He showed no CO_2 in the desorption products (middle plot of Figure 8), confirming this suspicion. This result indicates that, even after presulfiding the catalyst at $400^\circ C$, thiophene (or its products) is capable of reacting with residual oxide still left on the catalyst.

Another interesting result of this experiment is the shift in the thiophene and butene peaks to higher temperatures. The reacted state of the catalyst (after being exposed to thiophene/ H_2 under catalytic reaction conditions for an extended time) is considerably different from the original presulfided state. The activity differences for these catalyst persist for a considerable period of time before a constant steady-state activity is achieved.⁴ Apparently, this is due to catalyst structural changes as well as coke formation during this period.⁸ Similar structural changes have been recently reported.⁸

The effect of subsequent pyridine poisoning on this reacted catalyst is shown in the lower plot of Figure 8. Smaller thiophene and butene peaks are observed and the high temperature thiophene peak is absent. Thus, poisoning has resulted in the loss of some active sites and has caused a change in the adsorption energetics of the remaining sites.

Conclusions

- 1) The original stirred, microbalance reactor for gas-phase feeds was inadequate for liquid feeds. After modifications, the reactor exhibited excellent performance with a model test reaction.
- 2) A catalyst poisoning technique was developed to measure the number of active sites on the catalyst under steady-state conditions.
- 3) Hydrodesulfurization of benzothiophene increased with temperature and H_2 pressure, but decreased with benzothiophene and H_2S pressure.
- 4) Equilibrium adsorption data for H_2S over the sulfided catalysts followed a Langmuir isotherm. Poisoning reduced the amount of H_2S adsorbed.
- 5) Temperature programmed desorption of thiophene in He showed a complex pattern, including desorption of thiophene from several different sites and decomposition to butene and H_2S . Poisoning affected the desorption process in a complicated matter.

6) The state of the sulfided catalyst changes after reaction with thiophene for an extended period. Thiophene is active in removing residual amounts of oxygen left on the sulfided catalyst.

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Figure 1
Constant Stirred, Flow Microbalance Reactor

Figure 2

Constant Stirred, Flow Microbalance Reactor

Figure 3. Constant Stirred, Flow Microbalance
Reactor Modified.

Figure 4

Coking Profile of Benzothiophene and Ethylbenzene

Conditions Used (CP = Coking Precursor)

*In the case of ethylbenzene a 50:50 mixture of H_2/N_2 was used over the $Mo/\gamma-Al_2O_3$ catalyst

FIGURE 5. Effect of Pyridine Poisoning on Catalyst Activity.

Figure 6. H_2S Adsorption Isotherms - Effect of Pyridine. Values are Weights of Pyridine Added.

Figure 7. Thiophene TPD over 1% CoMo/Al₂O₃ catalyst. Catalyst presulfided at 400°C.
A. TCD response (1) blank run (2) thiophene run (3) blank run after (2).
B. FID response (1) thiophene run (2) repeat after poisoning with quinoline.

Figure 8. TPD of thiophene over 3% CoMo/Al₂O₃ catalyst.
 Symbols: ▲-thiophene, ○-butene, △-H₂S, ●-CO₂.
 (A) Fresh sulfided. (B) Aged in thiophene (C) Pyridine added.

Table 1. Effects of Reaction Conditions on Benzothiophene Conversion and Catalyst Weight Changes.

Catalyst Wt = 236.2 mg; Reactor Flow = 40 cc/min; Reactor Temp = 347°C;
Pressure = 650 mmHg; Catalyst = 8% Mo/ γ -Al₂O₃

Run ^{a,b}	10 ^c	11	12	13	14 ^c	15	16	17	18	19 ^c
P _T ^O	2.09	2.09	2.09	2.09	2.09	5.32	5.32	5.32	5.32	2.09
P _H ^O	579	227	554	162	579	572	220	547	161	5.79
P _S ^O	0	7.35	24.96	0	0	0	7.28	24.6	0	0
P _N ^O	0	345	0	417	0	0	348	0	415	0
P _T	1.43	1.98	1.90	1.81	1.45	4.15	5.05	4.95	4.88	1.53
P _E	0.65	0.12	0.20	0.28	0.65	1.16	0.27	0.36	0.44	0.57
P _H	577	226	553	161	577	568	220	547	160	577
P _S	0.65	7.48	25.2	0.28	0.65	1.16	7.55	24.8	0.44	0.57
% Conv	31.0	5.7	9.2	13.3	30.9	21.9	5.0	6.8	8.3	27.0
ΔW(mg)	+0.2	+0.8	+1.0	+0.7	+0.4	+0.7	+1.3	+1.3	+1.0	+0.7

^aSubscripts represent: T=benzothiophene, H=hydrogen, S=hydrogen sulfide, E-ethylbenzene, N-nitrogen.

^bP in mmHg.

^cStandard condition.

Table 2

Effect of Temperature and the Amount on Pyridine an K and b.

<u>Amount of Pyridine added mmol/g</u>	<u>Temperature °C</u>	<u>K_s atm⁻¹</u>	<u>b mmoles g</u>	<u>Δb mmoles g</u>
0	400	51	0.105	--
0.034	400	86	0.076	0.029
0.066	400	88	0.065	0.040
0	350	99	0.100	--
0.034	350	91	0.091	0.009
0.066	350	109	0.078	0.022

Table 3

Results of TPD of Thiophene.

Catalyst	Relative Amount Desorbed	Activation Energy of Desorption, kcal/mol Approximate Peak Temp °C		
		<u>150°</u>	<u>170°</u>	<u>230°</u>
Al ₂ O ₃	0.4	10	--	--
+ Quinoline	0.2	10	--	--
Mo/Al ₂ O ₃	1.1	--	15	19
+ Quinoline	0.8	--	15	23
1% CoMo/Al ₂ O ₃	1.0	--	15	--
+ Quinoline	0.8	--	--	18

Fundamental Studies on Hydrogen Transfer Over
Coal Conversion Catalysts

Faculty Advisor: S.W. Cowley

Introduction

Zinc chloride is a well-known coal liquefaction catalyst. Zielke et al.¹⁻⁴ and Weller⁵ have used zinc chloride in a molten salt process for coal liquefaction and found that it demonstrated high catalytic activity for selective conversion to products in the gasoline boiling range. Wood and Wiser⁶ used a small amount of zinc chloride with coal in a turbulent flow hydrogen reactor and found that it was active for an exceptionally rapid conversion of coal to a heavy liquid which, after upgrading, would provide a substitute refinery feedstock. Reactor space utilization of 2000 lb coal per cubic foot of reactor volume per hour were achieved. Because of the desirable products and excellent space utilization, zinc chloride based coal liquefaction processes may have considerable economic value as conventional refinery feedstocks dwindle.

The development of a viable zinc chloride-coal liquefaction process requires an understanding of the role played by zinc chloride and more information about the fundamental chemistry of zinc chloride. The effects of zinc chloride upon the hydrogenation of coal and coal derived liquids have been investigated,^{5,7,8} but the products are complex mixtures, and little information about the catalytic action or the chemical mechanism have been obtained from those studies.

Zinc chloride is known as a weak Lewis acid, that is, it accepts an electron pair with its associated entity to form a covalent bond. However, the Lewis acidity does not satisfactorily explain its catalytic behavior in coal liquefaction. Ferric chloride is a stronger Lewis acid than zinc chloride, but is less active for coal liquefaction. Aluminum chloride, a much stronger Lewis acid, is active but yields different products.⁹

Zielke et al.⁸ suggested that zinc chloride acts as a Friedel-Crafts acid, forming a complex with water and functioning as a proton donor or Bronsted acid:

Zinc chloride has long been used as a Friedel-Crafts catalyst.¹⁰ Dermer et al.¹¹ compared the activity of several metal chlorides for a known Friedel-Crafts ketone synthesis and found that the activity decreased in the order $\text{AlCl}_3 > \text{SbCl}_5 > \text{FeCl}_3 > \text{TiCl}_2 > \text{SnCl}_4 > \text{TeCl}_4 > \text{BiCl}_3 > \text{ZnCl}_2$. Similar comparisons by others^{12,13}

agree in putting ZnCl_2 at the bottom of the list. Thus a Friedel-Crafts mechanism does not explain why ZnCl_2 is a superior coal hydrogenation catalyst.

Zinc metal is not a good coal hydrogenation catalyst.⁶ However, Peretyaka et al.¹⁴ reported exchange between hydrogen and deuterium with zinc, but only with the metal vapor, not with solid metal.

The ability of zinc chloride and zinc metal to participate in well defined hydrogen transfer reactions was studied in this laboratory. Specific reactions were used to compare the acid properties of zinc chloride to the acid properties of well known catalysts. The hydrogen exchange properties of reduced zinc metal were also compared to the hydrogen exchange properties of metallic hydrogenation catalysts.

Three materials were selected for reference catalysts which are representative examples of different types of acidity. A fourth material, silica (S), has no acidic properties and was occasionally used as a blank. The acidic materials included solid phosphoric acid (SPA), which consists of polymerized orthophosphoric acid on a support. It is a strong Bronsted acid¹⁵ previously used for making high octane gasoline by polymerization of light olefins.¹⁶⁻¹⁸ It has not been reported to have Lewis acidity, and it is not an oxidizing agent.¹⁹

Another acidic material, silica-alumina (SA), is more complex, and several researchers²⁰⁻²⁸ have established that both Bronsted and Lewis acid sites are normally present. Addition of small amounts of water convert some Lewis acid sites to Bronsted acid sites.

Gamma-alumina (A) is a well-known Lewis acid^{29,30} with a very complex surface which also contains strong base sites.^{31,32} Hydration poisons the catalytic activity of gamma-alumina leaving only a very weak or 'passive' Bronsted acidity, but the normal Lewis acidity and its catalytic activity are restored by prolonged exposure to a vacuum at temperatures below 900°C.³³⁻³⁶ Acid properties of the reference catalysts used in this study are included with the summary in Table 1.

Four hydrogen exchange reactions were used to characterize the acid catalysts in terms of whether or not each reaction occurred. The first reaction was a hydride exchange over a Lewis acid and is shown in Figure 1a. The second reaction was a hydride exchange over a Bronsted acid, made possible by the presence of a small amount of olefin in the feed, as shown in Figure 1b. The third reaction was an exchange between the primary hydrogen of the hydrocarbon and the deuterium on the catalyst surface in the presence of a Lewis acid and is illustrated in Figure 2a. A fourth reaction was an exchange between olefinic molecular hydrogen and the deuterated catalyst surface with Bronsted acid

sites and is shown in Figure 2b. This reaction is often less useful than the others because of the competing olefin polymerization reaction which occurs readily over acid catalysts. The type of acidity exhibited by zinc chloride catalysts and the zinc chloride coal combination could be characterized relative to the reference catalysts using these reactions.

Experimental

A procedure similar to one given by Rosenblatt and Davis³⁷ for a Grignard reaction was used to prepare 2-methylpropane-2-d. The 2-chloro-2-methylpropane (99%) and deuterium oxide (99.8 atom %) were obtained from the Aldrich Chemical Company. Tetrahydrofuran and magnesium turnings were reagent grade. Fifty ml each of 2-chloro-2-methylpropane and tetrahydrofuran were added to a 500 ml flask and a trap was attached. A crystal of iodine and 2.5 g magnesium were added. The system was purged with a continuous helium flow. When the reaction was completed, the trap was immersed in liquid nitrogen. Three ml of deuterium oxide were mixed with a drop of phosphorous trichloride and drawn into a syringe for injection (dropwise) into the 500 ml flask through a septum. The 2-methylpropane-2-d was carried by the helium flow into the trap where about 3 ml of liquid were collected.

The trap was transferred to the vacuum system for purification by vaporization and condensation cycles. Olefins were removed by circulating the product over silica-alumina²² at 60°C.

A supported zinc chloride catalyst with low water content was prepared by reacting zinc metal with anhydrous hydrogen chloride gas at 540°C and vapor depositing the product on a previously dried support. Isotope dilution methods were used to establish that the mole percent water in the catalyst was less than 0.06%. Hydrated zinc chloride catalysts were prepared by evaporating a slurry mixture of water, zinc chloride and silica support.

The reference catalysts were industrial materials. The macro-porous silica (S) was Houdry's development catalyst support number 532 CP-57. This was also the support used for the hydrated zinc chloride catalysts. The solid phosphoric acid (SPA) was a Universal Oil Products catalyst made by mixing polyphosphoric acids with kieselguhr to form composites which were calcined at 180-300°C. The silica-alumina (SA) was a Houdry 159 CP experimental catalyst. The gamma-alumina (A) was a Cyanamid Ketjen CK-300 catalyst. Properties of the acidic reference catalysts are summarized in Table 1.

The metal reference catalyst was a supported nickel, Harshaw's Ni 0102T with 55% nickel (as NiO) on kieselguhr. The zinc metal catalyst was prepared by placing clean 20 x 30 mesh zinc granules in the bottom of a reactor, heating in hydrogen to 540°C, and vapor depositing the zinc metal on the glass wool packing and reactor walls above the granules. This procedure produced a reduced zinc metal surface.

The coal was from the Beehive mine in Utah and was typical of the subbituminous coals mined in Utah and southwestern Wyoming, see Table 2.

A glass vacuum system, shown in Figure 3, contained a closed loop with an inert pump (A) to circulate gases through the catalyst bed. The system included gas storage bulbs (B) and (C) and detachable U-tube traps (E) and (F), which were used both to transfer volatile liquid reagents into the vacuum system and to hold the catalyst bed. The exchange reactions were followed with a quadrupole mass spectrometer (not shown), a Varian VGA-100 gas analyzer with 1 amu resolution over 0-100 amu operable range.

The catalyst samples were given a standard pretreatment. Each sample was ground and sieved to 10 x 40 mesh and heated in air at 500°C to oxidize organic matter (heat treatment omitted for the volatile substances), then it was placed in a vacuum.

Further treatment was given to some of the catalysts. The deuterated catalysts were prepared by exchange with D₂ gas at 500°C. When a hydrated catalyst was required, the temperature was lowered between 200 and 300°C and exposed to H₂O or D₂O vapor until water uptake had ceased. Finally, each catalyst was placed in a vacuum prior to running the exchange reaction. The normal time for vacuum exposure was one hour, but a few, termed heavily hydrated, were given only a 15 minute vacuum exposure, a procedure which left more water on the catalyst.

The coal and the zinc chloride-coal combination were each heated in flowing helium to about 400°C, then they were transferred to the vacuum system for deuteration at 300°C by exchange with D₂O vapor and finally exposed to a vacuum for 1 hour prior to running the exchange reactions.

Table 3 lists the catalysts, reactants, reaction conditions and observed reactions.

Results and Discussion

The solid phosphoric acid catalyst did not undergo exchange reactions between catalyst deuterium and the hydrogen of paraffin molecules. However, the exchange reaction between catalyst deuterium and the hydrogen of olefin molecules occurred readily. Deuterium in the tertiary position of a paraffin molecule did not exchange with hydrogen in any position of nonlabeled paraffin molecules.

This result was the same whether an olefin was present or not. An exchange apparently occurred between the deuterated SPA surface and the hydrogen of 2-methylbutane when 2-methylpropene was present. This reaction was slow and was accompanied by increases in mass spectral peaks which were due to pentenes and decreases in the peaks due to 2-methylpropene.

The silica support, a nonacidic material, did not undergo exchange between surface deuterium and the hydrogen of either an olefin or a paraffin. However, a reaction occurred between 2-methylpropene and 2-methylbutane which produced pentenes.

Using the silica-alumina catalyst, exchange occurred readily between the surface deuterium and the hydrogen of a paraffin. The first products of this reaction contained several deuterium atoms per molecule. In addition, the hydride exchange reaction between deuterium and hydrogen in the tertiary positions of paraffin molecules occurred over both hydrated and nonhydrated catalysts. This reaction did not require the presence of an olefin and occurred between tertiary positions exclusively.

Using the gamma-alumina catalyst, exchange occurred between the surface deuterium and the hydrogen of a paraffin, when the catalyst surface was not hydrated. Hydrogen exchange did not occur when the surface was hydrated. In contrast to silica-alumina, the first products had only one deuterium atom in the molecule, and the molecules acquired additional deuterium atoms by subsequent exchange with the surface.

A hydride exchange reaction occurred with the deuterium in the tertiary position of paraffin molecules over gamma-alumina, but deuterium in the exchanged products was not restricted to the tertiary positions. The molecules had only one tertiary position, but they acquired more than one deuterium atom. The reaction was accompanied by paraffin dehydrogenation. These effects were not observed with the silica-alumina. The expected and observed exchange reactions using the reference catalysts are summarized in Table 4.

The catalytic activity of zinc chloride is sensitive to the amount of water present.³⁸⁻⁴¹ Consequently, supported zinc chloride catalysts were prepared with several states of hydration, including the anhydrous preparation with less than 0.06 mole percent water, based on the $ZnCl_2$. The hydride exchange reaction between hydrogen and deuterium in the tertiary positions of paraffin molecules did not occur over any zinc chloride catalyst. This result did not change when an olefin was added to the gas mixture. Furthermore, exchange did not occur between the surface deuterium of the zinc chloride catalyst and the hydrogen of a paraffin. When an olefin was present, exchange occurred, but only between the surface deuterium and the olefinic hydrogen exchange. This reaction was repeated at several temperatures to obtain rates. The average percent deuteration was calculated for each of a series of mass spectra taken at a single temperature. The rates of approach to equilibrium were calculated assuming the reaction was first order. The results are shown on an Arrhenius plot (Figure 4). The activation energy for the exchange reaction was about 16 kcal/mole.

The exchange reactions between adsorbed hydrocarbons and surface deuterium were attempted on coal both with and without the catalyst. No exchange reaction was observed between the

deuterated catalyst/coal combination and the hydrogen of a paraffin. However, exchange occurred readily between the deuterated catalyst/coal surface and the hydrogen of the olefin. The olefin exchange reaction was repeated using a separate sample of coal which was deuterated. Some exchange occurred between the deuterated coal surface and the hydrogen of the olefin, but at only about one sixth the rate observed with the catalyst/coal combination (see Figure 5).

Following the experiments involving coal, samples of both the zinc chloride treated coal and the untreated coal were analyzed by X-ray fluorescence for zinc. The analysis confirmed that the untreated coal had not been contaminated and that the zinc chloride in the treated coal had not been lost by volatilization.

The total amount of exchangeable hydrogen present in both the zinc chloride treated coal and in the untreated coal was calculated based on isotope dilution in the 2-methylpropene. Finally a portion of each sample was analyzed for total hydrogen by a CHN analysis. The results indicated that about 1.8% of the hydrogen in the zinc chloride treated coal participated in exchange compared to about 1.5% of the hydrogen in the untreated coal. The difference is probably not significant.

The experiments with metallic catalysts indicated that reduced zinc metal probably did not play a role in coal hydrogenation catalysis. Most metallic hydrogenation catalysts catalyze exchange between deuterium gas and ethane at temperatures below 200°C as was observed with the reduced nickel catalyst. Since no reaction occurred at 400°C, solid zinc metal does not demonstrate hydrogen exchange activity.

Conclusions

The exchange between the deuterated SPA surface and an olefin indicates that the SPA surface acts as a proton donor to the olefin, forming a carbonium ion as indicated in Figure 2a. However, even though carbonium ions were formed, they did not extract hydride ions from tertiary positions of paraffins as indicated in Figure 1b. Although exchange apparently occurred between the deuterated SPA surface and the hydrogen of 2-methylbutane in the presence of 2-methylpropene, examination of the mass spectra showed that all the peaks originally assigned to deuterium exchanged 2-methylbutane, could have been due to deuterium exchanged pentene which was formed at the same time. Thus, the exchange did not occur between the surface and paraffin molecules.

The exchange reactions over silica-alumina were consistent with the view that both Lewis and Bronsted sites are present on the surface. The Lewis sites were apparently capable of polarizing the paraffin molecules sufficiently that surface exchange could proceed as shown in Figure 2a. Also, the hydride exchange between the hydrogen in tertiary positions occurred readily, apparently via Lewis sites as shown in Figure 1a. Bronsted

sites were also present, which indicates that hydride ions did not combine with or exchange with surface hydrogen held at Bronsted sites, because although the surface deuterium exchanged readily with the hydrogen in primary positions, there was no exchange between tertiary and primary positions.

With gamma-alumina, surface deuterium exchanged with the hydrogen of paraffins with no olefin present, indicating that Lewis acid sites or possibly base sites capable of polarizing the molecule were present. The reaction proceeded stepwise, which indicates a different mechanism than that which occurred over silica-alumina. A further difference was shown in that tertiary deuterium exchanged with both tertiary and nontertiary hydrogens with simultaneous dehydrogenation. This could occur if the molecule were diadsorbed with the molecule donating a hydride from the tertiary position to a Lewis acid site and a proton to a base site. Evidently the hydride and the proton could combine to yield molecular hydrogen. Reversal of these reactions could lead to deuterium in nontertiary positions even though the starting materials were deuterated solely in tertiary positions. Table 4 summarizes the expected and observed hydrogen exchange reactions for the reference catalytic materials.

The results of the exchange reactions using zinc chloride, summarized in Table 5, indicate that hydrated zinc chloride behaved solely as a Bronsted type acid. The role of water is of considerable importance. No reaction occurred in its absence, but the reactions occurred at a slower rate when excessive water was present. Apparently there is an optimum amount of water for maximum catalytic activity.

Carbonium ions were formed from olefins with both the zinc chloride and the solid phosphoric acid catalysts, but in both cases the carbonium ions did not abstract hydride ions as expected. Because the carbonium ions were adsorbed onto the catalyst surface, there may be a steric reason for the lack of hydride abstraction (see Figure 6a). The hydride donor (I) must approach the carbonium ion (II) on the side opposite the catalyst surface. This would require the donor to form a free carbonium ion, not attached to the surface, which would have to exist long enough for the newly formed neutral molecule to desorb and move out of the way. This arrangement would also require a large net increase in the charge separation with a high energy requirement making the reaction very unlikely.

When Lewis acid sites are present, the molecule may be polarized in a direction parallel to the surface, as indicated in Figure 6b, or with the hydride ion between the carbonium ion and a Lewis acid site. Exchange could then occur by a disproportionation mechanism requiring neither free carbonium ions nor large increases in the net charge separation.

Results of the exchange reactions using coal, summarized in Table 5, indicate that the zinc chloride/coal combination also behaves as a Bronsted acid. Furthermore, untreated coal exhibits

a weak Bronsted acidity. The post reaction CHN analyses indicated that the deuterium oxide used to deuterate the coal and the zinc chloride/coal combination was not retained by the zinc chloride or the coal. Therefore, the hydrogen available for exchange must have originated in the coal structure. The amount of structural hydrogen available for exchange was only slightly higher in the zinc chloride treated coal than in the untreated coal. These observations support the view suggested by Massoth⁴² that the presence of zinc chloride does not provide new reaction pathways to hydrogen transfer, but rather it enhances pathways which were already available to untreated coal.

Exchange reaction rates for the treated and untreated coal are shown in Figure 5. Based on the kinetic data obtained earlier for the supported zinc chloride catalyst, the exchange reaction rate for the zinc chloride/coal combination was very slow. Also, polymerization of the 2-methylpropene began to occur over the supported zinc chloride catalyst at 123°C, but was absent over the zinc chloride/coal combination at 300°C. The treated coal has a much lower acid strength than the supported zinc chloride alone.

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Table 1. Properties of reference catalysts

Property	Catalyst			
	S	SPA	SA	A
Composition (%)				
SiO ₂	99	n.d	87.3	0
Al ₂ O ₃	0.1	n.d	12.4	99.2
Na ₂ O	0.1	n.d	0.25	0.0018
Surface Area (m ² /g)	350	2-4	290-315	192
Acid Type	None	Bronsted only	Bronsted and Lewis	Lewis only*

* Base sites are also present.

Table 2. Ultimate and proximate analysis of Beehive Mine, Utah coal

Ultimate Analysis MAF*

Carbon	76.1%
Hydrogen	5.7%
Nitrogen	1.5%
Oxygen	16.0%
Sulfur	0.7%

Proximate Analysis**

Volatile Matter	49.6%
Ash	7.5%
Fixed Carbon	42.9%

* Moisture and ash free basis

**Moisture free basis

TABLE 3

HYDROGEN-DEUTERIUM EXCHANGE REACTIONS

Catalyst ^(a)	Treatment ^(b)	Reactions Tested ^(c)	Gaseous Reagents		Temp. (°C)	Observed Reaction
			Mat'l ^(d)	P (torr)		
SPA	Deuterated Hydrated (D ₂ O)	3	I	60	300	None in 24 hr
SPA	Deuterated Hydrated (D ₂ O)	2,4	I II	60 6	300	Exchange
SPA	Hydrated (H ₂ O)	1	III I	120 40	300	None in 48 hr
SPA	Hydrated (H ₂ O)	2	III I II	120 40 15	300	Reaction
S	Deuterated	3	IV	200	350	None in 24 hr
S	Deuterated	4	II	200	350	None in 24 hr
S	Hydrated (H ₂ O)	(e)	I II	180 20	300	Reaction
SA	Deuterated Hydrated (D ₂ O)	3	IV	20	225	Exchange
SA	Hydrated (H ₂ O)	1	III V	120 30	200	Exchange
SA	Standard only	1	III V	80 40	225	Exchange

TABLE 3 (continued)

Catalyst (a)	Treatment (b)	Reactions Tested (c)	Gaseous Reagents		Temp. (°C)	Observed Reaction
			Mat'l (d)	P (torr)		
A	Deuterated Hydrated (D ₂ O)	3	IV	20	350	None in 4 hr
A	Deuterated	3	IV	20	135	Exchange
A	Exposed to vacuum overnight	1	III I	120	300	Exchange
ZnCl ₂	Deuterated Hydrated (D ₂ O)	3	I	120	300	None in 48 hr
ZnCl ₂	Deuterated, Hydrated (D ₂ O)	4	I II	120 14	300	Exchange
ZnCl ₂	Deuterated, Heavily Hydrated (D ₂ O)	4	I II	120 14	300	Exchange
ZnCl ₂	Deuterated, Hydrated (D ₂ O)	4	II	80	45-125	Exchange
ZnCl ₂	Hydrated (H ₂ O)	1	III I	120 40	300	None in 24 hr
ZnCl ₂	Hydrated, Exposed to vacuum overnight	1	III I	120 40	300	None in 24 hr
ZnCl ₂	Anhydrous Preparation	1	III V	180 90	300	None in 24 hr

TABLE 3 (continued)

Catalyst (a)	Treatment (b)	Reactions Tested (c)	Gaseous Reagents		Temp. (°C)	Observed Reaction
			Mat'l (d)	P (torr)		
ZnCl ₂	Anhydrous Preparation + 0.4 mole % H ₂ O added	1	III	180	300	None in 24 hr
			V	90		
ZnCl ₂	Hydrated (H ₂ O)	2	III	120	300	None in 24 hr
			I	40		
			II	35		
ZnCl ₂ /Coal	Deuterated, Hydrated (D ₂ O)	4	II	90	300	Exchange
ZnCl ₂ /Coal	Deuterated, Hydrated (D ₂ O)	3	IV	90	300	None in 3 days
Coal	Deuterated, Hydrated (D ₂ O)	4	II	90	300	Exchange
Ni	Reduced in H ₂	(f)	VI	25	150	Exchange in one hr
			VII	200		
Zn	Vapor deposited on Glass wool and reactor walls	(f)	VI	23	400	No exchange in 15 hours
			VII	183		

(a) SPA = Solid phosphoric acid, SA = Silica Alumina, S = Silica Support, A = Gamma Alumina, Ni = Nickel catalyst, Zn = Reduced Zinc Metal

(b) Catalyst pretreatment in addition to the standard pretreatment

(c) Reaction 1 = Fig 1a; Reaction 2 = Fig 1b; Reaction 3 = Fig 2a; Reaction 4 = Fig 2b

TABLE 3 (continued)

- (d) I = 2-methylbutane, II = 2-methylpropene, III = 2-methylpropane-2d, IV = 2-methylpropane, V = 3-methylpentane, VI = Ethane, VII = Deuterium Gas
- (e) Performed to test the reaction: $C_4H_8 + C_5H_{12} \longrightarrow C_4H_{10} + C_5H_{10}$
- (f) Performed to test the reaction: $C_2H_6 + nD_2 \longrightarrow C_2H_{6-n}D_n + nHD$

Table 4. Exchange of hydrogen over catalysts of known acid type.

Catalyst Tested	Acid Type	Hydride Transfer LA	Hydride Transfer BA	Surface Exchange Primary H	Surface Exchange Olefin
A	L	No (Yes)	-- (No)	Yes (Yes)	-- (No)
SA	L+B	Yes (Yes)	-- (Yes)	Yes (Yes)	-- (Yes)
SPA	B	No (No)	No (Yes)	No (No)	Yes (Yes)
S	None	No (No)	No (No)	No (No)	No (No)

A = alumina, SA = silica alumina, SPA = solid polyphosphoric acid, S = silica, L = Lewis acid and B = Bronsted acid.
Values in () are predicted.

Table 5. Exchange of ZnCl_2 on various supports.

Catalyst Tested	Hydride Transfer LA	Hydride Transfer BA	Surface Exchange Paraffin	Surface Exchange Olefin
$\text{ZnCl}_2/\text{SiO}_2$	No	No	No	Yes
$\text{ZnCl}_2/\text{-Al}_2\text{O}_3$	No	--	--	Yes
$\text{ZnCl}_2/\text{Coal}$	--	--	No	Yes
Coal	--	--	--	Yes

Figure 1. Hydride transfer between deuterium labeled and non-labeled hydrocarbons over (a) a Lewis acid [L] and (b) a Bronsted acid [BH].

(b)

Figure 2 . Exchange between deuterated catalyst surface and non-deuterated (a) alkanes or (b) olefins

Figure 3. Recirculating reactor and vacuum system including pump (A), gas storage bulbs (B,C), pressure gauge (D), traps (E,F), capillary inlet to mass spectrometer (G), vacuum trap (H), vacuum gauge (I), gas inlet manifold (J), D₂O storage (K), temperature controller (L), oven (M) and vacuum pump (N).

Figure 4. First order rate constant vs $1/RT$ for the hydrogen exchange reaction between 2-methylpropene and hydrated zinc chloride.

Figure 5. Effect of zinc chloride on the rate of 2-methylpropene-coal hydrogen exchange reaction at 300°C (a) untreated coal and (b) coal treated with zinc chloride.

Figure 6. Hydride transfer mechanism over (a) a Bronsted acid and (b) a Lewis acid.

Mechanism of Catalytic Hydrogenation by
Metal Halide Catalysts

Faculty Advisor: D.M. Bodily

Introduction

Metal halides such as ZnCl_2 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ are effective catalysts for coal hydrogenation. Work at the University of Utah using an entrained-flow reactor has demonstrated that these metal halides are active at short residence times.¹ A general model of the liquefaction process involves two stages.² In the first stage, covalent bonds are broken by thermal and/or catalytic processes to produce unstable intermediates. In the second stage, the intermediates may be stabilized by hydrogen transfer to produce low molecular weight product or they may polymerize to form char or coke. A catalyst may be effective in one or both stages. Work in this laboratory demonstrated that ZnCl_2 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ interact with coal and are active in the bond scission stage of the reaction, producing high liquid yields at short reaction times during coal hydrogenation.³ The metal halides dehydrogenated the coal at low temperatures under pyrolysis conditions, resulting in the suppression of devolatilization.⁴ The nature of the interaction of the catalyst and the coal is not certain, although under pyrolysis conditions the acid properties of the catalyst were destroyed below hydrogenation temperatures and free-radical scavengers had little effect on the interaction.^{5,6}

The mechanism of catalytic hydrogenation of coal by metal halide catalysts was further studied in this investigation. The products of hydrogenation reactions were analyzed to provide information on how changes in the catalyst effected the yield and nature of the products. The heavy liquid was separated and the fractions were characterized. The liquid products from coal hydrogenation were compared with coal liquids produced by other processes. The activity of metal halide catalysts was compared with that of other catalyst systems.

Experimental

Coal samples were hydrogenated in a coiled-tube, entrained-flow reactor.¹ Hydrogen pressures were 12.4 MPa and the temperature ranged from 400 to 510°C. Flow rates were adjusted to provide turbulent flow through the small diameter tube. Residence times in the heated reaction zone varied from 8 to 372 seconds, depending on flow rate, reactor length and degree of conversion. Water soluble catalysts were impregnated on the coal from aqueous solution. Insoluble catalysts were crushed and fed with the coal into the reactor. Heavy oil was collected in a water cooled condensor.

Lighter liquids were collected in subsequent condensers. The heavy oil has an initial boiling point of about 150°C.

A typical separation scheme for heavy oil is shown in Figure 1. In some cases the scheme was modified to include initial extraction of the char and heavy liquid with pyridine at room temperature and with hot pyridine. The extractions with pyridine, benzene and hexane were performed in soxhlet apparatus. The extractions with dilute acid and base were performed in separatory funnels. Hexane soluble oils were separated by gradient elution chromatography from columns packed with silica and alumina. Saturate, one-ring aromatic, two-ring aromatic, three to four-ring aromatic and polar fractions were obtained. The acidic and basic fractions were also separated by liquid chromatography. Gel permeation chromatography, GPC, was applied to each of the fractions.

Fractions were characterized by proton and carbon-13 nuclear magnetic resonance, NMR, at 100 MHz for protons and 25 MHz for carbon. Fourier transform techniques were used to record the carbon spectra. The proton spectra was divided into protons attached to aromatic rings, H_a , those attached to carbons alpha to aromatic rings, H_α , and those attached to aliphatic carbons not alpha to aromatic rings, H_o .

Molecular weights were determined by vapor pressure osmometry in dilute solutions. Carbon, hydrogen and nitrogen contents were determined by combustion followed by determination of CO_2 , H_2O and N_2 .

The elemental analysis and proton NMR results were used to determine average structural parameters for the liquid fractions according to the equations in Table 1. In some studies, these equations were extended and density and molecular weight included in the data base to optimize the determination of the parameters by computer.

Results and Discussion

The yields of hydrogenation products are listed in Table 2 for three samples with 1.5, 3.0 and 6.0 percent zinc as zinc chloride catalyst.⁹ These samples were separated by GPC as shown in Figure 2. Structural parameters for each of the subfractions are shown in Figures 3-7. The samples were hydrogenated under nearly identical conditions to give similar liquid yields. The yield of liquid increases slightly with increasing amount of catalyst. Much of the increased liquid yield is in the form of heavy liquid. Although the yield of heavy liquid increases through increased conversion as the amount of catalyst is increased, the average molecular weight of the heavy liquid decreases significantly with increasing catalyst. This is shown by the decreased yield of asphaltenes in samples 0.03 and 0.06 and by the GPC curves in Figure 2. Compounds with large molecular volumes elute first in GPC experiments. The asphaltenes show a slight shift to longer elution volumes (smaller molecular size) as the catalyst content increased. The effect is very pronounced for the aromatic oil in sample 0.06. Although the yields

of various products is changing, the nature of the products does not change as shown in Figures 3-7. Subfractions eluted under a certain set of conditions show the same structure independent of the amount of catalyst used during hydrogenation.

The chemical structure that evolves from the structural analysis is that of a condensed ring aromatic system with phenolic, naphthenic and aliphatic substituents.⁹ Heteroatoms may replace carbons in the ring structures or form functional groups on the periphery. The analysis treats each condensed ring system as a separate unit. The molecules may contain several units cross-linked together. Figure 7 shows that the molecules of the aromatic oil are composed of single units for the most part, while those of the asphaltene are polymers of the unit structures. The asphaltene fractions contain from 2.5 to 4 condensed rings on the average and the molecular weight varies from 400 to 1400. The aromatic oil fractions contain from 1 to 3 condensed rings and the molecular weights are between 250 and 700.

The progressive decrease in molecular weight of the liquid products of hydrogenation as the amount of catalyst is increased is interpreted as due to continuous degradation of the coal during reaction. The structural units observed in the asphaltene and oil fractions are postulated to be similar in nature to the structural units of the coal. Liquefaction by hydrogenation involves breaking of crosslinks between unit structures to produce extractable fragments. Only the more reactive functional groups are thought to react during the initial stages of liquefaction. The carbon backbone of the coal is not thought to be appreciably altered. Liquefaction thus involves the breaking of a limited number of covalent bonds, associated with disruption of polar interactions and the three-dimensional structure of the coal.

The hexane-soluble oil from sample 0.06 was separated by gradient elution chromatography as shown in Figure 8.¹⁰ The fractions were further separated by GPC as shown in Figure 9. Structural parameters calculated for the subfractions are shown in Figures 10-12. The higher molecular weight subfractions of each compound type contain long aliphatic chains which reduce the aromaticity. The lower molecular weight subfractions consist of aromatic and naphthenic rings.

The subfractions were analyzed by carbon-13 NMR (CMR).^{11,12} The aromaticities are shown in Figure 13. The ¹³C NMR results confirm the structures based on structural analysis. The aromatic carbons are slightly under estimated in CMR while the structural analysis approach requires an estimation of the C/H ratio in aliphatic groups. Although both methods contain inherent errors, the agreement between the methods is sufficient to confirm the structures proposed.

The saturate fraction was analysed by proton NMR, CMR and gas chromatography.¹² The fraction is composed largely of long chain paraffins with little branching. The results are listed in Table 3. It is not certain whether the paraffins originate

from the body of the coal or from a resinous component.

The structural analysis approach was used to compare four samples of coal liquids.¹³ Two solvent refined coals (SRC) and two hydrogenation liquids were selected. The yield of various product types is shown in Figure 14. The yields vary greatly among the samples. The synthoil sample shows a high asphaltene content while the two SRC samples show a high content of benzene insoluble material. The University of Utah coal hydrogenation liquid shows a high yield of hexane soluble oil. The structural parameters calculated by computer optimization are shown in Table 4. The molecular structure of the products is similar to that calculated for the coal-hydrogenation heavy oil, although the various structural parameters vary significantly among the samples.

Acidic and basic fractions were analyzed according to the scheme shown in Figure 15. The polar nature of the molecules complicates the analysis and the recovery of the sample from chromatography columns was low. Structural parameters for the subfractions are shown in Figure 16.

Zinc chloride was compared with cobalt-molybdate, presulfided red mud, red mud plus sulfur and no catalyst for effectiveness in coal hydrogenation.¹⁴ Conversions and analyses of products are shown in Table 5. The structural analysis of the products is shown in Figure 17. About 20% of the coal is liquefied without any catalyst at 500°C. Similar conversions are obtained with the solid catalysts tested. The structural analyses of the products are also similar indicating that these catalysts are inactive for coal hydrogenation at these residence times. The residence time is low in these cases due to lack of appreciable reaction. However, for ZnCl_2 catalyst under similar conditions, about 75% conversion is achieved and the residence time is increased. The conversion and residence time can be reduced by using shorter reactors. The results suggest that during liquefaction by catalytic hydrogenation, up to 20% of conversion is achieved noncatalytically and the products of this stage of the reaction are richer in hydrogen and have a lower heteroatom content than products of later stages of the reaction. Zinc chloride is effective even at the initial stage of the reaction producing a product under conditions where the noncatalytic reaction does not occur. The product of the reaction is more nearly like that produced at later stages. The products of the noncatalytic portion of the reaction is thought to originate in the hydrogen rich portions of the coal which produce the tar during pyrolysis. Coal may thus be viewed as having a dual structure with catalytic and noncatalytic or thermal reactions occurring simultaneously during hydrogenation.

Conclusion

The heavy liquid from coal hydrogenation has been separated to fractions of similar chemical properties and molecular size.

The subfractions have been characterized by analytical procedures to determine the average chemical structure of the constituent molecules. The heavy liquids are composed of molecules of condensed-ring aromatic systems with naphthenic, aliphatic and phenolic substitution. One or more of the condensed-ring aromatic systems form a molecule. The number of rings and the relative amounts of aliphatic and aromatic carbons vary significantly with the subfractions. High molecular weight molecules generally contain long aliphatic groups. These basic structural units are also observed in solvent refined coals and in synthoil products.

The structure of coal is thought to be similar to that of the hydrogenation products. Coal is composed of the same basic structural units, but they are highly crosslinked to form a solid material. The hydrogenation process involves rupture of these crosslinks to produce lower molecular weight products. As the size is decreased the fragments became more soluble in conventional solvents used to determine conversion. The carbon backbone structure of the units is thought to be little effected by hydrogenation, although more reactive functional groups may react.

Zinc chloride is an effective coal hydrogenation catalyst. It is active in bond scission during the initial stages of the reaction. Solid catalysts such as cobalt molybdate and ferric oxide are inactive in this stage of the reaction. As catalyst concentration, temperature or other conditions become more severe, the degree of degradation of the coal increases, altering the yield of various product types, but the basic nature of the structural units is not changed.

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Table 1
Structural Parameters

$$f_a = \frac{C/H - H_{\alpha}/HX - H_o/HY}{C/H} \quad (1)$$

$$H_{au}/Ca = \frac{H_a/H + H_{\alpha}/HX + O/H}{C/H - H_{\alpha}/HX - H_o/HY} \quad (2)$$

$$\sigma_t = \frac{H_{\alpha}/HX + O/H}{H_a/H + H_{\alpha}/HX + O/H} \quad (3)$$

$$H_o/H_{\alpha} = \frac{H_o/HY}{H_{\alpha}/HX} \quad (4)$$

$$M(us) = 12 Ca(us) + 14 Cp(us) \sigma_{al} \left(\frac{H_o}{H_{\alpha}} + 1 \right) + Cp(us) (1 - \sigma_{al} + 15 \sigma_o) \quad (5)$$

Definitions used in these equations are as follows:

f_a = fraction of aromatic carbons

H_{au}/Ca = ratio of the hydrogens in a hypothetical unsubstituted aromatic molecule to the aromatic carbons

σ_t = total substitution on the aromatic ring

σ_{al} = aliphatic substitution on the aromatic ring

σ_o = oxygen substitution on the aromatic ring

$\frac{H_o}{H_{\alpha}} + 1$ = length of aliphatic chain

$M(us)$ = molecular weight of the unit structure

Ca = aromatic carbon

Cp = peripheral carbon

X = H/C at alpha aliphatic carbon

Y = H/C at other aliphatic carbons

Table 2

Conversion and Products from Extraction of Heavy Oil

<u>Products</u>	<u>Percent Yield</u>		
	<u>Sample 0.015</u>	<u>Sample 0.03</u>	<u>Sample 0.06</u>
Solid	45.1	46.9	40.8
Liquids	42.9	49.8	50.4
Heavy Oil	25.6	31.8	31.3
Light Oil	12.1	10.9	13.2
Water	5.2	7.1	6.0
Gas (by difference)	12.0	3.3	8.8
Heavy Oil (% of coal)	25.6	31.8	31.3
Asphaltene (% of heavy oil)	17.3	6.6	6.0
Oil (% of heavy oil)	34.0	63.6	62.2
Saturates	8.9	11.9	6.9
Aromatic	91.1	88.1	93.1
Acidic (% of heavy oil)	9.5	17.4	12.9
Basic (% of heavy oil)	1.5	1.8	2.2
Residue (% of heavy oil)	28.4	5.3	3.3
Loss	9.3	5.3	12.9

Table 3
Structure of GPC Paraffin Sub-Fractions

	¹ H-NMR	¹³ C-NMR		G.C.			
	Branching ^a	C _n ^b	% of n-paraffin	C _n ^d	C min.	- C max. ^e	% of n-paraffin
Fr-1-P	0.088	50~60 ^c	67	33	27	- 40	68
Fr-2-P	0.054	34	86	28	21	- 33	81
Fr-3-P	0.168	23~28 ^c	54	22	16	- 27	68

a $\frac{H_Y/3}{H_O/2}$

b average number of carbon in n-paraffins

c indicated possible range of average carbon numbers in n-paraffins

d carbon number of n-paraffins at maximum in distribution

e distribution of n-paraffin

Table 4. Structural Parameters for the Fractions Calculated by Computer.

	M	FA	PAI	CTotal	RA	RN	CP(T)	CI (T)	CA	CPA	CIA	CN	CAL	CBL	CL	CP	N	L
SRC (P & M)																		
C ₆ H ₆ Soluble	1.0	0.764	0.245	32.22	7.18	1.23	19.29	14.82	29.97	17.62	12.35	4.13	5.22	3.40	0.63	5.11	4.75	4.
Asphaltene	1.0	0.766	0.469	55.66	11.05	2.52	24.06	25.14	42.66	22.56	20.10	6.53	7.03	5.14	0.83	6.46	5.00	5.
Oil	1.0	0.755	0.030	31.95	5.23	1.02	16.36	10.50	24.11	15.66	8.45	2.74	4.22	3.07	0.54	5.09	2.67	2.
SRC (U)																		
C ₆ H ₆ Soluble	2.0	0.905	1.000	23.24	4.70	0.00	15.63	5.40	21.03	15.63	5.40	0.00	1.59	0.49	0.13	2.21	1.59	2.
Asphaltene	3.0	0.883	0.786	65.36	14.80	0.27	34.78	24.13	58.31	34.72	23.60	0.60	3.84	3.49	0.36	7.10	2.36	4.
Oil	1.0	0.877	0.000	23.27	4.42	0.58	14.00	8.00	20.41	13.56	6.85	1.60	1.28	1.48	0.11	1.27	0.13	0.
Synthoil (ERDA)																		
C ₆ H ₆ Soluble	1.0	0.673	0.781	22.85	3.60	1.08	10.64	7.35	15.39	10.19	5.19	2.60	3.18	3.76	0.54	4.87	1.53	1.
Asphaltene	2.0	0.856	0.220	79.64	16.66	0.50	38.89	30.31	68.20	38.89	29.31	1.00	5.55	5.25	0.64	10.44	3.56	4.
Oil	1.0	0.665	0.885	21.11	3.29	0.51	10.07	5.61	14.04	9.45	4.59	1.64	2.75	3.64	0.68	5.43	2.33	2.
Coal Hydrogenated Oil (U of U)																		
Asphaltene	1.0	0.757	0.336	42.11	7.63	1.13	19.68	14.97	31.30	18.58	12.72	3.34	5.25	4.72	0.79	7.47	4.03	4.
Oil	1.0	0.610	0.405	23.45	3.03	0.93	12.71	5.13	11.28	3.29	7.99	4.57	4.90	1.46	1.46	7.60	4.03	4.

All parameters show values per average molecule of each fraction.

M = Number of fused ring systems	CIA = Number of internal aromatic carbons
FA = Fraction of aromatic carbon	CN = Number of naphthenic carbons
PAI = Ring compactness factor	CAL = Number of benzylic carbons
C Total = Number of total carbons	CBL = Number of nonbenzylic carbons bonded to one or two hydrogens
RA = Number of aromatic rings	CL = Number of aliphatic carbons bonded to three hydrogens except benzylic carbons
RN = Number of naphthenic rings	CP = Number of paraffinic carbons
CP(T) = Number of total peripheral carbons	N = Number of alkyl chains
CA = Number of aromatic carbons	L = Number of attachments of alkyl chains to rings
CPA = Number of peripheral aromatic carbons	CI(T) = Number of total internal carbons

Table 5. Yield of products from hydrogenation

Catalyst	Temp. (°C)	Tube length (m)	Time (sec)	Product distribution (% d.a.f.)							Conversion (%,d.a.f.)
				Liquid				Gas	Residue		
				Aqueous phase	Oil	Asphal- tene-I	Total		Asphal- tene-II	Toluene insolubles	
ZnCl ₂	400	36	13	1.7	1.3	0.6	3.6	2.0	0.6	93.8	6.2
	450	36	13	4.0	2.7	3.0	9.7	3.2	2.5	84.6	15.4
	500	12	3	4.2	4.4	3.4	12.0	2.0	3.7	82.3	17.7
		18	21	4.9	7.9	11.2	24.0	3.5	8.0	64.5	35.5
		24	3	3.9	4.8	4.8	13.5	2.9	2.3	81.3	18.7
		36	372	7.4	35.1	3.7	46.2	11.0	17.0	25.8	74.2
Co-Mo	500	36	12	3.3	6.3	4.1	13.7	2.6	2.9	80.8	19.2
Presulfided red-mud	500	36	12	4.5	5.3	6.5	16.3	4.1	2.5	77.1	22.9
Red-mud plus sulfur	500	36	12	4.3	4.5	7.5	16.3	3.3	2.5	77.9	22.1
No	500	36	10	2.9	5.5	5.1	13.6	3.4	3.0	80.0	20.0

Figure 1. Separation scheme.

Figure 2. GPC chromatograms.

Figure 3. Carbon aromaticity vs. elution volume for oils and asphaltenes.

Figure 4. The average length of aliphatic carbon chain vs. elution volume for oils and asphaltenes.

Figure 6. Values of the degree of the substitution of the aromatic system (g) vs. elution volume (Ve) for oils and asphaltenes.

Figure 5. The atomic hydrogen to ratio of the hypothetical unsubstituted aromatic material (H_{au}/C_a) vs. elution volume (V_e) for oils and asphaltenes.

Figure 7. Experimental and calculated molecular weights vs. elution volume.

Figure 8. Elution curve from liquid chromatography.

Figure 9. Elution curves from gel permeation chromatography.

Fig. 10: f_a vs. elution volume.

Fig. 11. σ vs. elution volume.

Fig 12. H_{α}/Ca and $\frac{H_o}{H_{\alpha}} + 1$ vs. elution volume.

Fig 13. f_a derived from ^{13}C -NMR vs. elution volume.

Figure 14. Yield of liquid products.

GPC SEPARATION OF ACID

LC SEPARATION OF ACID

LC SEPARATION OF BASE

FIG. 15. SEPARATION SCHEME OF ACID AND BASE

Figure 16. Structural parameters for acid and base fractions.

Figure 17. Change of structural parameters of products with conversion.

	Liquid	Asphaltene-II	Oil
ZnCl ₂	○	●	●
Co-Mo	△	▲	
Presulfided Red-Mud	□	■	
Red-Mud plus Sulfur	◇	◆	
No Catalyst	▽	▼	

The Mechanism of Pyrolysis of Bituminous Coal

Faculty Advisor: W. H. Wiser

Introduction

Coal liquefaction is usually conducted in the temperature range of 400-500°C in an effort to maximize the production of liquids. In this temperature range, coal liquefaction is usually understood to involve thermal rupture of the bonds connecting the aromatic and/or hydroaromatic structures in the coal, followed by stabilization of the resulting free radicals to produce stable molecules. In coal pyrolysis, this stabilization is understood to involve abstraction by the free radical of hydrogen from the hydroaromatic portion of the coal. In other approaches to coal liquefaction, such as solvent extraction with a hydrogen donor solvent or catalytic hydrogenation, the thermal bond rupture to produce free radicals is still a major step in the liquefaction operation, followed by radical stabilization from the various available sources.

It has been observed that in a solvent extraction system utilizing a coal-derived hydrogen donor solvent, as much as 30 percent or more of the coal is converted to liquids and gases without any net reduction in the hydrogen donor capability of the solvent. This is interpreted to mean that the utilization of the hydrogen donor capability of the coal, characteristic of the coal pyrolysis reactions, is operative in the early stages of the liquefaction process and occurs more readily than abstraction of hydrogen from the donor solvent molecules. Understanding the mechanisms involved in coal pyrolysis in the temperature range of 400-500°C is thus very important to the understanding of the mechanisms of coal liquefaction.

According to current understanding of bituminous coal structure, the principle structure in the coal consists of condensed aromatic configurations averaging about three rings per cluster, with a considerable amount of hydroaromatic structures of similar size. These condensed configurations are joined by short bridges consisting principally of ether linkages, short aliphatic bridges, a combination of these such as methoxy bridges and perhaps some biphenyl linkages. The complexity of the structure of bituminous coal presents extreme difficulty in trying to discern the mechanism of the pyrolytic reactions when it is not possible to know precisely the chemical makeup of the starting materials which would produce particular product molecules. It was, therefore, considered to be useful to examine the pyrolysis of model compounds which contain the important features of the coal structures.

Experimental

A series of model compound configurations was prepared on paper, each containing a cluster consisting of several condensed aromatic rings, with one hydroaromatic ring as part of the condensed configuration, and joined through a typical connecting bridge of the ether or short aliphatic type to a single ring aromatic structure. The theory was to prepare a structure which would pyrolyze in a manner similar to the pyrolysis of bituminous coal, namely the thermal rupture of the bond connecting two configurations and the abstraction of hydrogen from the hydroaromatic portion to produce stable molecules. Inasmuch as coal pyrolysis studies are usually conducted by measuring the weight loss of the coal as a function of time, the attempt was made to obtain compounds which would remain solid in the temperature range 400-450°C, thus permitting following the reaction with a thermal gravimetric apparatus. However, we were unable to obtain such compounds. All of the chemical synthesis laboratories contacted considered synthesis of these types of compounds to be too difficult and too time-consuming and they were not willing to attempt it.

We finally were able to obtain samples of 9-benzyl, 1,2,3,4-tetrahydrocarbazole. Since this compound would not remain solid to a temperature high enough to promote rupture of the connecting bridge at atmospheric pressure, it was necessary to construct equipment to permit the reaction to occur in the liquid or gaseous phase. A diagram of the reactor is shown in Figure 1. Several reactor vials were placed in a support ring and suspended in a fluidized sand bath. A carefully determined amount of 9-benzyl tetrahydrocarbazole was placed in each vial and the vial sealed. At a given time interval, one vial was removed from the sand bath and quenched. At the second time interval a second vial was removed and quenched and so on until all vials were removed and quenched at specified times. This provided for the time measurement of the kinetic determinations. The vial was opened and the products analyzed. The initial samples were analyzed by both gas chromatograph and mass spectrometer. After determining which compounds were produced in the reactions, only the gas chromatograph was subsequently used to determine the amounts of these various compounds.

Results and Discussion

The principal compounds produced in the pyrolysis of 9-benzyl, 1,2,3,4-tetrahydrocarbazole are shown in Figure 2. Only toluene, 1,2,3,4-tetrahydrocarbazole, carbazole and 9-benzylcarbazole appeared in any significant amounts, along with the unreacted 9-benzyl, 1,2,3,4-tetrahydrocarbazole. Other theoretically possible products were not detected or were detected in only trace amounts. Consideration of the compounds produced in the reaction leads to the conclusion that two principle pathways are possible. In all cases, the bond between the benzyl group and the nitrogen in the carbazole was ruptured. No other bonds were observed to rupture during

the initial pyrolytic reaction. The two alternatives then involve the manner in which the benzyl radical was stabilized to produce toluene. The stabilization could occur by hydrogen transfer from the hydroaromatic portion of the same molecule which produced the benzyl group. The second pathway would involve abstraction of hydrogen by the benzyl group from a different molecule than the one which produced the benzyl group. These two pathways are illustrated in Figure 3. If the benzyl group moved to a different molecule than the one which produced it in order to abstract hydrogen, the first pathway was followed leading to increasing concentrations of tetrahydrocarbazole. If the benzyl group received hydrogen from the same molecule which produced it, one would observe increasing concentrations of carbazole. It should be noted that in order to draw conclusions from the changing concentrations of these two products, one needs to look at the early stages of the reaction, because as the reactions proceed an equilibrium tends to be established among the various species in the system including the carbazole and the tetrahydrocarbazole.

The relative amounts of the various products of concern in determining the reaction path are shown in Table 1. At temperatures above 400°C the reaction proceeded so rapidly that the establishment of equilibria among the species already commenced by the time of the first sample analysis, namely 4 minutes. At the lower temperatures, however, it is observed that the initial reactions produced tetrahydrocarbazole with no carbazole appearing in the first 4 minutes. The tetrahydrocarbazole was produced faster than the carbazole even when the carbazole began to appear. The rate of production of 9-benzylcarbazole paralleled the rate of production of tetrahydrocarbazole in these beginning stages of the reaction. An equilibrium ratio of tetrahydrocarbazole to carbazole was approached at the longer times with a different ratio for each temperature.

Referring to Figure 3 one draws the following conclusions relative to the pathway of the stabilization reaction. The rupture of the bond between the benzyl group and the nitrogen of the tetrahydrocarbazole group produces a tetrahydrocarbazole radical and a benzyl radical. The absence of any carbazole or carbazole derivatives other than the tetrahydrocarbazole in the products in the initial stages of reaction indicates that the benzyl group did not receive hydrogen from the structure which produced it. The hydrogen abstraction was from a parent molecule, producing the 9-benzylcarbazole whose rate of appearance was roughly parallel to the rate of appearance of the tetrahydrocarbazole. Thus two parent molecules were utilized in the production of one toluene molecule.

One observes that the abstraction of hydrogen from a parent molecule by the benzyl group involves a two-body collision. The abstraction of hydrogen by a residual tetrahydrocarbazole radical also involves a two-body collision involving a parent molecule. It is of interest to observe whether these two-body collisions are involved in the slow and rate-determining steps

in the overall kinetics of the reaction, thereby yielding overall second order reaction kinetics.

An attempt was made to follow the rate of the reaction at constant temperatures by measuring the production of toluene as a function of time. The results obtained to date are somewhat less than satisfactory due to scatter of the data. The rate expression used for kinetic analysis of the data is:

$$\frac{dx}{dt} = k (a-x)^n \quad (1)$$

In this equation "x" is the micromoles of toluene formed, "a" is the micromoles of 9-benzyl 1,2,3,4-tetrahydrocarbazole initially placed in the vial, "k" is the reaction velocity constant and "n" is the kinetic reaction order. If n is 1 for a first order reaction, the integrated form of equation (1), with x = 0 when t = 0, is:

$$\ln \frac{a}{a-x} = kt \quad (2)$$

Figure 4 contains a plot of this equation at 392°C and Figure 5 contains a plot at 405°C. There appears to be a distinct concave-downward character to these curves plotted under first-order conditions, indicating that the reaction order is greater than one.

If n is set equal to 2 for a second order reaction, the integrated form of equation (1) with x = 0 when t = 0, is:

$$\frac{x}{a(a-x)} = kt \quad (3)$$

A plot of the experimental data under second-order conditions at 392°C is contained in Figure 6 and a plot at 405°C is contained in Figure 7. It appears that the best fit of these data is obtained by drawing a straight line through the data points. One concludes that there is an indication of overall second order kinetics in these data. However, the data points at the other three temperatures exhibited so much scatter that it was not possible to draw a reasonable conclusion concerning whether the data fit a straight line or a curve. At this point one must state that the kinetics, whether first order or second order, are inconclusive. Further experimental data must be obtained under improved experimental conditions to reduce the data scattering.

It is of interest to note that second order overall kinetics would most reasonably indicate a two-body collision in the rate determining step. This would be explained from these data by the observation that two of the parent molecules are actually involved in the production of one toluene molecule, since abstraction of hydrogen was observed to occur from a different molecule than the molecule which produced the benzyl

group. First order overall kinetics could conceivably be explained in terms of the thermal bond rupture being involved in the rate determining step.

It is noted in passing that considerable experimental data obtained from coal pyrolysis at constant temperature in the temperature range 400-500°C have yielded overall second order kinetics. On the other hand, coal pyrolysis at a constant heating rate through the temperature range 400-500°C have usually yielded first order kinetics according to the technique used to analyze the experimental data when the temperature is not constant. It is hoped that future kinetic studies with the right types of model compounds which can best represent pyrolysis of the coal structure may help to resolve this obvious conflict in pyrolysis studies on bituminous coal.

Conclusions

The compound 9-benzyl 1,2,3,4-tetrahydrocarbazole (9-BTHC) was chosen as a model compound to represent types of structural configurations and connecting bridges believed to be present in bituminous coal. It was pyrolyzed isothermally at 376-436°C. Closed-tube vapor-phase pyrolysis was done with a sample size of about 10 mg. A reliable reactor system was developed to study the kinetics of pyrolysis reaction. Reaction tubes were retrieved at different time intervals from the reaction-tubes-holder and quenched in liquid N₂. The products of pyrolysis were analyzed through a GC-MS for product confirmation and GC for quantitative analysis. A 10 ft x 1/8 inch stainless steel column packed with 3% OV-17 supported on chromosorb 100/120 WHP was used.

Carbazole, 1,2,3,4-tetrahydrocarbazole, toluene and 9-benzyl carbazole were observed to be the important products of pyrolysis. Small amounts of bibenzyl were observed whereas no benzene or biphenyl was detected.

The kinetic study indicated that the data fit better for second order than for first order. Furthermore, the stabilization of radicals formed by thermal rupture is effected principally by hydrogen abstraction from a second molecule. These observations indicate that the pyrolysis of the model compound 9-Benzyl, 1,2,3,4-tetrahydrocarbazole is second order under isothermal conditions with radical stabilization as the rate-determining step. Inasmuch as this model compound has been chosen to represent the structures and linkage believed to exist in bituminous coal, one might infer that the pyrolysis of bituminous coal is second order under isothermal conditions. Pyrolysis study of a few more model compounds with ether (-O-) and methylene (-CH₂-CH₂-) groups may give more evidence to this observation.

TABLE 1

RELATIVE AMOUNTS OF THC, CARB. AND 9 BENZ·C

<u>376°C</u>	<u>4 min</u>	<u>9 min</u>	<u>14 min</u>	<u>19 min</u>	<u>24 min</u>	<u>30 min</u>
THC	0.018	0.059	0.175	0.256	0.481	0.510
Carb.	0.0	0.005	0.004	0.016	0.114	0.115
Ratio $\frac{\text{THC}}{\text{Carb.}}$		12.0	44.0	16.0	4.2	4.4
9-Benz. C	0.048	0.150	0.353	0.431	0.534	0.551
 <u>390°C</u>	 <u>4 min</u>	 <u>7 min</u>	 <u>10 min</u>	 <u>14 min</u>	 <u>19 min</u>	 <u>23 min</u>
THC	0.070	0.204	0.372	0.552	0.700	0.952
Carb.	0.0	0.078	0.110	0.221	0.255	0.344
Ratio $\frac{\text{THC}}{\text{Carb.}}$		2.6	3.4	2.5	2.7	2.7
9-Benz. C	0.160	0.322	0.446	0.559	0.627	0.435
 <u>405°C</u>	 <u>5 min</u>	 <u>10 min</u>	 <u>15 min</u>	 <u>20 min</u>		
THC	0.247	0.558	0.595	0.725		
Carb.	0.141	0.319	0.343	0.442		
Ratio $\frac{\text{THC}}{\text{Carb.}}$	1.75	1.75	1.73	1.64		
9-Benz. C	0.156	0.272	0.247	0.311		
 <u>422°C</u>	 <u>4 min</u>	 <u>6 min</u>	 <u>8 min</u>	 <u>10 min</u>	 <u>12 min</u>	 <u>14 min</u>
THC	0.78	1.29	1.50	1.83	1.71	1.88
Carb.	0.40	0.78	0.96	1.42	1.17	1.36
Ratio $\frac{\text{THC}}{\text{Carb.}}$	1.95	1.65	1.56	1.29	1.46	1.36
9-Benz. C	0.46	0.72	0.74	0.74	0.41	0.52
 <u>436°C</u>	 <u>4 min</u>	 <u>6 min</u>	 <u>8 min</u>	 <u>10 min</u>	 <u>12 min</u>	 <u>14 min</u>
THC	0.58	0.80	1.26	1.09	1.21	1.23
Carb.	0.32	1.37	1.73	2.31	2.21	2.14
Ratio $\frac{\text{THC}}{\text{Carb.}}$	1.81	0.58	0.73	0.47	0.54	0.57
9-Benz. C	0.19	0.73	0.64	0.37	0.38	0.31

EXPERIMENTAL SET-UP FOR PYROLYSIS OF MODEL COMPOUND

TECAM FLUIDISED BATH SBS-4

Figure 1. Experimental Set-Up for Pyrolysis of Model Compound

PRINCIPAL PRODUCTS OF PYROLYSIS OF 9-BENZYL, 1,2,3,4 - TETRAHYDROCARBAZOLE

Figure 2. Principal Products of Pyrolysis of 9-Benzyl, 1,2,3,4-Tetrahydrocarbazole.

PYROLYSIS OF 9-BENZYL, 1,2,3,4 - TETRAHYDROCARBAZOLE POSSIBLE REACTION PATHS

3. Benzene and biphenyl are negligible.

4. Bibenzyl is present in very small amounts.

Figure 3. Pyrolysis of 9-Benzyl, 1,2,3,4 - Tetrahydrocarbazole
Possible Reaction Paths.

Figure 4. First Order Kinetic Plot at 392°C

Figure 5. First Order Kinetic Plot at 405°C.

Figure 6. Second Order Kinetic Plot at 392°C.

Figure 7. Second Order Kinetic Plot at 405°C.

Heat Transfer to Gas-Solid Suspensions in
Vertical Cocurrent Downflow

Faculty Advisor: J.D. Seader

Introduction

Recent applications of transport chemical reactors to coal gasification and liquefaction processes have prompted a new interest toward the understanding of transport phenomena in a gas-solids suspension flow. For example, in the University of Utah short-residence-time coal hydrogenation process, hydrogen and coal particles flow cocurrently downward through a tubular reactor, while being heated through the tube wall. Under these conditions, the reaction rate is greatly affected by transport phenomena, such as heat transfer and flow characteristics of the gas-solids suspension. Hence, it is important to understand momentum and heat transport mechanisms in such a vertical, cocurrent downflow system.

While numerous investigations on flow characteristics and heat transfer of gas-solids suspensions have been conducted in the past in connection with pneumatic transport or nuclear reactor cooling applications¹⁻⁴, most have been concerned with vertical-upflow or horizontal-flow systems; the vertical downflow system has been largely neglected. Recently, limited data on the vertical downflow case have been reported by Shimizu et al.⁵ for pressure drop and by Wahi⁶ for heat transfer. However, Shimizu et al. studied the pressure drop for a vertical-downflow system as a peripheral problem to their investigation for the vertical-upflow case, and they conceded that their data were not complete or trustworthy. Wahi investigated the effect of test section orientation on heat transfer for a limited range of solids-loading ratios.

The work reported here is a two-part study on heat transfer and pressure drop in cocurrent, downward flow of gas-solid suspensions at conditions of Reynolds number, particle size, and solids loading that are typical of coal reactors. The first part used suspensions of 329-micron glass spheres and was aimed at investigating the effects of flow orientation (upflow vs. downflow). The second part of the study used actual coal particles with the objective of determining the effects of particle shape and size distribution.

In the study, experimental data on both pressure drop and heat transfer from the wall to the suspension have been obtained. In addition, particle holdup or velocity in the tube have been measured to permit the calculation of the frictional component from the total pressure drop. A new, dimensionless parameter for correlating the data has been derived from a similarity analysis of the momentum equations.

STUDIES WITH GLASS BEADS

Experimental

The overall experimental apparatus for studies with air and glass beads consisted of three systems: gas and particles flow system, pressure drop and holdup test section, and heat transfer test section. A schematic flow diagram of the experimental apparatus is shown in Fig 1 with the holdup measurement section installed. Compressed air was drawn through regulators and rotameters and through a mixing chamber where particles, fed by a vibratory feeder, were mixed with air. The two-phase suspension flowed downward through the approach section (22 ft in length, corresponding to about 500 L/D) and the holdup (or heat transfer) test section and then to a receiving hopper where the air was exhausted into the room through a screen filter.

The test tubes were made of type 304 seamless stainless-steel tubing with 0.51 inch I.D. On the approach section 10 pressure taps, 20 $\frac{3}{8}$ inches apart for 7 taps and 40 $\frac{3}{4}$ inches apart for the rest, were attached to measure pressure drop profiles. The 3 ft long holdup test section, positioned after the approach section, had a set of slide valves attached at both ends. The slide valves were operated by pneumatic pistons connected to a series of activating mechanisms. A common electrical switch was used to close the two slide valves and open an air bypass solenoid, which was positioned before the rotameters.

Heat transfer experiments were conducted by replacing the holdup test section with a heat transfer test section, which, as shown in Fig 2, had 16 thermocouples attached on the outside surface of the tube at 13 axial positions. Since the heat transfer test section was directly heated by flowing electrical current through the tube wall, it was separated from the other sections by phenolic insulators. The copper flanges at both ends, which also served as bus bars for the electrical cables, were silver soldered.

A D.C. welder that could continuously deliver up to 300 amperes provided low-voltage, high-current electrical power. Signals from all thermocouples along with voltage drops through the tube and shunt (25 channels all together) were read by a data-logging system, which consisted of a digital meter, a scanner, a digital recorder, and a terminal panel. The data logger was interfaced to a Wang computer, which was programmed to take all readings, process the input data, and give print-outs of the raw data and final results.

Initial system calibration runs were made with air alone at various Reynolds numbers up to 30000 to check the operation of the apparatus. During the heat transfer calibration runs with air alone, heat losses through the insulation were experimentally determined, and by keeping the outlet tube-wall temperature constant at 250°F, the same heat-loss correction was applied for the experiments with glass bead-air suspensions.

For pressure drop and holdup measurements with suspensions, the air flow rate was first set at the desired value, and the particles were introduced into the air stream. At higher Reynolds numbers, just the rotameter was read, since the air flow rate was often changed by the addition of the particles. Except for the cases where complete pressure drop profiles were desired, only the pressure drop between the last two pressure taps was measured. The particle holdup was measured by closing the top and bottom slide valves simultaneously and weighing the particles trapped.

The procedure for the heat-transfer experiments involved first setting the desired air flow rate and adjusting the electrical power to yield an outlet tube-wall temperature of 250°F. After a steady-state condition was established with the flow of air alone, particles were introduced into the flow. As the tube-wall temperature decreased due to the addition of particles, the electrical power had to be readjusted to keep the outlet wall temperature constant. When the system reached steady-state again, the air inlet temperature upstream of the mixing chamber, the tube-wall temperatures, and the voltage drops were measured and processed by the computer. The air temperatures were calculated by solving thermal energy equations along with the particle Nusselt number equation.

The total pressure drop in a suspension flow may be regarded as the sum of accelerational, frictional, and static pressure drop. Thus,

$$\Delta P_t = \Delta P_a + \Delta P_f - \Delta P_{pp} \quad (1)$$

Since the manometer line was filled with air, the static head due to the gas is not included in Eq (1). The negative sign before ΔP_{pp} appears because the downward flow direction is taken as positive. Neglecting the acceleration pressure drop in the fully developed region, the friction pressure drop can be obtained from the measured pressure drop and the particle holdup data by the following equations:

$$\Delta P_f = \Delta P_t + \Delta P_{pp} \quad (2)$$

$$\Delta P_{pp} = E_p \rho_p L g / g_c \quad (3)$$

$$E_p = m_p / \rho_p V_H \quad (4)$$

where m_p is the weight of particles trapped in length L , and V_H is the volume of the holdup test section. The holdup data also permitted calculation of particle velocity and slip velocity by the continuity relation:

$$V_s = \frac{U_{sg}}{(1-E_p)} - \frac{U_{sp}}{E_p} \quad (5)$$

The suspension friction factor, defined by the following equation, was correlated in terms of gas Reynolds number and a dimensionless parameter, α , derived from a similarity analysis of the momentum equations of a suspension flow following the methods proposed by Hellums and Churchill:⁷

$$f_{tp} = \frac{\Delta P_f D}{2\rho_g U_{sg}^2 L} = 4 \left[\frac{DU_{sg}\rho_g}{\mu_g}, \alpha \right] \quad (6)$$

where $\alpha = \frac{C_D E_p D}{(1-E_p)d_p}$.

The net heat input to the suspension was obtained by subtracting the average heat loss of 25 Btu/hr, which represented 3 to 8 percent of the net heat input, from the generated heat in the tube-wall. Heat transfer results are presented in terms of local Nusselt numbers, which are defined by the following equation based on the temperature difference between the tube-wall and the local mean temperature of the gas phase:

$$Nu_s = \frac{g_i D}{k_g (T_{wi} - T_{gm})} \quad (7)$$

Results and Discussion

Friction factors and Nusselt numbers obtained from the test runs with air alone show good agreement with correlations for single-phase flow, e.g., Nikuradse equation for the friction factor and Kays equation for the Nusselt number. These results indicate the reliability of the measurements.

Axial pressure drop profiles reveal that the hydraulic entry length is considerably extended, up to an L/D of 300, by the addition of particles, and that it is dependent only on particle flow rates, being in agreement with the findings of Rose and Duckworth.⁸ The pressure drop profiles also show that a fully developed flow condition was ensured at the holdup (or heat transfer) test section.

At low gas flow rates, negative total pressure drops were observed; however, the frictional pressure drop calculated by Eq (2) always became positive and then increased with solids-loading ratio. Comparison of the present downflow data with upflow data reported in the literature shows that the friction pressure drop for a downflow system is smaller than that for an upflow system, the difference becoming larger as the solids-loading ratio increases.

Figure 3 shows the suspension friction factor plotted against the superficial gas Reynolds number with α as a parameter. The apparent transition from laminar flow to turbulent flow is delayed as the value of parameter α increases. This phenomenon may also be stated that, as more particles are added, the suspension flow becomes stabilized in the transition region. An empirical correlating equation was obtained from Figure 3. Generalization of the relation between the suspension friction factor and α was attempted by extending the similarity considerations to a packed bed, which represents an upper limit of the particle holdup. The pressure drop in a packed bed as given by Ergun's equation was correlated again in terms of α for the same range of variables as covered by Ergun's equation. The results are shown at the right-hand upper corner of Figure 4. The curves for the dilute-phase transport are shown at the left-lower corner. Although the dilute-phase transport curves do not extrapolate perfectly to the packed bed limit, Figure 4 indicates a possibility that the parameter α may be a universal correlating parameter. As α involves variables such as the particle holdup and drag coefficient, which are difficult to obtain from the input variables, further investigation of systems other than those of immediate interest here is needed to prove the generality of this parameter.

The effect of particle size on particle temperature was studied by a simultaneous solution of the particle- and gas-phase energy equation. The temperature difference between the gas and particles of 329 micron diameter was substantial being about 70°F. Hence, Nusselt numbers based on the suspension mean temperature as used by many investigators cannot represent true heat transfer processes occurring in large particle suspensions.

Figure 5 shows asymptotic Nusselt numbers for three different gas Reynolds numbers as a function of solids-loading ratios. At the gas Reynolds number of 10000, no change in asymptotic Nusselt numbers is observed for all solids-loading ratios studied. Above a gas Reynolds number of 10000, however, Nusselt numbers decreased with an increase in the solids-loading ratio. These contrary results for low and high Reynolds numbers may be due to the opposing effects of particles on suspension flow; boundary-layer thinning effect, which is caused by the sweeping action of particles when they hit the tube-wall, enhancing the heat transfer rate; and the effect of reduced wall eddy diffusivity, which is caused by reduced turbulence near the wall because of the large momentum relaxation time of the particles, decreasing the heat transfer rate. Despite the reduced Nusselt numbers, the amount of heat transferred to suspensions was always greater than that transferred to gas alone.

STUDIES WITH COAL PARTICLES

Experimental

The experimental apparatus for the studies with coal particles consisted of four systems: a gas supply and metering system, a solids handling system, a pressure drop and particle velocity measurement system, and a heat transfer system. The gas supply and metering system consisted of a compressor, primary and secondary regulators, a filter-dryer, and a rotameter. The maximum air output was approximately 10 scfm. The solids handling system consisted of a vibratory feeder, storage and receiving hoppers, a gas-solids mixing section, a cyclone separator, and a pneumatic return line connecting the two hoppers. The maximum output of the feeder was approximately 300 pounds of coal per hour, depending on the particle size.

Figure 6 is a diagram of the pressure drop and particle velocity measuring system. The flow section was constructed of 5/8 inch O.D. x 0.065 inch wall seamless 304 stainless steel tubing. A bank of two-way switching valves selected any two of fourteen pressure taps, and two manometers measured absolute and differential pressures. Particle velocity was measured by injecting a few tagged particles into the flowing suspension near the entrance of the flow section and then detecting passage of the injected particles at two downstream locations. The tagging agent was a phosphorescent powder pigment used in the paint industry and was attached to the coal particles using a sodium silicate solution as the "glue." Photomultiplier (PM) tube detectors and an oscilloscope and camera system measured the lag time, which could then be used to calculate the particle velocity.

The heat transfer system in Figure 7 was installed between the flange connections in the flow section of Figure 6. The tube was heated electrically by a 300 amp D.C. rectifier type welder. Twenty-one thermocouples (Type K) measured the local tube-wall temperature, and a digital multimeter and laboratory computer recorded and processed the data.

Pulverized coal for the experiments was obtained from the Castlegate Mine in Helper, Utah, and three size fractions were prepared by screening: -28/+48 mesh, -48/+100 mesh, and -100/+200 mesh. These three size fractions are referred to as L (large), M (medium), and S (small), respectively. Only experiments using the L coal, which had an average screen size of approximately 300 microns, are reported here.

The apparatus was first tested by measuring pressure drop for the flow of air alone, and the results compared favorably with accepted correlations for the friction factor. Heat transfer measurements for the flow of air alone were also made to determine the correction for heat lost to the surroundings during the subsequent runs with coal particles. The asymptotic wall Nusselt number for the flow of air alone compared favorably with accepted correlations.

Particle velocity was measured in suspensions of L coal where the gas velocity varied from 30 to 140 feet per second, and the solids flow rate varied from zero to 300 pounds of coal per hour. Two sizes of tagged particles were injected: -24/+28 mesh and -42/+48 mesh. The effect of the phosphor coating was investigated by coating some of the particles lightly and others heavily. Approximately 20 particles (one milligram) were injected for each measurement.

The 14 pressure taps provided 13 pressure tap intervals for pressure drop measurement at various axial locations. The pressure drop was measured at all locations for two gas Reynolds numbers (10000 and 30000) and two solids flow rates (85 and 235 lb/hr). The resulting axial pressure drop profiles were used in evaluating the performance of the pressure drop measuring system with solids present in the gas stream and the effect of solids on the hydraulic entry length. Two-phase-flow pressure drops between taps P12 and P13 and between P13 and P14 in Figure 6 were abnormally high due to slight wall disturbances associated with flange connection C1 and detector D2. Thus, the pressure drop for fully developed flow was subsequently measured for three gas Reynolds numbers (10000, 20000 and 30000) and a wide range of solids flow rates (0 to 300 lb/hr) at the interval between taps P11 and P12 rather than at the lowest position.

Results and Discussion

Particle velocity measurements indicate negligible slippage between coal particles and gas. No effect of particle size, level of phosphor coating, or solids flow rate was observed.

The equation of motion for a single particle accelerating in a uniform gas field is given by

$$\frac{dU_p}{dt} = g + C_D \frac{\rho_g A_p}{2\rho_p V_p} (U_g - U_p) |U_g - U_p| \quad (8)$$

where C_D is a function of $|Re_p|$, given by

$$Re_p = \frac{\rho_g d_s (U_g - U_p)}{\mu_g} \quad (9)$$

Equation (8) was solved numerically by a Runge-Kutta method and integrated to obtain particle velocity as a function of distance. The effect of particle shape was investigated by using both the standard drag curve and a drag curve for mineral particles.⁹ Particle velocity calculated by this method is compared with measured particle velocity in Figures 8 and 9. The effect of particle shape is negligible for the smaller coal particles.

The hydraulic entry length was considerably prolonged by the addition of solids and was equal to approximately ten feet (250 tube diameters). It was more dependent on solids loading ratio than on gas flow rate.

The total frictional pressure drop in fully developed, downward flow is given by

$$\Delta P_f = \Delta P_t + \Delta P_{pp} \quad (10)$$

In calculating the static head due to solids, ΔP_{pp} , the slip velocity between the gas and solids was assumed to be negligible.

The frictional pressure drop was then divided into components due to the gas and solids:

$$\Delta P_f = \Delta P_{fg} + \Delta P_{fs} \quad (11)$$

The ΔP_{fg} is the gas frictional pressure drop in the absence of solids, and ΔP_{fs} is the additional frictional pressure drop when solids are present. The ΔP_{fs} was correlated in terms of a solids friction factor, f_p , defined by

$$f_p = \frac{\Delta P_{fs}}{2 \left(\frac{\Delta z}{D} \right) \rho_p E_p U_s^2} \quad (12)$$

and plotted in Figure 10. The calculation is imprecise at low values of solids loading, causing the data to scatter in this range, where, however, ΔP_{fs} is small in comparison with ΔP_f ; and a constant value for f_p of 0.00023 was chosen to represent the data. This constant value for f_p allows calculation of the total frictional pressure drop, ΔP_f , to within 4 percent of the experimental value for all measurements.

Conclusion

Differences in particle density between the coal and glass beads made comparison of data difficult. The effects of particle shape and size distribution are also difficult to establish. For the conditions of this study, the velocity of fully accelerated coal particles in downward transport is approximately equal to the gas velocity. Since the additional frictional pressure drop caused by the coal particles is only a small portion of the total frictional pressure drop at low solids loadings, the additional frictional pressure drop can be correlated in terms of a particle friction factor, which has a constant value for a particular coal particle suspension.

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Nomenclature

A_p	Particle cross-sectional area
C_D	Drag coefficient in a suspension
d_p, D	Particle and tube diameters
d_s	Average screen size
E_p	Particle holdup
f_p	Particle friction factor
f_{tp}	Suspension friction factor
ΔP_a	Acceleration pressure drop
ΔP_f	Friction pressure drop
ΔP_{fg}	Gas frictional pressure drop
ΔP_{fs}	Solids frictional pressure drop
ΔP_t	Total pressure drop
ΔP_{pp}	Static pressure drop due to particles

Δz	Distance between pressure taps
k_g	Thermal conductivity of gas phase
L	Length
Nu_s	Nusselt number based on the gas mixed-mean temperature
q_i	Input heat flux
Re_p	Particle Reynolds number
Re_{sg}	Gas Reynolds number
t	Time
T_{gm}	Gas mixed-mean temperature
T_{wi}	Inside tube-wall temperature
U_g	Actual gas velocity
U_p	Particle velocity
U_{sg}, U_{sp}	Gas and particle superficial velocities
V_p	Particle volume
V_s	Slip velocity
α	A parameter defined below Eq (6)
μ_g	Gas viscosity
ρ_g, ρ_p	Gas and particle density

Figure 1. Schematic diagram of the overall apparatus

Figure 2. Detailed diagram of the heat transfer test section

Figure 3. Suspension friction factors

Figure 4. Universal correlation for gas solids suspension flows

Figure 5. Asymptotic Nusselt numbers

Figure 6. Pressure drop and particle velocity measuring system

Figure 7. Heat transfer section

Figure 8. Comparison of calculated particle velocity with measured particle velocity of -42/+48 mesh coal

Figure 9. Comparison of measured particle velocity with single particle calculation

Figure 10. Solids friction factor for L coal suspension

Coal Particle and Catalyst Characteristics for
Hydrogenation Evaluation and Testing

Faculty Advisor: R.E. Wood

Introduction

The objective of this project was to study the effect of coal and catalyst properties and pretreatment procedures on the hydrogenation of Western coals in the University of Utah short residence time, entrained flow reactor.¹ In practice, it has been necessary to restrict this broad scope and concentrate in a rather narrow area. The result has been a study of the effect of coal particle size and temperature on the conversion of high volatile bituminous coal in an entrained flow reactor. One product of the study has been the development of equations to describe the liquefaction of coal under varying conditions of temperature, pressure and particle size. Extrapolation of these equations provides a prediction that the use of very small particles (20-30 microns) would permit relaxation of temperature and pressure without a drop in conversion.

An important consideration in the economics of coal liquefaction is that of capital investment. Capital investment may be reduced to some extent by reduction of the size and complexity of process equipment. Most current coal liquefaction processes are descendants of German processes developed during the 1920-1940 period. These processes require high pressure reactors, residence time of about one hour, pressures greater than 14 MPa, temperatures of 400-500°C and coal that is mixed with a coal derived liquid prior to the reaction. Because of these conditions, process equipment is large and costly. Desirable improvements would be to reduce pressure and/or residence time, and to avoid the use of a vehicle liquid. These improvements may be possible by careful consideration of catalyst and coal particle size.

A reaction mechanism based on the reaction of an individual coal particle is suggested by the data. This mechanism is based on the unreacted-core-shrinking mechanism.² A chemical reaction mechanism is also suggested, which describes the chemical reaction at the surface of the unreacted core.

Hopefully, these ideas will lead to a better designed reactor system for coal liquefaction. This system would be based on the optimum adjustment of process variables such as temperature, pressure, catalyst amount and type and particle size.

By proper adjustment (500°C, 6% ZnCl₂, 12.4 MPa, 105 micron coal particle size), high volatile bituminous coals may be reacted to 85% liquids and gases in a few seconds with a large liquids to gas ratio. This is accomplished by reaction in an entrained flow reactor. Coal is fed continuously into a stream of hydrogen. The coal and hydrogen are then transported together into a long, small I.D. tubular reactor. The hydrogen provides the force to carry the hot, sticky coal particles through the reactor.

Experimental

The residence time of coal particles in the reactor is measured by the time required for an iron tracer to pass through. Powdered iron is detected at the beginning of the preheater and at the end of the reactor. The magnetic iron is detected by an oscillating magnetic field which has a resonant frequency of about 5 megacycles. When iron is in the vicinity of the magnetic field, the resonant frequency is slightly changed. This change in frequency may be monitored on a chart recorder using an electronic logic circuit. The time between the reading at the beginning of the preheater and the end of the reactor is indicative of the residence time.

A block diagram of the tubular (coiled tube) entrained flow reactor system is shown in Figure 1. The preheater consists of two 316 SS tubes which have a 4.8 mm I.D. and a 9.6 mm O.D. The tubes are 6.8 m in length and are coiled into 16 cm diameter closely wound helixes. The tubes are immersed in lead and each is heated electrically with as much as 12,000 watts. The tubes are connected in series. Additional 6.8 m long tubes, wound in a similar fashion, are connected in series to the preheater tubes. These tubes are 316 SS with a 6.4 mm I.D. and a 9.6 mm O.D. Each of these coils is immersed in lead and is heated with 1500 watts electrical energy.

The residence time of coal in the coiled tube reactor is measured by the detection of a powdered iron tracer at the points indicated OSC A and OSC B in Figure 1. Residence times vary from a few seconds to a few minutes. The gas residence time is calculated to be three seconds or less depending on the total length of the reactor. The coal particles tend to go through the tube much slower than the gas. This is because of the sticky nature of the heated coal particles. Particles tend to stick to the tube wall until dislodged by passing hydrogen or other coal particles.

The loaded and pressurized coal hopper holds about 5000 g of coal. The coal is fed to the reactor by a star wheel mechanism at the bottom of the hopper. The feed rate may be varied with a variable speed motor.

The series of vessels used for material handling following the reactor are all operated at the same pressure as the reactor. Each is made of 316 SS. The first in the series of product receivers is the catch tank. Here the reactor products enter the top in a downward direction. Vapors are swept into the first condenser. Solids and some high molecular weight liquids are permitted to fall to the bottom of the catch tank. A condenser consists of a water cooled tube and a liquids receiver or separation vessel. Three water cooled condensers are connected in series to separate liquids from the gas stream. Two filters are placed in series fitted with 5 micron cellulose filters. The gases pass through these filters to remove both residual particulate and droplet materials. The residual gases are then passed through a vessel containing a silica gel desiccant for water removal. The remainder of the gases, which contain some light hydrocarbons, sulfur compounds and primarily hydrogen, are recycled through the diaphragm compressor to the hopper.

The catch tank and condensers are designed to extract collected products at pressure. The condensers contain liquid materials which are easily removed through a valve. The catch tank, however, contains a solid or powdered material which is difficult to remove with the system at pressure.

Two gas compressors are used for this work. The first is a four stage piston type compressor with a capacity of $0.0017 \text{ m}^3/\text{sec}$ of hydrogen which will compress to as high as 97.8 MPa. This compressor is used to initially pressurize the entire reactor system. The second compressor is a two stage diaphragm type with a capacity of $0.017 \text{ m}^3/\text{sec}$ to as high as 14.8 MPa. This compressor is used to recycle hydrogen and gaseous reaction products through the system.

Temperature measurements are made along the length of the reactor by means of thermocouples attached at the end of each 6.8 m coil. Use of the magnetic iron detection device assumes that measurement of the iron residence time is also a measure of coal residence time. Experimental justification for this assumption was developed as part of the overall study.

The powdered iron tracer is injected into the coal-hydrogen stream by the use of a ball valve. This apparatus is intended to incorporate a pulse of iron into the stream with a minimal disturbance of the flow.

Unless otherwise stated, all samples are of Clear Creek, Utah coal. The coal was separated into -40 +60, -60 +100, and -100 +200 mesh size ranges by use of U.S. Standard screens. The weight average particle size of each of these ranges are 364, 195 and $105 \times 10^{-6} \text{ m}$, respectively. Table 1 shows the proximate analysis, Table 2 shows the petrographic analysis and Table 3 shows the ultimate and calorific analysis of each particle size range. The coal samples are mine run materials (grab

samples from a conveyor belt) and are not altered except for grinding and catalyst application. Clear Creek, Utah refers to the town near where this sample was obtained. It is from the Valley Camp Mining Company, Utah, Number One Mine located in the Wasatch Plateau area.

The catalyst is ZnCl_2 at 6.25% based on a moisture and ash free basis (MAF) unless otherwise stated. The ZnCl_2 is dissolved in sufficient water to wet the surface of the coal. The ZnCl_2 -water-coal mixture is then dried in an inert atmosphere until the temperature of the sample is 110-115°C.

Material balance is based on material fed into the reactor and all materials which are collected after the reaction, except gases. The mass of gases is the difference between solid materials fed and solid and liquid materials collected.

The routine measurement of the reactor volume is made following each test. This is necessary to make the material balance complete. At the end of any given experiment, a small amount of residue is left on the wall of the reactor. This consists of char with a greater concentration of ash and catalyst than the originally prepared coal sample. The density of this material was measured to be approximately 2 g/cm³. Other assumptions that lead to small errors in the measurement of the reactor volume are 1) nitrogen behaves as an ideal gas at low pressure and room temperature, 2) expansion of the gas is done adiabatically and 3) the process is reversible.

Three particle size fractions of Clear Creek, Utah coal were processed at four different reaction temperatures. These were -40 +60 (364 microns), -60 +100 (195 microns) and -100 +200 (105 microns) mesh. Temperatures were 471, 482, 493 and 504°C. Measurements on each trial included residence time in seconds, and percent product distribution, i.e., toluene insoluble residue (solids), light liquids (BP less than 150°C), heavy liquids (BP greater than 150°C), H_2O , gas and total conversion to gases and liquids. Chars were analyzed in terms of a standard proximate analysis, that is, moisture, ash, volatile matter and fixed carbon content. Calculations were then made in terms of the fractional conversion of the coal and volatile matter and fixed carbon originally in the coal, as a function of time at the reaction conditions.

Results and Discussion

A mathematical expression for a material production curve of the type obtained is

$$\frac{dx}{dt} = k(a-x)^n \quad (1)$$

where x is the fraction conversion, k is the temperature dependent Arrhenius constant, a is the maximum value of x , t is the time of reaction and n is the order of the reaction.

The integrated form of this equation is

$$kt = \frac{a^{(1-n)} - (a-x)^{(1-n)}}{1-n} \quad (2)$$

where $x=0$ at $t=0$.

The fractions of total coal matter, volatile matter and fixed carbon converted are represented by X_C , X_{VM} and X_{FC} , where

$$X_C = \frac{1-(X_C)_t}{(X_C)_0}$$

$$X_{VM} = \frac{1-(X_{VM})_t}{(X_{VM})_0}$$

$$X_{FC} = \frac{1-(X_{FC})_t}{(X_{FC})_0}$$

From the data obtained, 18 curves, 6 each for X_C , X_{VM} and X_{FC} have been calculated. Values for a , k and n (Eq 2) were calculated by choosing the maximum correlation coefficient for the data over a range of values for a and n with the restriction that $x=0$ at $t=0$. An example of these calculations is shown in Figure 2 where the 95% confidence limits are shown rather than the best single curve. This was done to demonstrate that the data is sufficiently reliable to show both temperature and particle size effects. A significant separation between the 95% confidence limits was found for the particle size effect particularly in the 50-200 second residence time range. Figure 3 shows the same calculations with respect to temperature variation for the 364 micron particle size sample. Here the separation between 95% confidence ranges is less well defined. Only data for fixed carbon conversion is shown.

From Figures 2 and 3, data can be extracted that will represent conversion of fixed carbon as a function of particle size and as a function of temperature. These numbers are shown in Tables 4 and 5. Further discussion will be in terms of conversion of fixed carbon, although similar remarks may be with respect to volatile matter and total carbon.

Figure 4 shows the relative rates of volatile matter and fixed carbon consumption from Clear Creek, Utah coal as a function of coal conversion. Initially, the Volatile matter is consumed at a much higher rate than the fixed carbon. At 60% coal conversion only 30% of the volatile matter remains, but more than 50% of the fixed carbon remains.

Heat produced in this reactor has been measured in terms of the volume of ambient air required to blow through the oven to prevent the temperature from rising above the set point. Below 75% coal conversion very little cooling air is required, indicating that pyrolysis is the primary reaction to this con-

version level. Above 75% conversion the requirement for cooling air increases markedly. This has been interpreted to mean that hydrogenation of high carbon, low hydrogen structures occurs with considerable heat produced and high volumes of hydrogen consumed at the higher conversion levels. Therefore, to minimize hydrogen consumption, conversion should be limited to 75-80% or below. This can be done readily in the 150-200 sec residence time range in the entrained flow reactor.

Very high space rate utilization factors are possible in a tubular reactor of the subject design. Figure 5 shows the space rate utilization factor versus conversion percent at 493°C, 12.4 MPa and the three particle sizes. Factors which have contributed to this reaction rate are 1) the addition of sufficient $ZnCl_2$, 2) sufficient partial pressure of hydrogen, 3) rapid transfer of energy to the coal particle and 4) sufficient temperature.

A reaction mechanism to describe the coal pyrolysis-hydrogenation reaction completely is very complex and beyond the scope of this report. However, in selecting a simple scheme to fit the reaction conditions, one may write

where P is the MAF coal, R is the semi-coke, $P^{\cdot}$ represents a thermally produced free radical, * is a catalyst molecule capable of interacting with molecular H_2 and H_{ar} is hydrogen attached to a hydroaromatic carbon but restricted to one hydrogen atom per hydroaromatic carbon atom.

The thermal bond rupture via Reaction (3) to produce $P^{\cdot}$ is fast, and the rate of the overall reaction is determined by the interaction of $P^{\cdot}$ to yield products. This is consistent with the second order kinetics observed in coal pyrolysis³⁻⁵ and dissolution.^{4,6}

With appropriate assumptions, the rate of production of reaction products is

$$R_{PH} = \frac{k_1 [P] (k_7[H-*) + k_8[H_{ar}])}{k_4 [P^{\cdot}] + (k_7[H-*) + k_8[H_{ar}])} \quad (9)$$

As $[H-^*]$ increases, $[k_7 H-^*] + k_8 [H_{ar}]$ may become large with respect to $k_4 [P']$. Then R_{PH} becomes nearly independent of $[H-^*]$. The form of this equation is then consistent with the shape of the production curves measured.

The coal hydrogenation reaction in the coiled tube reactor can be considered using the unreacted-core-shrinking model.² The solid reactant followed for this purpose is the fixed carbon. Mazumdar et al. has shown that the change in fixed carbon is directly proportional to the amount of hydrogen added to the coal.⁷⁻⁹

Measurements with Clear Creek, Utah coal with widely different residence times in the coiled tube reactor and consequently different conversion levels have led to the data of Figure 4. As shown, the volatile matter is initially reduced at a more rapid rate than is fixed carbon. As conversion becomes greater, the rate of consumption of fixed carbon increases and that of volatile matter decreases. This could indicate a mechanism which includes a reaction, whereby fixed carbon is transformed to volatile matter and hence to liquids and gases. A clear separation in the rates of volatile matter from that of the fixed carbon consumption is indicated. This suggests that the hydrogenation reaction may be followed by changes in fixed carbon mass.

Two equations which describe the reaction time for a given conversion are as follows:²

$$t = \frac{R}{k_S C_{A_0}} [1 - (1-X)^{1/3}] \quad (10)$$

$$t = \frac{a C_{S_0} R^2}{2 C_{A_0} D_{eA}} [1 - (1-X)^{1/3}]^2 \quad (11)$$

Equation (10) describes a chemically controlled reaction, and Equation (11) describes an inert layer diffusion controlled reaction. In the coal hydrogenation model, A is H_2 , X is X_{FC} , S is coal, t is the residence time of the coal, R is the particle radius or $D/2$ where D is the diameter of the coal particle and D_{eA} is the diffusivity of the diffusing specie in the inert layer.

Figure 6 shows a plot of $\ln t$ vs. $\ln 1 - (1-X_{FC})^{1/3}$ for Clear Creek, Utah coal processed at various temperatures and particle sizes. Points on a given line from left to right represent X_{FC} values of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6, respectively. The conversion levels of 0.1 to 0.3 show slopes of the lines which are approximately unity, indicating a reaction which is chemically controlled at the surface of the unreacted core. For temperatures of 471° and $482^\circ C$, the chemically controlled reaction continues to $X_{FC} = 0.6$. However, at higher temperatures the reaction reverts to physical control as shown by the slope of approximately two in the area where X_{FC} is

0.4 to 0.6. This probably happens because at the higher temperatures, the chemical reaction rate is increased. As the inert outer layer of the particle thickens, the flow of hydrogen through the inert layer to the unreacted core is inhibited. The slow step in the reaction, then, is transferred from chemical control to inert layer diffusion control.

For the diffusion rate controlled region, it is not possible to determine whether the mechanism is bulk, Knudsen or activated diffusion. Probably all three types of diffusion occur to some extent. This is true because the porosity characteristic of all three types of diffusion occur in coal chars. The average size of pores becomes larger in coal particles as they are heated and swell. However, bulk diffusion, characteristic of the larger pore sizes, is more prominent in coal chars than in the original coal.

It is not possible, with the data of Figure 6 to determine an accurate diffusivity or activation energy for the diffusion controlled regime. This is partly because, in each case, there is a wide region where the reaction rate is chemically controlled. The chemical rate constitutes the greatest possible rate at any given reactor condition. It is therefore desirable to keep the coal hydrogenation reaction in the chemically controlled regime to the highest conversion level possible.

Figure 6 shows data at four different temperatures. This data is sufficient to evaluate the activation energy for hydrogen addition to coal and the result is 44.5 Kcal per mole of hydrogen. The activation energy for diffusion of hydrogen in coal char has been reported as 8.5 Kcal per mole of hydrogen.¹⁰ The figure of 44.5 Kcal per mole of hydrogen is in the range ordinarily accepted for a chemically controlled reaction.

Various projections may be made by use of Equation (10) assuming that the chemical control mechanism holds for an extended range of temperature, hydrogen partial pressure and particle diameter. These projections may or may not be valid depending on the physical aspects of the system in which they are tested. Therefore, a reactor must be used where the particles remain essentially separated. Validity of the projections also depends on relative rates of reactions which do not contribute to the production of liquids. For instance, at high temperatures the production of gases is increased. This is especially true at temperatures greater than 600°C. The polymerization reaction may also be temperature and pressure dependent. Also, the projections based on Equation (10) represent the most rapid reaction that could be expected. This is because the system reversion to a diffusion control regime will give a reduced reaction rate.

Figure 7 illustrates the very rapid increase in reaction rate with an increase in temperature. However, elevated temperatures have operational problems. Temperatures in excess of 500°C

are troublesome because of particle agglomeration. Also, hydrogen consumption is increased and product gases increase at the expense of liquid production.

Figure 8 shows the effect of pressure on the rate of reaction. An increase in pressure is effective in increasing the reaction rate. Since the chemical rate is proportional to pressure, the rate increases with pressure until the depletion of hydrogen at the surface of the unreacted core exceeds the hydrogen made available by diffusion through the inert layer. At this point, the reaction rate is independent of the hydrogen pressure.

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

Figure 9 shows the effect of coal particle diameter on chemical reaction rate. The rate increases remarkably with a reduction of size. The smaller particles of coal (2.5 to 10 microns) are somewhat difficult to obtain because of grinding costs. However, recent advances in grinding technology have made the use of smaller particles possible.¹¹ The power requirements for grinding increase rapidly with a decrease in the average particle size. Medium particle sizes of 19, 11, 7, 4 and 3 microns were attained with a power requirement of 13, 80, 199, 402 and 842 kilowatt hours per ton of coal, respectively. This was accomplished with samples of Montana Rosebud coal in an "attritor" grinding device. An economic analysis would be required to discover what particle size coal should be used.

Figures 10 and 11 further illustrate the particle size effect. If coal is to be converted 75% ($X_{FC} = 0.6$) to liquids and gases at less than 500°C, the particle size should be less than 100 microns. This reaction may be done in 25 sec or less as shown in Figure 12. The time requirement becomes less as the particle size is reduced. If the time requirement was 10 sec or less, the particle size should be 32 microns or less. The pressure in these instances is 12.4 MPa H_2 . If the pressure is reduced, the time requirement for 75% conversion increases as shown in Figure 12. The projection is that 55 sec reaction time would be required for 75% conversion for 50 micron coal particles and a pressure of 3.5 MPa.

Conclusion

Conclusions drawn from the development and use of the residence time measurement device are 1) accurate information is obtained on the coal residence time distribution by the detection

of a -400 mesh iron or magnetite tracer, 2] the detection coil of the residence time measurement device may be used in a high temperature, high pressure environment as well as under less demanding conditions and 3) the residence time measurement device may be used to detect incremental samples of some high ash coals without added tracer.

. A coal hydrogenation reactor has been designed which 1) facilitates the feeding of dry coal particles instead of a liquid-coal slurry into a medium pressure and medium temperature reactor, 2) reacts the coal in a short time (1-200 sec) to produce liquids and gases and 3) has a large space rate utilization factor (1-150 Kg/m³ sec).

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

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

The data which lead to a chemical mechanism of coal pyrolysis-hydrogenation illustrates the following ideas: 1) The addition of molecular hydrogen without catalyst is very slow at temperatures below 600°C, 2) The hydrogenation reaction is very rapid with ZnCl₂ added as a catalyst to the coal, 3) The ZnCl₂ hydrogen complex provides an alternate source of hydrogen to the hydroaromatic hydrogen already available in the coal, 4) Thermally produced free radicals in the coal are stabilized by addition of hydrogen (catalytically or from the hydroaromatic) or by the recombination of two free radicals and 5) Addition of hydrogen tends to produce liquids and gases whereas the recombination of two free radicals tends to produce solids.

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TABLE 1
PROXIMATE ANALYSES OF CLEAR CREEK, UTAH
COAL FOR VARIOUS PARTICLE SIZES

Particle Size 10 ⁻⁶ Meters	Percent			
	H ₂ O	Ash	Volatile Matter	Fixed Carbon
364	6.49	5.04	41.09	47.38
195	6.00	10.00	38.40	45.60
105	6.33	8.96	40.15	44.54
364	Moisture	5.39	43.95	50.67
195	Free	10.64	40.85	48.51
105		9.57	42.86	47.55
364	Moisture		46.45	53.55
195	and Ash		45.71	54.29
105	Free		47.40	52.60

TABLE 2

PETROGRAPHIC ANALYSIS OF CLEAR CREEK, UTAH COAL AT
VARIOUS PARTICLE SIZES. DONE BY THE PENNSYLVANIA
STATE UNIVERSITY, COLLEGE OF EARTH AND MINERAL
SCIENCES, COAL RESEARCH SECTION, UNIVERSITY
PARK, PA

Particle Size 10 ⁻⁶ Meters	Vit	Pseudo Vit	Fus	Semi Fus	Mac	Mic	Ex	Res
364	95.4	0.0	0.4	2.2	0.2	0.1	1.6	0.1
195	93.6	0.3	0.2	3.1	0.1	0.6	1.8	0.3
105	95.4	0.0	0.7	1.8	0.1	0.9	1.1	0.0
% Vitrinite Types					Vitrinite Reflectance (Mean Maxima in Oil)			
	V ₄	V ₅	V ₆	V ₇	Range	Average		
364	3	54	43	0	0.48 - 0.69	0.589		
195	0	80	20	0	0.50 - 0.64	0.561		
105	1	57	41	1	0.47 - 0.70	0.590		

Items included: Vitrinite, pseudovitrinite, fusinite, semifusinite, macrinite, micrinite, exinite and resinite. Alginite and sclerotinite are always zero. Analysis is on a moisture and ash free basis.

TABLE 3

ULTIMATE AND CALORIFIC ANALYSIS OF CLEAR CREEK,
UTAH COAL AT VARIOUS PARTICLE SIZES.

Particle Size M	% (MF Basis)					Cal/g
	C	H	N	S	O(diff)	
364	70.81	4.96	1.52	0.62	16.70	7215
195	70.88	4.95	1.55	0.61	11.37	6996
105	66.99	4.75	1.43	1.31	15.95	6710
	% (MAF Basis)					MAF
364	74.84	5.24	1.61	0.66	17.65	7625
195	79.32	5.34	1.73	0.68	12.93	7766
105	74.08	5.25	1.58	1.45	17.64	7420

TABLE 4

RESIDENCE TIME IN SECONDS FOR VARIOUS VALUES
OF X_{FC} AS DEPICTED BY THE CURVES OF FIGURE 40

X_{FC}	Particle Size, μ (10^{-6} Meters)		
	105	195	364
0.1	4.1	5.4	12.3
0.2	9.0	12.3	27.6
0.3	15.3	21.7	47.0
0.4	24.0	35.4	72.7
0.5	37.2	56.9	109
0.6	61.6	95.7	164
0.7	142	188	260

TABLE 5

RESIDENCE TIME IN SECONDS FOR VARIOUS VALUES
OF X_{FC} AS DEPICTED BY THE CURVES OF FIGURE 43

X_{FC}	Temperature, °C			
	471	482	493	504
0.1	27.0	21.5	12.3	9.0
0.2	54.0	44.0	27.6	19.9
0.3	81.0	68.3	47.0	33.4
0.4	108	95.0	72.7	50.9
0.5	135	125	109	75.5
0.6	163	162	164	116
0.7			260	221

Figure 1. Block diagram of "coiled tube" reactor system
*Oscillator

Fig 2. Residence time vs. X_{FC} for Clear Creek, Utah coal at various particle sizes processed in the coiled tube reactor at 493°C and $12.4 \text{ MPa} \cdot \text{H}_2$ and with $6.25\% \text{ ZnCl}_2$ added to the coal.

Fig 3. Residence time vs. X_{FC} for $-40 +60$ mesh (364μ) Clear Creek, Utah coal at various temperatures processed in the coiled tube reactor at 12.4 MPa H_2 with $6.25\% \text{ ZnCl}_2$ added to the coal.

Fig 4. Percent volatile matter and fixed carbon remaining in char after liquefaction treatment in the coiled tube reactor set at 12.4 MPa H_2 and 471-504°C. The sample is Clear Creek, Utah coal with 6.25% $ZnCl_2$ added.

Fig 5. The space rate utilization vs. conversion for various particle sizes of Clear Creek, Utah coal processed in the coiled tube reactor set at 493°C and 12.4 MPa H_2 with 6.25% $ZnCl_2$ added to the coal.

Fig 6. Graph showing chemical and diffusion controlled regimes for the hydrogenation of Clear Creek, Utah coal in the "coiled tube reactor" set at 12.4 MPa H_2 and with 6.25% ZnCl_2 added to the coal. (Slopes listed on lines)

Fig 7. X_{Fc} vs. time for various temp ($^{\circ}\text{C}$ listed on lines). Pressure is 12.4 MPa H_2 and initial particle diameter in 50×10^{-8} meters.

Fig 8. X_{Fc} vs. time for various press (MPa listed on lines). Temp is 500°C and initial particle diameter is 50×10^{-8} meters.

Fig 9. X_{FC} vs. time for various initial particle diameters (10^{-6} m listed on curves). Temp is 500°C and press is 12.4 MPa H_2 .

Fig 10. Time vs. temp for various sizes of coal particles, (10^{-6} meters listed on curves) to reach $X_{FC} = 0.6$ (approx 75% coal conversion). Press is 12.4 MPa H_2 and catalyst is 6.25% ZnCl_2 on Clear Creek, Utah coal.

Fig 11. X_{FC} vs. particle diameter for various times (sec listed on curves). Temp is 500°C and press is 12.4 MPa H_2 .

Fig 12. Time for various temperatures and pressures (Atm listed on curves, 1 atm = 0.1013 MPa) to reach $X_{FC}=0.6$ which is equivalent to about 75% total conversion. Catalyst is 6.25% $ZnCl_2$ on Clear Creek, Utah coal. Particle diameter = 50×10^{-6} meters.

The Effect of Structure on Coal Reactivity

Faculty Advisor: D.M. Bodily

Introduction

The physical and chemical properties of coals vary over a wide range of values. The properties of coals are indicated by the rank of the coal, but even within coals of the same rank, large differences in properties are observed. Properties such as pore size distribution, hydroaromatic content, chemical functionality and covalent bonding will determine the reactivity towards a specific reaction. They will determine the behavior of the coal when it is heated, the softening and swelling and the decomposition reactions. They will determine its interaction with solvents and the bond scission reactions in hydroliquefaction processes. It is important to understand the effects of structure on chemical reactivity.

Two aspects of coal structure were studied in this project. The first study involves the effect of coal rank on the interaction of coal with a hydrogenation catalyst, ZnCl_2 . The reactions of a high volatile bituminous coal impregnated with ZnCl_2 have been studied.¹⁻⁵ Zinc chloride reacted with the coal below the temperature of pyrolysis reactions. The coal was dehydrogenated in the range 200-400°C. The pyrolysis reactions occurring in the region of 400°C were suppressed and the total evolution of volatile products reduced. Concurrent with these reactions was an increase in the pore volume of the coal. The surface acidity of the ZnCl_2 impregnated on the coal surface was also destroyed below 400°C. In this study, these experiments were extended to a wider range of coals. A lignite sample and a medium volatile bituminous coal sample were studied and compared with the high volatile bituminous coal sample. The object of the study is to elucidate structural effects on the pyrolysis of coal-catalyst systems.

The second study deals with the structure of coal-derived asphaltenes and the effects of structure on the processing of the asphaltenes. Results of studies under Project B-4 of this report indicate that many of the chemical bonding features of coal are retained by the asphaltene fraction of the liquid products. Information on the structure and reactions of the asphaltenes will be used to help understand the mechanism of coal hydroliquefaction and to propose new schemes for liquefaction.

Experimental

A lignite (40.2% VM), a high-volatile bituminous coal (44.1% VM) and a medium volatile bituminous coal (24.6% VM) were impregnated with ZnCl_2 from aqueous solution. The coal and ZnCl_2 solution were mixed to wet the coal surface and the water was evaporated.

Samples with up to 20% by weight ZnCl_2 were prepared for each coal.

Pyrolysis experiments were performed by thermal gravimetric analysis using a Cahn electrobalance. Ten milligram samples were heated to 900°C at $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Temperature and sample weight were continuously recorded. Sample weights were corrected for loss of ZnCl_2 to determine the weight loss of the coal.

Pyrolysis gases were collected at 50°C intervals from larger coal samples. Analysis of hydrocarbons was performed by gas chromatography with a silica gel column and flame ionization detector. Hydrogen evolution was measured on an alumina column with a thermal conductivity detector.

The asphaltene sample was obtained from the hydrogenation of Hiawatha, Utah coal (44.1% VM) with 6% ZnCl_2 catalyst at 492°C and 12.4 MPa hydrogen pressure. The liquid hydrogenation products were extracted with hexane to remove light oils and then extracted with benzene to obtain the asphaltene fraction. The asphaltene was catalytically dehydrogenated and reacted with HCl to obtain products for analysis.

The method of Reggel et al.⁶ developed for solid coals was used for dehydrogenation of the asphaltene. A catalyst of 1% Pd on CaCO_3 was refluxed with phenanthridine and asphaltene at 374°C . Effluent gases were analyzed by gas chromatography.

The asphaltene was dissolved in benzene for reaction with HCl .⁷ The HCl gas was bubbled through the solution containing 7.5 g of asphaltene for 4 hours at a rate of 1 cc/min at room temperature. The base- HCl adduct precipitated and was recovered by filtration. The acid/neutral fraction remained in solution and was recovered by evaporation of the solvent. The base fraction was redissolved in tetrahydrofuran, washed with NaOH to remove the HCl and the solvent evaporated to recover the base fraction. The acid fraction represented 63% and the base fraction 17% of the total asphaltene fraction.

The asphaltenes and reacted asphaltenes were separated on the basis of molecular size by gel permeation chromatography (GPC). Micro styragels (Bio-beads SX-1 and SX-2) with pore sizes of 500 and 10,000 Å diameter were used as GPC packing. A 5% solution of methanol in benzene was used as the solvent. Recovery of the asphaltenes was of the order of 94%. Eluted materials were combined to provide samples for further analysis.

The samples separated by GPC were analyzed by elemental analysis, vapor pressure osmometry, nuclear magnetic resonance (NMR) and infrared spectroscopy. Elemental analysis for C, H and N was performed on a Perkin-Elmer model 240, elemental analyzer. Molecular weights were determined in chloroform solution on a Coroan-Wescan Model 117 Osmometer. Concentrations were from 0.25 to 0.40 mg/g. Infrared spectra were measured in CCl_4 solution.

Proton NMR spectra were measured at 300 MHz in deuterio pyridine or deuterio chloroform solution. Signals from 2 to 3 δ were assigned to protons on carbons α to an aromatic ring. Signals from 0 to 2 δ were assigned to protons attached to other aliphatic carbons. The signals at 6 to 8.5 δ were assigned to protons attached to carbons of aromatic rings. The elemental analysis and proton NMR results were used to calculate structural parameters by the method of Brown and Ladner.⁸

Results and Discussion

Pyrolysis results are shown in Figures 1-3. Each sample shows weight loss in the range 300-600°C. The temperature of maximum weight loss and the extent of weight loss varies with the rank of the sample. In each case, the presence of ZnCl_2 inhibits the evolution of volatile matter. The effect is most pronounced in the high volatile and medium volatile coals, but also occurs in the lignite sample. Analysis of methane and other hydrocarbon gases evolved from the samples during heating indicates little change in the composition of the gases at each temperature, but a significant decrease in the yield of gases.

Previous work on high volatile bituminous coals demonstrated that the suppression of volatilization was due to dehydrogenation of hydroaromatic groups by the ZnCl_2 . Evolution of hydrogen is shown in Figures 4-6. In each case, significant hydrogen is evolved below the temperature of pyrolysis reactions in the presence of zinc chloride. The effect is least for the lignite sample, but very pronounced for the high volatile and medium volatile coals.

Gel permeation chromatography elution curves for the asphaltene, dehydrogenated asphaltene and acid and base fractions of the asphaltene are shown in Figures 7-10. The separation of the samples into fractions is shown on the curves. The fractions were analyzed by proton NMR and elemental analysis, and the equations listed in Table 1 were used to calculate structural parameters. The structural parameters are listed in Table 2.

The asphaltene fraction shows a bimodal distribution in the molecular weight, typical of asphaltenes.⁹ The fractions have aromaticities in the range of 0.55 to 0.80. After dehydrogenation, the aromaticities increase to the range of 0.65 to 0.93, and a fraction of low aromaticity is produced that can only be eluted with THF solvent. The number of aromatic rings per structural unit and the molecular weight of the structural unit increases upon dehydrogenation. This indicates that the asphaltenes contain hydroaromatic units connecting condensed ring systems that can be aromatized during dehydrogenation. This conclusion is supported by the decrease in aliphatic substitution of the condensed ring system, apparently by removal of the shorter aliphatic groups (i.e., hydroaromatic links).

The acid/neutral fraction obtained by reaction with HCl is of higher molecular weight than the whole asphaltene, while the

basic fraction is of lower molecular weight. The acid/neutral fraction is composed of molecules which contain larger condensed ring systems and longer alkyl constituents. The acid/neutral fraction represented 63% of the original asphaltene. This yield is much higher than that reported by Sternberg et al.⁷

Conclusions

The effect of ZnCl_2 on the properties of a medium volatile coal are similar to those observed with a high volatile coal. Upon heating the coal impregnated with ZnCl_2 , hydrogen is evolved from hydroaromatic groups in the range 200-400°C. In the absence of ZnCl_2 , hydrogen is not evolved below 400°C. The change in the hydroaromatic structure of the coals results in lower volatile matter evolution above 400°C. A similar effect is observed in lignite, but the magnitude is much less due to the lower hydroaromatic content.

Asphaltenes obtained by coal hydrogenation are shown to contain hydroaromatic structures that can be catalytically dehydrogenated with Pd. The asphaltenes can be reacted with HCl to produce acidic and basic fractions. The acidic fractions are of higher molecular weight and contain larger condensed ring aromatic systems and larger alkyl group substituents. The basic fraction is of lower average molecular weight. The asphaltenes contain many of the structural features of the original coal.

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Table 1

Structural Parameters and Definitions from PMR Spectra

$$f_a = \frac{C/H - H_\alpha/HX - H_o/HY}{C/H}$$

$$H_{au}/C_a = \frac{H_\alpha/H + H_\alpha/HX = O/H}{C/H - H_\alpha/HX - H_o/HY}$$

$$\sigma_t = \frac{H_\alpha/HX + O/H}{H_\alpha/H + H_\alpha/HX = O/H}$$

$$H_o/H_\alpha = \frac{H_o/HY}{H_\alpha/HX}$$

$$M(us) = 12 C_a(us) + 14 C_p(us) \sigma_{al} \left(\frac{H_o}{H_\alpha} + 1 \right) + C_p(us) (1 - \sigma_{al} + 15 \sigma_o)$$

Definitions used in these equations are as follows:

f_a = fraction of aromatic carbons

H_{au}/C_a = ratio of the hydrogens in a hypothetical unsubstituted aromatic molecule to the aromatic carbons

σ_t = total substitution on the aromatic ring

σ_{al} = aliphatic substitution on the aromatic ring $\left(\frac{H_\alpha/HX}{\frac{H_\alpha}{H} + \frac{H_\alpha}{HX} + \frac{O}{H}} \right)$

σ_o = oxygen substitution on the aromatic ring $(\sigma_T - \sigma_{al})$

$\frac{H_o}{H_\alpha} + 1$ = length of aliphatic chain

$M(us)$ = molecular weight of the unit structure

C_a = aromatic carbon = $\frac{3}{\left(\frac{H_{au}}{C_a} - 5 \right)}$

C_p = peripheral carbon = $\left(\frac{H_{au}}{C_a} \right) \cdot C_a$

X = H/C at alpha aliphatic carbon

Y = H/C at other aliphatic carbons

R_a = number of aromatic rings

Table 2

Structural Parameters from HNMR for Bulk Fractions FA and FD

<u>Ve(ml.)</u>		<u>Ho/H+1</u>	<u>Fa</u>	<u>σ_T</u>	<u>σ_{al}</u>	<u>σ_o</u>	<u>Ca</u>	<u>Cp</u>	<u>Hau/Ca</u>	<u>M(us)</u>
400	FA1	3.191	0.5576	0.5609	0.3507	0.2102	14.3541	10.1771	0.7090	355.61
470	FA2	2.955	0.5943	0.4203	0.2612	0.1591	7.8288	6.9144	0.8832	190.27
530	FA3	1.715	0.6410	0.4669	0.3601	0.1068	7.3800	6.690	0.9065	161.40
600	FA4	1.693	0.7505	0.2953	0.2733	0.0220	13.6923	9.8461	0.7191	238.49
680	FA5	1.711	0.8072	0.2672	0.2424	0.0148	40.107	23.054	0.5748	637.73
345	FD1	5.114	0.6404	0.4083	0.2435	0.1648	61.100	27.55	0.4509	1302.44
450	FD2	3.903	0.6490	0.3519	0.2180	0.1399	22.124	14.062	0.6356	473.50
535	FD3	2.935	0.6932	0.2980	0.2108	0.0872	13.787	9.794	0.7176	271.89
630	FD4	1.802	0.9208	0.0789	0.0675	0.114	14.670	10.335	0.7045	205.04
680	FD5	1.313	0.9320	0.0790	0.0790	0.	14.771	10.385	0.7031	201.90
835	FD6	6.05	0.7236	0.2178	0.1026	0.1152	24.814	15.402	0.6207	472.05
2000	FD7	5.69	0.4214	0.4816	0.2794	0.2022	8.1411	7.071	0.8685	281.61

Table 2 (Continued)

Structural Parameters from HNMR for Bulk Fractions FAC and FB

<u>Ve(ml.)</u>		<u>Ho/H+1</u>	<u>Fa</u>	<u>σ_T</u>	<u>σ_{al}</u>	<u>σ_o</u>	<u>Ca</u>	<u>Cp</u>	<u>Hau/Ca</u>	<u>M(us)</u>
400	FAC1	4.398	0.6040	0.1874	0.1712	0.0162	8.1345	7.067	0.8688	179.68
485	FAC2	3.333	0.5611	0.4087	0.2673	0.1414	7.903	6.951	0.8796	201.37
570	FAC3	4.516	0.4513	0.5614	0.3911	0.1703	15.789	10.894	0.690	493.30
600	FAC4	4.866	0.4675	0.4865	0.3583	0.1282	19.206	12.603	0.6562	570.42
780	FAC5	4.162	0.6252	0.3540	0.2098	0.1442	15.865	10.933	0.6891	356.32
2000	FAC6	17.22	0.4247	0.5882	0.1263	0.4619	21.818	13.909	0.6375	793.84
500	FB1	3.335	0.5727	0.4731	0.3542	0.1189	22.455	14.214	0.6330	539.10
695	FB2	3.0	0.5720	0.4197	0.3368	0.0829	12.381	9.19	0.7423	296.09
760	FB3	1.673	0.7399	0.3789	0.3470	0.0319	14.191	10.100	0.7114	269.80
820	FB4	1.890	0.8362	0.2263	0.1481	0.0782	15.053	10.527	0.6993	243.20
2000	FB5	3.588	0.6085	0.5090	0.2422	0.2668	12.371	9.185	0.7425	303.92

Figure 2. TGA of High Volatile Coal.

Figure 1. TGA of Medium Volatile Coal.

Figure 3. TGA of Lignite.

Figure 4. Hydrogen Evolution from Medium Volatile Coal.

Figure 5. Hydrogen Evolution from Lignite.

Figure 6. Hydrogen Evolution from High Volatile Coal.

Figure 7. Elution Curve for Asphaltene.

Figure 8 . Elution Curve for Dehydrogenation Reaction.

Figure 9. Elution Curve for Acid/Neutral Fraction.

Figure 10. Elution Curve for Basic Fraction.

The Separation and Characterization of
Coal-Derived Liquids

Faculty Advisor: R.R. Beishline

Introduction

This project dealt with the investigation of promising methods for analyzing the lighter fractions of coal hydrogenation liquids. The objectives of the study were (1) to determine whether fractionation through a spinning band (SB) distillation column can separate pure compounds directly from complex coal-derived liquids; (2) to determine the effectiveness of SB distillation in combination with preparative gas chromatography (PGC) as a method for separating and isolating pure compounds from complex coal-derived liquids, and to identify the isolated compounds and (3) to develop a general analytical scheme for the characterization of the light fraction of coal hydrogenation liquids.

Experimental

Crude coal liquid samples were obtained from the University of Utah coal hydrogenation reactor. These samples contained water in addition to the crude coal liquids.

Rough distillations were done to clean up crude coal liquids or to obtain a narrower boiling distillate from a wide boiling range sample of previously rough distilled crude coal liquid. Rough distillations were conducted by fractionating the sample through a 1 x 16 cm column packed with 6 mm glass helices. Some of these distillations were conducted at atmospheric pressure and others under vacuum. When the pot charge was a crude coal liquid containing water, the pot was magnetically stirred through the heating mantle to avoid the severe bumping that otherwise occurs after most of the water has been removed. If water was present, the aqueous and organic phases were separated, and the organic phase was dried over anhydrous magnesium sulfate. The distillate fractions obtained from these rough distillations are referred to as rough cuts.

The crude coal liquid containing water was rough distilled until all the water had been removed from the pot. The volatile hydrocarbons that codistilled with the water were recovered, dried and added back into the pot. The reconstituted pot charge was redistilled (rough distillation), and all the distillate up to 100°C, 10 torr was collected. The distillate was extracted with aqueous 6N sodium hydroxide and hydrochloric

acid to remove tar acids and bases, respectively, washed with water, dried over anhydrous magnesium sulfate and gravity filtered to remove the drying agent.

The pot charge was fractionated through the SB distilling column at atmospheric pressure, 200:1 reflux ratio and 10-20 drops/min boil up rate. The distillation was equilibrated at total reflux for at least thirty minutes before any distillate was taken.

The components of the neutral, light hydrocarbon fraction were analytically separated on a 2 m x 1/8" stainless steel column packed with 80/100 mesh carbopack C/0.10% picric acid. The helium flow rate was 60 ml/min. Temperature program: 55°C isothermal, 5 min; 2°C/min, 10 min; 6°C/min to 120°C; 120°C isothermal, 40 min.

The bromine number, a method of determining unsaturation, is defined as the number of grams of bromine consumed by the double bonds in a 100 gram hydrocarbon sample. The bromine number was determined according to ASTM method D1158-59T. The method consists of treating the sample with excess bromide-bromate solution, reducing the excess bromine with potassium iodide, and titrating the liberated iodine to the disappearance of the starch-iodide blue color with standard sodium thiosulfate solution.

Large samples (50-500 µl) were separated on a 20 ft x 3/8" aluminum column packed with 20% SP 2100 on 45/60 mesh Chromosorb A. The helium flow rate was 200 ml/min. Temperature program: 75°C isothermal, 5 min; 2°C/min, 20 min; 6°C/min, 10 min; 175°C isothermal, 10 min; 8°C/min up to 200°C. In most cases, the amount of a given compound collected was equivalent to a column of liquid 1-2 cm high in a melting point capillary.

The GC-MS analysis of coal liquids was done at the Flammability Research Center at the University of Utah. The GC column described in this experimental section was used in the GC part of the GC-MS instrument.

Results and Discussion

The SB distillation column has a fractionating capability of the order of two-hundred theoretical plates,¹ and has been used to separate compounds having boiling point differences of one degree C or less.²⁻⁴ Therefore, its usefulness was evaluated for separating the complex hydrocarbon mixtures that are produced by coal hydrogenation. SB distillations cannot be carried out above 185°C, however, due to excessive wear on the teflon parts above this temperature. The investigation was therefore limited to the lighter fractions of coal hydrogenation liquids.

A large number of coal liquid samples were subjected to precision SB distillation, and the fractions collected were analyzed on the analytical GC column described in the experimental section. The results obtained in the following example are typical:

A rough cut coal liquid fraction (54 ml, boiling range 80-100°C) was obtained by rough distilling a neutral, light hydrocarbon fraction from a crude coal liquid. This 80-100°C rough cut was shown by GC to contain 27 components. Precision SB distillation of the rough cut separated material boiling as low as 49°C and as high as 114°C. The largest SB fraction of the rough cut (8.9 ml, 70-79°C boiling range) was shown by GC to contain thirteen components, four of which made up 74% of the total fraction. This 70-79°C fraction was redistilled through the SB column to determine how effectively it could be separated. The results of this redistillation are shown in Table 1. The four principal compounds in the 70-79°C SB fraction (methylcyclopentane, 1-methylcyclopentene, cyclohexane and cyclohexene) were separated and collected by PGC and identified by MS, NMR and IR.

Five rough cut fractions boiling from 24°C (atm press) to 94°C (10 torr) were obtained by rough distilling a neutral, light hydrocarbon coal liquid fraction. The unsaturation in these rough cuts was evaluated by determining their bromine numbers. The results are shown in Table 2. The average number of carbon atoms per double bond in Table 2 was taken as the n value in the C_nH_{2n} (empirical formula for a monoalkene) that gave a molecular weight nearest to the grams sample per mole of double bonds.

Using SB distillation in combination with PGC, the components in an 80-100°C (atm press) coal liquid fraction were separated and isolated, and compounds representing about 70 volume % of the fraction were spectroscopically identified (MS, IR, NMR).

The following procedure was followed to accomplish the separation, isolation and identification: (1) The 80-100°C rough cut of the neutral hydrocarbon fraction (fraction 2, Table 2) was precision distilled through the SB column into 33 small fractions. (2) Each fraction was analyzed by GC. (3) Selected fractions were combined to give new mixtures having the best combination of GC resolution and concentration for a limited number of components. (4) The combined fractions were separated by PGC, and the individual peaks collected. The gas chromatograms of the total 80-100°C rough cut, and some typical combined SB fractions from which individual compounds were isolated are shown in Figure 1. (5) Samples of the collected peaks were re-examined on analytical GC columns to determine how well a particular peak had been resolved from neighboring peaks, and whether the isolated peaks consisted of single or multiple compounds. (6) The IR, NMR and mass spectrum of each collected peak was obtained and interpreted, and the identity of the compound (or compounds) determined.

The identified compounds are shown in Table 3. In some cases the specific isomers were not identified and are shown by formula only. From a combination of analytical GC (see Step (5) above) and spectral information, several individual SP2100 peaks (B,E,I,K,L and Q in Table 3) were shown to consist of two compounds.

In the course of characterizing a coal hydrogenation liquid, the crude material is commonly solvent fractionated, and in this process, the lighter hydrocarbons are lost into the fractionating solvents. Though these light hydrocarbons usually make up only a small percentage of the total coal liquid, it is nevertheless necessary to qualitatively and quantitatively characterize them. To this end, a relatively simple scheme has been developed for characterizing the room temperature - 80°C (645 torr) fraction of coal liquids. Solvent fractionation is not used, thereby circumventing the aforementioned problem.

The procedure consists of three parts: (A) sample preparation, (B) precision SB distillation and (C) GC analysis. The initial part of the sample preparation was a rough distillation of a crude coal liquid containing water (see the experimental section). Distillate was collected up to 150°C (atm press).

The crude coal liquids contain ammonia, amines and phenols, and if these materials carried through the procedure, they could conceivably degrade the GC column resolution (phenols boil above 150°C, the highest head temperature in the crude distillation, but some phenols could be carried into the crude distillate azeotropically, or by steam distillation). To evaluate the possibility that amines and phenols, if present, might degrade column resolution, a single crude distillate was divided into five aliquots which were treated as follows:

- Sample 1. Control, no additional treatment.
- Sample 2. Washed with water and dried.
- Sample 3. Extracted with 6N aqueous sulfuric acid, washed with water and dried.
- Sample 4. Extracted with 6N aqueous sodium hydroxide, washed with water and dried.
- Sample 5. Extracted with 6N aqueous sulfuric acid and sodium hydroxide, washed with water and dried.

The control and all the treated samples were precision distilled through the SB column, and distillate from each was collected up to 80°C. The SB distillate from Sample 5 was first analyzed on the GC column since amines and phenols, if present, would have been removed by the pretreatment. The SB distillates of the control and Samples 2-4 were next analyzed on the GC, and finally, the distillate from Sample 5 was analyzed a second time. This sequence of analyses would (1) show an example of optimum resolution (Sample 5), (2) show whether the control or any other of the variously treated samples gave degraded resolution relative to the optimum and (3) answer the question: If any of the samples gave degraded resolution, would the degraded

resolution persist to a subsequent sample that was free of amines and phenols? The first and last gas chromatograms of distillate from Sample 5 were identical, and the gas chromatograms of distillates from Samples 1-4 were identical to each other and to Sample 5. Therefore the pretreatment of the crude distillate before SB distillation is unnecessary. Apparently small quantities of amines are not detrimental to the GC column, and phenols are not present in sufficient concentration to be a problem.

The dried, crude distillate was precision fractionated through the SB column and the distillate collected in a cooled receiver (dry ice - acetone) up to a head temperature of 80°C.

Triplicate precision SB fractionations of a representative crude distillate (see Table 4) gave a standard deviation of 7.0% in the volume of distillate. The representative crude distillate was made by mixing the dried, crude distillates obtained from the hydrogenation of several different Utah coals (University of Utah Coal Reactor).

The SB distillates (rm temp - 80°C fractions) were analyzed on a gas chromatograph coupled to an electronic integrator (see Experimental Section). A typical gas chromatogram is shown in Figure 2. The resolution is not outstanding, but considering that the mixture contains alkanes, cycloalkanes, monoalkenes, dienes and cycloalkenes, this is not surprising.

The identity of the GC peaks was established by GC-MS and by peak enhancement (addition of known compounds to the total rm temp - 80°C coal liquid fraction and observation of the GC peaks that increased in size). This work is summarized in Table 5, and the peak numbers listed in Table 5 correspond with those of Figure 2.

The average standard deviation of the integrated area percents for triplicate GC analysis of a single rm temp-80°C fraction was 0.62 percent. This represents the average combined error in the reproducibility of sample injection, column resolution, detector response and electronic integration. The results of a typical triplicate analysis are shown in Table 6. Table 6 indicates that the larger standard deviation are associated with peaks that are merged in the gas chromatogram.

Finally, the F test⁵ was applied to the mean GC analytical data for triplicate SB distillations of the same crude distillate, i.e., three aliquots of the same crude distillate were distilled (see Table 4), the SB distillates from the three fractionations were each analyzed in triplicate by GC (see Table 6 for the triplicate analysis of one of the SB distillates), and the mean data from the triplicate GC analyses were subjected to the F test. The F test calculates the statistical probability that the three distillates are really three samples of the same mixture, where the degree of "sameness" is based on the degree to which the analyses of the separate distillates show the same

statistical variances. The F test was significant at the 1% level, i.e., there is a 99% chance, based on the above criteria, that the three distillates are identical.

Liquids produced by hydrogenation of five different Utah coals in the University of Utah coal hydrogenation reactor (identical hydrogenation conditions for each coal) have been subjected to the above analytical procedure, and the rm temp-80°C fractions collected and analyzed. The results are shown in Tables 7 and 8.

Conclusions

In addition to conclusions, a brief summary of the results obtained with respect to the three objectives stated in the introduction will also be presented in this section.

A method has been developed to isolate a neutral, light hydrocarbon fraction from crude coal liquids. The bromine numbers of five light hydrocarbon rough cuts were determined, and indicated that the respective rough cuts contained an average of thirteen to twenty-four carbon atoms per double bond. The results of a number of fractionations indicate that precision SB distillation of light hydrocarbon rough cuts boiling up to 150°C (atm press) does not give distillates consisting of pure compounds, but does effectively cut the pot charges into much less complex fractions.

Using precision SB distillation in combination with PGC, the components in an 80-100°C (atm press) coal liquid rough cut have been separated and isolated, and compounds representing about 70 volume % of the fraction have been spectroscopically identified (MS, IR, NMR). This method of separation, isolation and identification is very time consuming, however, and has largely been superceded by GC-MS.

In some cases, the SB-PGC procedure is both useful and necessary, e.g., when, as is frequently the case with GC-MS, a particular compound can be identified by empirical formula but not by the specific isomer. (This happens if a compound is a relatively rare isomer, and known reference compounds or reference spectra are not available for comparison. In such an instance, the specific isomer can often be identified from its NMR spectrum, and it is not only useful, but mandatory that a finite sample of the compound be isolated for the NMR study.

A method of characterizing the light hydrocarbons (boiling range: rm temp - 80°C) in a coal liquid has been developed and applied to the analysis of the light hydrocarbons produced in the hydrogenation of five different Utah coals (University of Utah coal hydrogenation reactor).

The similarities of the rm temp - 80°C fractions of these coal liquids are much more striking than their differences. The rm temp - 80°C fraction constitutes a very small percentage of the total coal liquid in all cases. The percentage is largest

for Swisher #4. Swisher #2 and Consolidated Coal #6 have larger amounts of high molecular weight compounds in their rm temp - 80°C fractions than do the other coal liquids.

References

1. "250 Plate Calibration Mixture Separation," Nester/Faust Distillation Equipment Applications Bulletin, 1971.
2. "Auto Annular Distillation Applications," Nester/Faust Data Sheet, Figures 3-6, 1968.
3. "Plastic Component Pilot-Scale Separation," Nester/Faust Distillation Equipment Applications Bulletin, 1971.
4. "Organic Synthesis Fraction Purification," Nester/Faust Distillation Equipment Applications Bulletin, 1971.
5. W.J. Youden, Statistical Methods for Chemists," John Wiley & Sons, Inc., New York, 1951, pp 29-32.

Table 1. Redistillation of 70-79°C SB Fraction

Fraction	Vol. (mL)	Boiling Range °C 645 torr	Composition (%)				
			Methyl-	1-Methyl-	Cyclo-	Cyclo-	Other
			cyclo- pentane BP760 72°	cyclo- pentene BP760 76°	hexane BP760 81°	hexene BP760 83°	
Initial							
Pot Charge	7.9	70-79	12	12	18	32	26
1	0.10	63-66	63	2	0	1	34
2	0.15	66-68	32	51	0	0	17
3	0.15	68-70	16	62	7	0	15
4	0.10	70-71	14	44	25	0	16
5	0.20	71-72	7	25	50	0	18
6	0.20	72-73	8	20	58	7	7
7	0.40	73-74	8	10	58	11	13
8	0.50	74-74	8	9	32	44	7
9	0.35	74-78	0	2	17	78	3
Pot	---	---	0	5	1	25	69
Residue							

Table 2. Bromine Numbers of Rough Cuts of a Neutral Hydrocarbon Fraction from a "Light Ends" Coal Hydrogenation Sample (University of Utah Coal Hydrogenation Reactor)

Fraction	Press. (Torr)	Boiling Range (°C)	Vol. (mL)	Bromine Number	Grams Sample per Mole of Double Bonds	Ave. No. of C atoms per Double Bond
1	645 ^a	24-80	23	89.57	178.4	13
2	645 ^a	80-100	38	88.13	180.9	13
3	100	24-100	70	81.32	196.5	14
4	10	24-64	30	55.47	282.3	21
5	10	64-94	52	48.04	332.6	24

^a645 Torr is the average atmospheric pressure at Weber State College where the experimental work was done.

Table 3. Composition of the 80-100°C (645 Torr) Rough Cut

Compound	Peak Letter (see Figure 1)	Approx. Retention ^a Time (min)	Approx. % of Total
4-Methyl-2-pentene	B	16.6	4
Hexane	B	16.6	1
Methylcyclopentane	D	19.6	6
1-Methylcyclopentane	E	21.7	5
Benzene	E	21.7	1
Cyclohexane	F	23.2	8
Cyclohexene	G	24.7	8
Heptane	I	26.7	10
Trans-2-heptene	I	26.7	1
Methylcyclohexane + C ₇ H ₁₂	K	29.5	9
C ₇ H ₁₂ + C ₇ H ₁₄	L	30.5	7
C ₇ H ₁₂	M	31.8	3
Toluene	N	32.4	10
Octane (most)	Q	35.0	5
Trans-2-octene (least)	Q	35.0	

^aGas chromatograph conditions: Identical to those listed for the SP2100 prep column in part II of the experimental section of this report.

Table 4. Reproducibility of the SB Distillation of Aliquots of a Single Crude Distillate

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

Table 5. Compounds in the Rm. Temp. - 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 ₅ H ₁₀	pentene ^a	
2	68	C ₅ H ₈		
3	72	C ₅ H ₁₂	pentane ^a	1-pentene ^c
4	84	C ₆ H ₁₂	hexene ^a	
5	84	C ₆ H ₁₂		cyclohexane, methylcyclopentane
6	84	C ₆ H ₁₂	ethylcyclobutane	2,3-dimethylbutane ^c
7	82	C ₆ H ₁₀		1-methylcyclopentene cyclohexene ^c
8	86	C ₆ H ₁₄		3-methylpentane
9	82	C ₆ H ₁₀	dimethylbutadiene ^a	
10	82	C ₆ H ₁₀	hexyne ^a	2-methyl-1-pentene ^c , n-hexane ^c 2-methylpentane ^c
11	84	C ₆ H ₁₂		trans-2-hexene
12	84	C ₆ H ₁₂		cis-2-hexene
13	86	C ₆ H ₁₄	hexane ^a	1-hexene ^c
14	86	C ₆ H ₁₄	hexane ^a	
15	78	C ₆ H ₆	benzene	
16	93	C ₇ H ₁₄	dimethylcyclopentane ^a	
17	93	C ₇ H ₁₄	dimethylcyclopentane ^a	methylcyclohexane ^c
18	96	C ₇ H ₁₂	heptyne ^a or heptadiene ^a	2,4-dimethylpentane ^b
19	96	C ₇ H ₁₂	heptyne ^a or heptadiene ^a	
20	100	C ₇ H ₁₆		3-methylhexane
21	100	C ₇ H ₁₆	methylhexane ^a	2-heptene ^c 1-heptene ^c
22	98	C ₇ H ₁₄		trans-3-heptene toluene ^c
23	100	C ₇ H ₁₆		n-heptane

^aSpecific isomer unknown^bEluted on top of sample peak but was not present in original sample^cEluted between peaks in sample

Table 6. Triplicate GC Analysis of Distillate #1

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

Table 7. Rm. Temp. - 80°C Distillates from the Hydrogenation of Utah Coals

	Swisher #2	Swisher #4	Braztah #3	Consol. Coal #6	Beehive Emery Co.
Pot Charge, vol (mL) (crude distillate)	10	25	20	12	17.5
A-80 Distillate					
Vol (mL)	0.78	3.4	1.6	0.70	1.4
% of pot charge	7.8	14	8.0	5.8	8.0
Norm. % of total anhyd. coal liquid ^a	0.19	0.34	0.20	0.27	0.28

^aThe normalized % of the total anhydrous coal liquid is defined as the percent of the total anhydrous coal liquid the rm. temp. - 80°C fraction would constitute if the rm. temp. - 80°C fraction were quantitatively recovered from the total anhydrous coal liquid.

Table 8. Composition of Rm. Temp. - 80°C Distillates from Utah Coal Hydrogenation Liquids

Peak Number	AREA PERCENT					Identity (GC-MS and Peak Enhancement Methods)
	Swisher #2	Swisher #4	Braztah #3	Consol. Coal #6	Beehive-Emery Co.	
1	2.30	3.60	4.32	1.43	2.32	pentene ^a
2	1.02	1.67	1.79	0.35	1.00	C ₅ H ₈ ^a
3	2.11	5.35	5.34	0.68	1.48	pentane ^a
4 } 5 }	7.81	10.94	11.81	14.05	12.09	hexene ^a cyclohexane, methylcyclopentane
6	11.96	16.43	16.78	12.78	15.04	ethylcyclobutane
7	9.20	11.24	10.80	11.31	15.39	1-methylcyclopentene
8	1.47	2.01	2.07	1.29	1.81	3-methylpentane
9 } 10 }	11.28	13.96	12.30	8.30	12.39	dimethylbutadiene ^a hexyne ^a
11	4.60	2.55	4.45	4.21	5.44	trans-2-hexene
12	0.55	1.49	1.68	1.72	1.32	cis-2-hexene
13 } 14 }	6.29	8.69	13.30	12.68	10.93	hexane ^a hexane ^a
15	0.82	--	--	--	1.05	benzene
16	3.41	6.37	3.09	5.59	4.25	dimethylcyclopentane ^a
17	6.55	2.14	1.38	4.79	2.09	dimethylcyclopentane ^a
18	4.73	1.72	1.29	2.60	2.97	heptyne ^a or heptadiene ^a
19	7.40	2.22	1.98	4.90	3.81	heptyne ^a or heptadiene ^a
20	2.22	1.38	0.63	2.18	2.38	3-methylhexane
21	1.23	1.49	0.91	1.83	2.08	methylhexane ^a
22	1.27	--	0.23	1.09	0.81	trans-3-heptene
23	6.52	--	1.09	6.87	0.47	n-heptane

^aSpecific isomer unknown

Figure 1. Gas Chromatograms (SP2100 Prep Column) of the Total Coal Fraction (80-100°C Rough Cut), and Combined SB Fractions from which Individual Compounds were Isolated.

I: Total coal fraction
 Rough cut boiling range:
 80-100°C (645 Torr)
 SB boiling range: 49-114°C (645 Torr)

II: Combined SB fractions 1-9
 Boiling range: 49-75°C (645 Torr)

III: Pot residue from redistillation of
 combined SB fractions 12-19. Boiling
 range (before redist): 76-86°C (645 Torr)

IV: Combined SB fractions 25-27
 Boiling range: 92-100°C (645 Torr)

V: SB fraction 31
 Boiling range: 106-109°C (645 Torr)

Figure 2. Gas Chromatogram of the Rm Temp-80°C Coal Liquid Fraction:
Garbopack C/0.19% Picric Acid Column.

A Pyrolysis-Gas Chromatography Study of Coals and
Related Model Compounds

Faculty Advisor: R.R. Beishline

Introduction

The scope of this proposal encompasses the study of coal pyrolysis and the pyrolysis of model compounds chosen either to elucidate coal structure or various aspects of the mechanism of coal hydrogenation. All of the research has been model compound work and can be divided into two categories: (1) the zinc chloride catalyzed decomposition of 1,2-dihydronaphthalene (1,2-DHN) at 165°C and (2) the pyrolysis of 1,2-DHN (380-410°C) and the pyrolysis of 1,2- and 3,4-dihydrophenanthrene (1,2-DHP and k,3-DHP) (300°C).

Zinc chloride is used as a coal hydrogenation catalyst, but the catalysis mechanism has not been established. Zinc chloride catalyzed nonhydrogenation reactions presumably also occur during coal hydrogenation, and a knowledge of these reactions, which is the subject of the zinc chloride research, constitutes a necessary background to the understanding of the hydrogenation chemistry.

The details of the zinc chloride research have been written into a paper for submission to J. Org. Chem. The zinc chloride work will therefore be treated very briefly in this report and further information can be obtained in the form of a preprint from the author.

In the hydroliquefaction of coal using tetralin (Tet) as a solvent, the Tet donates hydrogen to the coal and is converted into naphthalene (Nap). Careful analysis has shown that 1,2-DHN is an intermediate in the hydrogen transfer process. The objective of the pyrolysis research is to learn how 1,2-DHN and its DHP analogues participate in intrasolvent hydrogen transfer reactions which likely occur concurrently with the solvent-coal hydrogen transfer reactions.

Experimental

The 1,2-DHN was synthesized by the method of Yagi and Jerina.¹ Anhydrous zinc chloride was prepared by treating stock zinc chloride with thionyl chloride (24 hr, rm temp). The thionyl chloride was removed under vacuum and the zinc chloride vacuum distilled (0.1 - 1 torr, 450-500°C).

In a dry box, 10-15 mg of anhydrous zinc chloride were weighed into pyrex tubes (5 x 50 mm) which were then closed with rubber

caps. Water and 1,2-DHN were added through the rubber caps with syringes, to give water: zinc chloride mole ratios of 0.2 - 2.3 and 1,2-DHN:zinc chloride ratios of 1.5:1. The tubes were degassed, sealed under vacuum, agitated in an oil bath (165°C, 10 or 15 min), quenched in a water bath, and their contents analyzed by GC. After the tubes were opened, 2-methylnaphthalene in benzene was added as an internal standard.

For deuterium tracer studies D₂O was used in place of H₂O, and tube volumes and reactant quantities were scaled up by a factor of 100. No internal standard was added, and the reaction mixture was separated and collected by preparative gas chromatography (PGC). Deuterium incorporation was established by IR, and quantitative deuterium analysis was done by NMR, i.e., integration loss of deuterated samples relative to non-deuterated samples.

The molecules 1,2-DHP; 3,4-DHP and 1,2,3,4-THP were synthesized by the methods shown in Scheme 2. The numbers under the arrows in Scheme 2 are literature references.

Different known initial concentrations of 1,2-DHN were sealed in calibrated evacuated pyrex tubes and all of the tubes were heated (380-420°C) for the same length of time (20-30 min). The tube contents were analyzed for the final concentration of 1,2-DHN by GC.

The subject compounds were sealed in evacuated pyrex tubes and heated (300°C) for 30 min. The tube contents were then analyzed by GC.

Results and Discussion

Scheme I shows a mechanism for the reaction that is consistent with the experimental evidence. According to this mechanism, zinc chloride functions as a Lewis acid by coordinating with a water molecule, and the zinc chloride-water complex (a Bronsted acid) donates a proton to the double bond of 1,2-DHN to form the more stable benzylic carbonium ion intermediate I⁺. Intermediate I⁺ reacts with an additional molecule of 1,2-DHN by two different pathways. Via the major route, I⁺ attacks the double bond of 1,2-DHN to form a new benzylic dimer intermediate, II⁺, which eliminates a proton to produce dimer 2, or cyclizes to give dimer 3. Via the minor pathway, I⁺, by abstracting a hydride from 1,2-DHN, becomes Tet, and the molecule of 1,2-DHN that donated the hydride loses a proton to become Nap.

That water participates in the reaction has been quantitatively demonstrated by a series of sealed tube experiments in which the molar ratio of 1,2-DHN to zinc chloride was held constant while the molar ratio of water to zinc chloride was varied from 0.02-2.2. A plot of % reaction vs. the molar ratio of water to zinc chloride gave a curve which displayed a maximum % reaction at a water to zinc chloride mole ratio of one.

The carbonium ion nature of the reaction is supported by the structures of the products and also by the deuterium tracer experiments. If the reaction occurs by a carbonium ion mechanism, then substitution of D₂O for H₂O should put deuterium in the β position when 1,2-DHN is deuterated to form I⁺. The Tet that is formed from I⁺ should then also contain D in the β position. The results of the deuterium tracer experiments showed that this is indeed the case.

The structures of the dimers are consistent with the proposed mechanism, and with their mass spectra and their IR, 75 MHz ¹³C and/or 300 MHz ¹H NMR spectra.

When 1,2-DHN is pyrolyzed (380-420°C), the products are Tet and Nap, with the Nap being formed in slight excess. A few percent (1-6%) of side reaction products (believed to be free radical in origin) are also formed (dimers of 1,2-DHN, and products lighter than Tet). Pyrolysis studies show that the side reaction products do not come from Nap or Tet and must therefore come from 1,2-DHN decomposition. The slight excess of Nap suggested concurrent reactions (1) and (2) with reaction (2) predominating. The rate

law for concurrent reactions (1) and (2) takes the form

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

By integrating this rate law, taking the antilog of the integrated form and algebraically rearranging, expression (3) is obtained.

$$1/[1,2\text{-DHN}] = e^{k_1 t} / [1,2\text{-DHN}]_0 + k_2/k_1 (e^{k_1 t} - 1) \quad (3)$$

Contrary to the usual kinetic situation, expression (3) requires that t (time) be constant and that $1/[1,2\text{-DHN}]$ and $1/[1,2\text{-DHN}]_0$ be variable. If expression (3) is followed, a plot of $1/[1,2\text{-DHN}]$ vs. $1/[1,2\text{-DHN}]_0$ will be linear with the slope equal to $e^{k_1 t}$ and the intercept equal to $k_2/k_1 (e^{k_1 t} - 1)$. Note that the slopes of the plots are functions of both k_1 and t , i.e., (a) since k_1 increases as temperature increases, the slopes will increase with increasing temperature and (b) for constant temperature data, the plot of a kinetic run conducted for a longer time will have a larger slope even though the rate constants for the two runs will be the same. When the data were substituted into expression (3), the plots were linear, and values for k_1 were obtained from the slopes. Values for k_2 were then obtained from the intercepts using the known quantities k_1 and t . The slopes of the plots increased with increasing temperature, and at constant temperature, the slopes increased with increasing t while the values of k_1 and k_2 remained constant.

A simple second order rate expression can be cast into form (4), which also gives a linear plot of $1/[]$ vs. $1/[]_0$ at constant time. In the case of

$$1/[] = 1/[]_0 + kt \quad (4)$$

(4), however, the slope of the plot is always one regardless of the time or temperature of the kinetic run, and changes in time and temperature (and therefore k) are reflected in the intercept. The fact that expression (3) is followed clearly indicates that the kinetics are simultaneous first and second order and not simple second order.

Data from a tube half filled with fine glass beads fell on the same line as data from tubes containing no beads, indicating that surface effects are not important.

Reaction (2) is believed to be a concerted group transfer reaction governed by the Woodward-Hoffman orbital symmetry rules.⁷ If reaction (2) occurred by a free radical process, one would expect to find very much larger concentrations of free radical side reaction products than are observed.

The existence of reaction (1) has not been varified although it is inferred by the kinetics. It is possible to explain the simultaneous first and second order kinetics by alternatives other than reactions (1) and (2) although the alternatives are on no firmer ground than is reaction (1). One alternative is a series of free radical side reactions that produce Nap in addition to light products and dimers. If the summation of these side reactions approximated a first order rate process, then this summation would replace reaction (1) in the simultaneous first and second order scheme. Another alternative is side reactions that produce Nap and a smaller amount of Tet in addition to light products and dimers. If the overall rate expression for these reactions contained both first and second order terms, then the side reactions would account for all of the first order and part of the second order process. Experiments to qualitatively and quantitatively analyze for H_2 are planned as part of the effort to demonstrate the reality or nonexistence of reaction (1).

Rate constants, activation energies and the least squares correlation coefficients (r^2) for the rate and activation energy plots for reactions (1) and (2) are shown in Table 1. The rate constants in Table 1 contain errors from two sources:

(1) No correction has been made for side reactions, i.e., the rate constants have been calculated assuming all the 1,2-DHN that disappeared reacted via reactions (1) and (2).

(2) The rate constants were calculated using imprecise heat up corrections. Since the initial concentration in each tube is different in a given kinetic run, more reaction will occur in a more concentrated tube during heat up. A slightly

different correction should therefore be applied to each tube. In the calculation of the rate constants in Table 1, a single, constant empirical correction was applied to each tube in a given kinetic run. Efforts are now in progress to correct both of the above inaccuracies.

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

To determinate whether the disproportionation of 1,2-DHN into an aromatic plus a tetrahydroaromatic molecule is a general reaction for dihydroaromatic compounds containing alkene type double bonds, an investigation into the phenanthrene system has been initiated.

Exploratory pyrolyses of 1,2- and 3,4-DHP have given the following results: Both dihydrophenanthrenes disproportionate readily at 300°C (liquid phase, half life ~ 30 min) to give 1,2, 3,4-THP and phenanthrene, with the phenanthrene in excess. The 3,4-DHP reacts somewhat faster, which is to be expected, since the 3,4-dihydro compound has a less hindered double bond than 1,2-DHP. These results correspond closely to the behavior observed for 1,2-DHN.

Conclusion

The zinc chloride catalyzed decomposition of 1,2-DHN at 165°C occurs by a mechanism in which zinc chloride abstracts a hydroxyl ion from water and frees a proton which is donated to the double bond of 1,2-DHN to form a carbonium ion. The carbonium ion adds to the double bond of a second molecule of 1,2-DHN to yield a dimer ion from which two different dimers are produced. To a lesser extent, the initially formed carbonium ion abstracts hydride from 1,2-DHN to give tetralin, while the 1,2-DHN molecule that donates the hydride loses a proton and becomes naphthalene.

The thermal decomposition of 1,2-DHN (380-420°C) follows simultaneous first and second order kinetics, which is consistent with the following mechanism:

Rate constants and activation energies for the system have been obtained, but some refinements of the data are necessary, and these k and E_a values are therefore subject to revision.

Although 1,2-DHN can dehydrogenate a dihydroaromatic molecule to an aromatic molecule, experiments have shown that it will not dehydrogenate a tetrahydroaromatic molecule to a dihydroaromatic compound.

Exploratory pyrolysis of 1,2- and 3,4-DHP show that these compounds give products analogous in both structure and stoichiometry to those obtained from the pyrolysis of 1,2-DHN. No kinetic measurements have yet been made on the DHP system.

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SCHEME I

Table 1. Rate Constants, Activation Energies, and Least Squares Correlation Coefficients for Reactions (1) and (2).

	Temperature ($^{\circ}\text{C}$)					E_a (kcal/mole)
	380	384	396	409	410.7	
$k_1(\text{min}^{-1}) \times 10^2$	0.500	0.684	1.26	2.26	2.57	45.7, $r^2 = 0.998$
$k_2(\ell \text{ mole}^{-1} \text{ min}^{-1}) \times 10^2$	10.3	13.6	21.9	36.4	39.4	38.6, $r^2 = 0.999$
r^2	0.996	0.999	0.999	0.998	0.999	

Scheme 2

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

Faculty Advisor: A. G. Oblad

Introduction

Most petroleum upgrading or refining processes are operated in the fixed catalyst bed mode. For these processes fine catalyst particles cannot be used because of the excessive pressure drop developed. Also, neither fresh nor spent catalysts can be added or withdrawn continuously without reactor shutdown. However, with a fluidized bed reactor, it is possible to operate near isothermal conditions with fine catalyst particles to improve the effectiveness factor and to maintain constant catalyst activity by continuous injection withdrawal of catalyst into and from the reactor.

In this study, an experimental program was designed and carried out to 1) determine the feasibility of vapor-phase fluidized-bed hydrodesulfurization of potential commercial feedstocks obtained from coal, petroleum, oil shale or tar sand bitumens, 2) quantify the kinetics of sulfur removal from Solvent Refined Coal liquid (SRC-II) and 3) compare the extent of hydrodesulfurization of SRC-II liquid in a fluidized bed reactor and in a fixed bed reactor.

This report contains a brief description of the apparatus, analytical methods, program and the results obtained in this study.

Experimental

A bench scale one inch I.D. fluidized bed reactor system was built for this study (Figure 1). It consisted of two preheaters in series for heating hydrogen and oil liquid feed, a reactor fitted with a differential pressure gauge and product recovery units. The unit gave good reproducibility in repeated runs and was operated in this study within the ranges of the main variables studied (shown in Table 3).

The dew point temperatures and hydrogen/oil feed ratio were determined such that vapor-phase operation could be maintained for the desired range of operation. Minimum fluidization velocities at high pressure and high temperature conditions were experimentally determined by measurement of the pressure drop through the bed of solid particles.

In the operating range of this study, the selected feedstocks allowed smooth and stable operation of the fluid bed without agglomeration of the catalyst particles and consequent slugging in the bed.

Two feedstocks were used, one a heavy petroleum gas oil and the other a coal derived liquid (SRC-II). The heavy gas oil feedstock was obtained from the Salt Lake Refinery of the American Oil Company. It was used to check out the fluid bed hydrodesulfurization system. The properties of the feed are given in Table 1. The coal liquid (SRC-II) was obtained from the pilot plant at Tacoma, Washington, and was used in the main effort of this study. The properties of the coal oil feed used in this study are also given in Table 1.

The catalyst used for fluid bed hydrodesulfurization was obtained by grinding 1/8 inch tablets of a commercial cobalt-molybdenum oxide on alumina catalyst (Harshaw, Co Mo-0603T, 1/8") to average particle size of 49 microns and subsequently sulfiding the selected size fraction powder in a sulfiding reactor. For the fixed bed experiments, 1/8 inch tablets of the same catalyst, sulfided subsequently, were used. Properties and compositions of the catalyst used for fluid bed and fixed bed hydrodesulfurization studies are given in Table 2.

Sulfiding was done in a quartz tube system. The tube was loaded with 70 gms of the oxide catalyst powder supported on a bed of inert solids and was pressurized to about 10 psig with nitrogen. The reactor was then heated to 325°C with a temperature-controlled oven and the system was purged with a hydrogen stream containing 2% vol. H_2S . Hydrogen sulfide pressure was then increased to 15 psig and an H_2S -flow rate of 0.17 scf/hr was maintained for 4-6 hours, after which the catalyst and tube were cooled to room temperature. The catalyst was kept inside the tube under a flow of the hydrogen sulfide-hydrogen gas mixture or sealed from air until it was added to the fluid-bed reactor.

To have an idea of the hydrodesulfurization reaction conditions and H_2 /oil feed ratios such that the first requirement of this study can be met, dew point temperature of such high pressure hydrogen/hydrocarbon systems were estimated from the vapor-liquid equilibria data of Grayson and Streed.

Minimum fluidization velocity at high pressure and temperature conditions was determined according to the method recommended by Kunii and Levenspiel (1969).

For the hydrodesulfurization experiments, the reactor was loaded with a fixed amount of sulfided catalyst, the system was pressurized to about 15 psig with nitrogen and finally the reactor was heated close to the desired operating temperature. The system was then purged with hydrogen, pressurized with hydrogen to the desired operating pressure and hydrogen was allowed to flow at the estimated rate (based on H_2 /oil feed ratio and proposed experimental WHSV value). As the operating temperature and pressure stabilized, the oil was pumped at the estimated rate based on WHSV. Both the oil and H_2 flow were monitored frequently during the experiment and valves adjusted to maintain the desired oil flow and H_2 /oil ratio. Fluidization of the catalyst bed was indicated by the differential pressure indicator.

An aging run was carried out before the hydrodesulfurization studies, until the catalyst activity reached a steady state using the same feed oil used in the hydrodesulfurization reaction. Activity of catalyst for desulfurization showed a gradual and small decrease, but it was observed that the activity remained steady after about 40 hours running.

Hydrodesulfurization runs were carried out until about 200 ml of coal oil feedstock had been processed. Gas samples were taken periodically for analysis. At the end of the desired run time, the valve separating the gas/liquid separator, the collector was closed, the oil, H_2 flow were stopped and the wet test meter reading was noted. The collector was depressurized to recover the liquid product; the rest of the system was depressurized and flushed with nitrogen.

Catalyst activity was checked periodically during the kinetic experiments by checking the sulfur removed at standard conditions. Negligible change was observed.

The gaseous product was analyzed by gas chromatography using a Model 5830A gas chromatograph with a combination of flame ionization detector, thermal conductivity detector and a digital integrator. C_1 to C_4 hydrocarbon gases were determined using a 12 foot n- C_8 /porasilc column.

Amount of saturates and aromatics in the oil feed and products were determined by C_{13} -NMR analyses, done by the Chemistry Department, University of Utah.

Viscosity was determined by a Micro Viscometer manufactured by Wells-Brookfield Engineering Laboratories, Inc., Massachusetts.

Density was measured with a DMA 40 Density Meter manufactured by Anton Paar, Austria.

The boiling ranges of the feedstocks and the liquid products were determined by the ASTM D-86 distillation and simulated distillation methods.

The used catalyst was washed with dichloromethane and dried at $110^\circ C$ overnight. The weight% coke was determined by finding wt% carbon, hydrogen and nitrogen in the coked catalyst using a Perkin-Elmer CHN analyzer, Model 240.

Hydrogen consumption was determined by making a detailed material balance and elemental analysis of products for a series of runs to determine the relationship between sulfur removal and hydrogen consumption.

The fluid bed hydrodesulfurization of the Solvent Refined Coal liquid was carried out for a constant hydrogen/oil feed ratio of 5000 to 1 std. cc. H_2 /cc. oil, one specific catalyst bed weight (equivalent stationary bed heights of about 5 inches),

one catalyst particle size (49 micron average diameter) and a constant bed diameter (1 inch I. D.). Temperature, pressure and space velocity were varied to obtain their effects on sulfur removal. Material balances were generally over 98% (Table 4).

Results

The effects of temperature on sulfur removal of the Solvent Refined Coal liquid are shown in Figures 2, 3, and 4 when weight hourly space velocity was varied. The extents of sulfur removal increased with temperature. A definite correlation between severity and sulfur elimination can be noticed. The consumption of hydrogen vs. sulfur removal does not appear to be linear (Figure 5).

The effect of space velocity on sulfur removal of the Solvent Refined Coal liquid is shown in Figures 6, 7, and 8. The sulfur removal decreased with an increase in space velocity (decrease of contact time).

The effect of pressure on the fluid bed hydrodesulfurization of the Solvent Refined Coal liquid is shown in Figures 9, 10, and 11. As expected, increased pressure resulted in increased sulfur elimination.

A pseudo-second-order rate equation with respect to the sulfur content was found to be adequate to model sulfur removal in SRC liquid.

Assuming a plug flow regime, the second-order equation for the disappearance of the sulfur is

$$r = - \frac{dC}{dt} = KC^2 \quad (1)$$

where r = rate of reaction, wt %/hr.

C = sulfur content, wt %

K = apparent rate constant, (wt%⁻¹) (hr⁻¹).

t = apparent contact time or reciprocal of weight hourly space velocity, WHSV⁻¹.

In terms of the fraction of sulfur removed, x , the integrated form of the rate equation becomes:

$$x/(1-x) = C_0 K/\text{WHSV} \quad (2)$$

where C_0 = sulfur content in feed oil, wt%

x = 1-wt% sulfur in product oil/wt% sulfur in oil feed).

In Figures 12, 13, and 14 the experimental results obtained at 1000, 1250 and 1500 pressures were plotted with $x/1-x$ in the ordinate and the reciprocal of WHSV in the abscissa. The data showed good linearity; therefore, the above equation was assumed to represent the apparent rate equation.

Assuming that the temperature dependence of the rate constant follows the Arrhenius equation, the apparent activation energy was computed as follows:

$$K = A \exp (-E_a/RT)$$

(3)

where E_a = apparent activation energy, cal/g mole.

A = frequency factor, (wt%)-1(sec)-1.

R = gas constant, cal/(g mole) ($^{\circ}K$).

Figure 15 illustrates the Arrhenius equation for three pressures at the temperatures between 400 and 475°C. The frequency factors are 3.61×10^7 , 3.12×10^7 , and 4.21×10^7 respectively for pressures of 1000, 1250 and 1500 psig. The apparent activation energies are in the range of 14.9-15.5k cal/mole for sulfur removal. The results are depicted in Figure 15. These values suggest that chemical reaction is the rate limiting step.

The hydrodesulfurization of Solvent Refined Coal liquid was carried out at 0.47 to 1.26 WHSV over 1/8 inch catalyst pellets in a fixed bed. The effects of temperature, pressure and WHSV on sulfur removal using these two types of reactors were compared. Typical results of this comparison are shown in Figure 16.

It was interesting to note that the sulfur removal in the fluidized bed with an average catalyst particle size of 49 microns was less than that in the fixed bed with 1/8 inch pellets under the same reaction conditions.

Analysis of the data comparing effectiveness factors of the two systems showed that these were essentially the same.

Extensive mathematical analyses of model reactors for plug flow fixed bed, a fluid-bed reactor, and a completely mixed CSTR were made. The results of this work are shown in Figure 17.

It was concluded that the differences in sulfur removal between the fixed and fluid bed must be attributed to partial mixing in the fluidized bed reactor, i.e. a deviation from plug flow.

Conclusions

Fluidized bed operation has several advantages over the conventional fixed bed operation with respect to many catalytic reactions of industrial importance. In this study, an effort has been made to determine the feasibility of vapor-phase fluidized-bed hydrodesulfurization of a potential commercial feedstock obtained from coal (SRC-II liquid), over a commercial cobalt-molybdenum on alumina catalyst. Through experiments and theoretical analysis the following conclusions can be drawn:

1. It was possible to vaporize the heavy gas oil (280-389°C) completely using a hydrogen/oil feed ratio of 4000 std. cc/cc oil at 1500 psig and 400°C. The Solvent Refined Coal liquid (200-509°C) could be vaporized completely using a hydrogen/oil feed ratio of 5000 std. cc/cc oil at 1000 psig and 400°C or 1500 psig and 425°C. These operating conditions are in a suitable range for commercial application.

2. In the operating range of this study, the pressure drop readings over the catalyst bed had negligible fluctuations and the $\Delta P/\Delta P_{eq}$ ratio was near unity at gas velocities higher than U_{mf} . These results indicate the absence of channelling and slugging in the fluidized bed. This was expected for fluid bed operation at high pressure. Because excess gas available for bubble formation and expansion of bubbles due to bed pressure drop are essentially eliminated at high pressure and relatively low U/U_{mf} ratio, high pressure fluid-beds tend to fluidize smoothly.

3. The Solvent Refined Coal liquid feedstocks allowed smooth and stable operation of the fluidized bed without agglomeration of the catalyst particles in the operating range studied in this work. Data on material balance indicated that all of the reaction products went overhead into the product recovery units.

4. Extensive sulfur removal was obtained in the operating range studied. This sulfur removal is increased with increasing temperature and pressure and decreased with increased space velocity.

5. For the range of parameters studied regarding fluid-bed hydrodesulfurization of Solvent Refined Coal liquid, the mode of gas/solid contacting appeared to be plug-flow. This is true since the overall hydrodesulfurization reaction at constant total pressure followed pseudo-second-order kinetics with respect to sulfur concentration. The activation energy of hydrodesulfurization of the SRC liquid in the fluidized bed ranged from 14.9 to 15.5 Kcal/g mole; this suggests that chemical reaction is the rate-determining step.

6. The sulfur removal of SRC liquid in a fluidized bed reactor with average catalyst particle size of 49 microns was less than that in fixed bed with 1/8 inch tablets at the same reaction conditions. Because the chemical reaction rate was very slow under such conditions and the effectiveness factors in both fixed and fluidized bed reactors were essentially unity, the differences in sulfur removal were attributed to some mixing in the fluid bed reactor.

7. The comparison of the extent of sulfur removal in fluidized, fixed and completely stirred reactor showed the fluid-bed conversion was less than that calculated for the corresponding piston-flow reactor but higher than that calculated for CSTR. Back-mixing in fluid-bed lowered the conversion from that in the fixed bed. These factors and the relatively low U/U_{mf} ratio used in these studies resulted in a higher reactor efficiency for the fluidized bed than that obtained in a CSTR.

Table I

The Properties of Heavy Gas Oil and SRC-II Liquid

<u>Elemental Analysis</u>	<u>Heavy Gas Oil</u>	<u>SRC-II</u>
Hydrogen, wt %	12.45	8.12
Sulfur, wt %	1.60	0.33
Nitrogen, wt %	0.11	1.74
Oxygen, wt %	1.33	2.69
Carbon, wt %	84.51	86.83
<u>Inspections</u>		
Gravity, API	29.3	5.1
Specific Gravity, 15.6°C	0.88	1.04
Viscosity, CPS, 25°C	-	22.9
% C _A	-	73.18
<u>Distillation, °C</u>	<u>ASTM D-86</u>	<u>ASTM D-2887</u>
IBP	280	200
10%	338	244
20%	347	263
30%	358	275
40%	367	290
50%	376	303
60%	380	316
70%	385	329
80%	386	357
90%	389	394
EP	Residue loss	509

Table 2

Sources and Properties of Catalyst Used*

Catalyst	CoO - MoO ₃ /Al ₂ O ₃
Supplier	Harshaw
Composition, wt %	
CoO	3
MoO ₃	12
Apparent Bulk Density lbs./cu. ft.	64
Surface area, m ² /g	166
Pore volume, cm ³ /g	0.4
Average Side Crushing Strength, lbs	24

*The reported values were determined by the catalyst supplier.

Table 3

Ranges of Operating Conditions for the Vapor-Phase
Fluid-Bed Hydrodesulfurization of SRC-II Liquid

<u>Operating variables</u>	<u>Ranges of variables studied</u>
Temperature, °C	400-475
Pressure, psig	1000-1500
Hydrogen/oil feed ratio std. cc/cc oil	5000
WHSV, gm oil/gm cat-hr	0.47-1.26
Catalyst bed weight, gms	64.55
U/U _{mf} ratio	1.20-6.55
Catalyst particle size, microns	49

Table 4

Material Balance

<u>Run Number</u>	7	8	9	13	25
<u>Operating Conditions</u>					
Temperature, °C	475	450	425	425	425
Pressure, psig	1000	1000	1000	1250	1500
WHSV	0.93	0.93	0.93	0.47	0.47
<u>Liquid Product Properties</u>					
API Gravity	13.2	12.4	11.4	12.9	14.4
Carbon, wt %	88.42	88.26	88.10	88.59	88.63
Hydrogen, wt %	9.69	9.59	9.40	9.74	9.84
Sulfur, wt %	0.07	0.08	0.11	0.05	0.04
Nitrogen, wt %	1.45	1.51	1.55	1.32	1.25
Oxygen, wt %	0.37	0.56	0.84	0.30	0.24
<u>Sulfur Removal, wt %</u>	78.79	74.85	68.18	84.85	86.97
<u>Feed Charge</u>					
Oil, gms	100	100	100	100	100
H ₂ , gms/100gm oil	2.04	1.89	1.62	2.02	2.12
SCF H ₂ /Bbl oil	1396.75	1294.05	1109.18	1383.05	1451.52
	<u>102.04</u>	<u>101.89</u>	<u>101.62</u>	<u>102.02</u>	<u>102.12</u>
<u>Products</u>					
Oil, gms	95.24	94.77	95.29	95.88	96.03
Gases, gms	2.82	2.09	1.64	1.68	1.45
H ₂ O, H ₂ S, NH ₃ , gms	3.36	3.00	2.69	3.57	3.74
	<u>101.42</u>	<u>99.86</u>	<u>99.62</u>	<u>101.13</u>	<u>101.22</u>
<u>Coke & Material unaccounted, gms</u>	0.62	2.03	2.00	0.89	0.90

Figure 1 Flow Diagram of Hydrodesulfurization System

Figure 2. Effect of Temperature on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 3. Effect of Temperature on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 4. Effect of Temperature on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 5. Hydrogen Consumption versus Sulfur Removal

Figure 6. Effect of Space Velocity on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 7. Effect of Space Velocity on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 8. Effect of Space Velocity on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 9. Effect of Pressure on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 10. Effect of Pressure on Sulfur Removal in Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 11. Effect of Pressure on Sulfur Removal in Fluid Bed Hydrodesulfurization of SRC-II Liquid.

Figure 12. Second Order Plot of Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 13. Second Order Plot of Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 14. Second Order Plot of Fluid-Bed Hydrodesulfurization of SRC-II Liquid.

Figure 15. Arrhenius Plot.

Figure 16. Effect of WHSV on Sulfur Removal for Comparison of Fixed-Bed and Fluid-Bed Modes.

Figure 17. Effect of WHSV on Sulfur Removal in Various Reactors.

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