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CHEMISTRY AND CATALYSIS OF COAL
LIQUEFACTION, CATALYTIC AND THERMAL
UPGRADING OF COAL LIQUID, AND
HYDROGENATION OF CO TO PRODUCE FUELS

Quarterly Progress Report for the Period October—December 1983

By
Wendell H. Wiser

January 1984
Date Published

Work Performed Under Contract No. AC22-79ET14700

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

Quarterly Progress Report
for the Period Oct-Dec 1983

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CONTENTS

I	Cover Sheet	1
II	Objective and Scope of Work	3
III	Task 1 Chemical-Catalytic Studies	7
	Task 2 Carbon-13 NMR Investigation of CDL and Coal	9
	Task 3 Catalysis and Mechanism of Coal Liquefaction	Completed
	Task 4 Momentum, Heat and Mass Transfer in Co-Current Flow	Discontinued
	Task 5 The Fundamental Chemistry and Mechanism of Pyrolysis of Bituminous Coal	23
	Task 6 Catalytic Hydrogenation of CD Liquids and Related Polycyclic Aromatic Hydrocarbons	Completed
	Task 7 Denitrogenation and Deoxygenation of CD Liquids and Related N- and O- Compounds	59
	Task 8 Catalytic Cracking of Hydrogenated CD Liquids and Related Hydrogenated Compounds	Completed
	Task 9 Hydropyrolysis (Thermal Hydrocracking) of CD Liquids	Completed
	Task 10 Systematic Structural-Activity Study of Supported Sulfide Catalysts for Coal Liquids Upgrading	Completed
	Task 11 Basic Study of the Effects of Coke and Poisons on the Activity of Upgrading Catalysts	Completed
	Task 12 Diffusion of Polyaromatic Compounds in Amorphous Catalyst Supports	Inactive
	Task 13 Catalyst Research and Development	73
	Task 14 Characterization of Catalysts and Mechanistic Studies	Inactive
IV	Conclusion	77

OBJECTIVE AND SCOPE OF WORK

I. The chemistry and Catalysis of Coal Liquefaction

Task 1 Chemical-Catalytic Studies

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

Task 2 Carbon-13 NMR Investigation of CDL and Coal

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

Task 3 Catalysis and Mechanism of Coal Liquefaction

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

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

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

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

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

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

II. Catalytic and Thermal Upgrading of Coal Liquids

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

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

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

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

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

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

Task 9 Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

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

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

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

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

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

Task 12 Diffusion of Polyaromatic Compounds in Amorphous Catalyst Supports

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

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

III. Hydrogenation of CO to Produce Fuels

Task 13 Catalyst Research and Development

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

Task 14 Characterization of Catalysts and Mechanistic Studies

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

Task 15 Completion of Previously Funded Studies and Exploratory Investigations

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

Task 1

Comparison of Catalysts for Coal Conversion at Subsoftening Conditions

Faculty Advisor: L.L. Anderson
Graduate Student: T.C. Miin

Introduction

Catalytic coal liquefaction at subsoftening conditions by applying Lewis Acids as catalysts has been explained by the HSAB Principle in the previous reports. However, the reaction mechanisms need further study.

Project Status

Although the mechanism cited in the penultimate report is consistent with those mechanisms cited in the literature for similar coal research, some questions have been raised which could challenge the correctness of the mechanism. The questions are:

If the protonic form of the Lewis Acid is the only important form for weakening ether linkage bonding in the oval structure, there should be a sufficient amount of water required to be in the reactor, or the diffusion of trace-amounts of water would have to be fast enough to meet the demand during the liquefaction reactions. The latter is probably unlikely because the addition of the water molecule to the ether functional group is an acid-base adduct reaction. The water molecule is not able to diffuse if it is tightly associated with a base. For example,

If the water concentration is insufficient in the reactor, some of the catalysts should exist in the free form (some are in the protonic form). Step 1 shows the reaction which has the ratio of catalyst to water as 2:1.

where "☁" represents coal network parts.

Step 3:

The result should be 1) only some ether linkages are hydrogenolyzed, some are not, and 2) the water molecule is even more tightly bonded in the broken coal structure after the reaction. The water molecule in this circumstance would have difficulty in diffusing to other Lewis Acid sites because there is no protic solvent present. It may be argued that the phenolic proton produced can be a new protonic source. However, this has been proved to be incorrect by the poor results of the phenol-catalyzed experiments (i.e., the protonic acid is not a good catalyst because a phenolic proton is a hard acid).

Obviously, the above predicted results are in contradiction to our actual results (see previous reports). This forces us to admit that the free form of Lewis Acids is also another active form of catalyst. Further work will be done to determine the contribution of such catalytic action relative to other catalytic effects.

Future Work

The effects of water will be studied to answer the above questions raised by the experiments conducted. Water in different concentrations will be mixed with either coal or catalysts. Other experimental conditions will be the same as the previous experiments. Results should assist in identifying the correct reaction mechanism(s) involved in the catalytic conversion reactions being studied.

Task 2

Carbon-13 NMR Investigation of CDL and Coal

Faculty Advisor: R.J. Pugmire
Postdoctor: A. Beeler

Introduction

Conventional CP/MAS ^{13}C NMR studies of fossil fuels provide much needed structural information not readily available by other methods.^{1,2} Recent work indicates that additional information can be obtained by dipolar dephasing CP/MAS ^{13}C NMR spectroscopy.³ Consequently, several groups have applied these techniques to fossil fuel materials.⁴⁻¹⁶ The results of a study of the magnetic resonance of a Wyodak coal are presented in this report.

Project Status

Opella and Frey described the conventional CP/MAS and the basic dipolar dephasing CP/MAS NMR experiments. Others^{3a,18-21} have discussed the advantages of alternative dipolar dephasing CP/MAS NMR procedures. In the method used in this work (Figure 1), after a cross polarization for a time t_{cp} , both rf fields are turned off for a time $t_1/2$; and finally, carbon data acquisition with proton decoupling occurs for a time t_2 . A dipolar Hamiltonian evolves during t_1 , and a chemical shift Hamiltonian evolves during t_2 .²²

The spectra were obtained at 25.15 MHz with the Bruker CXP-100 spectrometer and Z32 PE/MAS probe.²³ Four acquisition parameters were the same for all spectra: (1) a contact time of 1 ms, which other studies^{12,15,24} have shown is usually adequate; (2) a delay of 300 ms without proton decoupling between the end of data acquisition and the 90° proton pulse (approximately 6 μs) beginning the next cycle so that the probe can cool and sufficient longitudinal relaxation of the proton magnetization can occur;²⁴⁻²⁶ (3) proton spin temperature inversion;²⁷ and (4) digitizer resolution of 12 bits.

The conventional CP/MAS spectrum of Wyodak coal is shown in Figure 2. The complexity of the coal limits the resolution, even with a line broadening factor of only 5 Hz.

The signal intensity near 175 ppm does not result from a spinning sideband and thus may be assigned to carbonyl carbon atoms. The carbonyl signal intensity downfield of 162 ppm constitutes approximately 8% of the total observed carbon signal.

The resonance bands from 162-150 ppm and from 89-49 ppm can be assigned with confidence to O-C (aromatic) and O-C (aliphatic) structures.^{28,29} The signal from 62-89 ppm suggests that aliphatic

carbon atoms in nonmethyl ethers or highly oxygenated, aliphatic functional groups are present.³⁰⁻³⁴

With the aliphatic region defined as shown in Figure 2, fa, the fraction of carbon that is sp^2 -hybridized, is 0.59 ± 0.02 . This value includes the contributions from the upfield and downfield spinning sidebands.

The carbon and hydrogen distributions in the coal can be determined as follows. Provided it is appreciated that modulations in signal intensities will occur at t_1 equal to $1/\omega_r$, $2/\omega_r$, etc. due to rotational modulations and at other dipolar dephasing times due to dipolar modulations, the exponential component of the decay of the signal intensity for different carbon atoms in coal can be recognized from logarithmic plots. The observed intensity (I) is given by the sum of the signal intensities (I_i) from the various carbon types in the coal:

$$I = \sum_i I_i \quad [1]$$

$$I = \sum_i I_i^0 \exp(-(t_1/T_{2i}')) \quad [2]$$

where i represents the different carbon types undergoing different dipolar dephasing behavior and the T_{2i}' values are the corresponding time constants for the decay processes.

If the approximation is made that the decay can be expressed in terms of constants T_{2A}' and T_{2B}' representing protonated and nonprotonated carbons, respectively, then the overall decay in the resonance signal is given by:

$$I = I_A^0 \exp(-(t_1/T_{2A}')) + I_B^0 \exp(-(t_1/T_{2B}')) \quad [3]$$

If $T_{2B}' \gg T_{2A}'$ and if t_1 is long enough for the protonated carbon signal to decay (i.e., $t_1 \approx 45 \mu s$) (2, 3a), Equation 3 becomes:

$$I = I_B^0 \exp(-(t_1/T_{2B}')) \quad [4]$$

Therefore, I_B^0 and T_{2B}' can be obtained from the $\ln I$ vs. t_1 plot at long times (generally, $t_1 > 45 \mu s$).

Since slowly decaying (i.e., nonprotonated) carbon signals experience only weak dipolar modulations, Equation 4 holds after the rapidly decaying (i.e., protonated) carbon signals have fully decayed ($t_1 \approx \mu s$) until the first rotational echo occurs ($t_1 \approx 240-280 \mu s$). A $\ln I$ vs. t_1 plot ($2 \leq t_1 \leq 200 \mu s$ so as to avoid the dipolar modulation) for the sample is shown in Figure 3 and at $t > 60 \mu s$ the relationship is logarithmic for relatively long t_1 values with $T_{2B}' = 380 \pm 100 \mu s$ and $I_B^0 = (0.65 \pm 5) I^0$ after least squares analysis and

standard analysis of uncertainty.³⁵

These values can be used to calculate I_A^0 and T_{2A}' since Equation 3 can be written as:

$$\ln[I - I_B^0 \exp(-t_1/T_{2B}')] = \ln I_A^0 - t_1/T_{2A}' = \ln I_A \quad [5]$$

A plot of $\ln[I - I_B^0 \exp(-t_1/T_{2B}')] vs. t_1$ at short times (i.e., $t_1 \leq 45 \mu s$) yields a value for T_{2A}' . Alternatively, a plot^{3a,6,28} of $\ln[I - I_B^0 \exp(-t_1/T_{2B}')] vs. t_1^2$ at short times according to Equation 6:

$$\ln[I - I_B^0 \exp(-t_1/T_{2B}')] = \ln(I^0 - I_B^0) - t_1^2/(2T_{2A}^2) = \ln I_A \quad [6]$$

yields the same value for T_{2A}' within experimental error. However, previous work^{3a,6,36} has demonstrated that the t_1^2 dependence holds for strongly coupled protonated carbon atoms; i.e., aromatic CH and aliphatic CH and CH₂ groups. Forcing a least squares fit of the calculated data according to Equation 5 causes the $\ln I_A$ -intercept to be too high by 20%,³⁶ while the $\ln I_A$ -intercept obtained from Equation 6 gives an I_A^0 value in agreement with the elemental analysis for an anthracite coal.³⁷ Hence, the t_1^2 dependence was used to fit the data and for the Wyodak coal, a double exponential fit of the data was employed using a t_1^2 dependence for T_{2A} and a t_1 dependence for T_{2B} for both aliphatic and aromatic regions of the spectra. The computed parameters are given in Table 1.

In model aromatic ring compounds, decay constants on the order of 12-20 μs and 100-200 μs have been found for methine and nonprotonated carbon, respectively.^{3a,8} The approach used here for separating protonated and nonprotonated carbon has also been successful on model compounds.^{3a} Hence, good agreement is found between the decay constants obtained on coals and model compounds.

The results clearly show that signal intensity data from dipolar dephasing experiments on coals can be confidently interpreted as two exponential decays from protonated and nonprotonated aromatic carbon. Even though the aromatic structures in coals differ, the dipolar dephasing method should be useful in calculating the fraction of aromatic carbon that is protonated in coals in which the fraction cannot be obtained from elemental analysis.

The dipolar dephasing CP/MAS spectra of this coal were obtained using 21 T_1 values from 2 to 200 μs . Destructive interference among the ¹³C-¹H dipolar interactions usually causes the signals for methine and methylene carbon atoms, which are strongly coupled to disappear at $t_1 \leq 50 \mu s$.³ Consequently, eleven different t_1 values $\leq 60 \mu s$ were used. The representative results shown in Figure 3 indicate that all the signals decay, but the loss of signal intensity is particularly evident around 25-35 ppm. Previous studies have shown that the signals for methyl and nonprotonated carbon atoms decay considerably more slowly than the signals for methine and methylene carbon atoms.³ Accordingly, most of the absorptions from

25-35 ppm can be assigned to methine and methylene carbon atoms. The decay of these signals leaves a broad band with two maximums corresponding to alkyl and aryl methyl shift positions as well as highly mobile methylene carbons. This observation indicates that the resonances of methyl carbon atoms contribute significantly to the aliphatic signal. In contrast, the position of maximum intensity in the aromatic region remains at about 130 ppm.

The carbon functional group distribution and the coal's atomic C/H ratio (100/84) provide a reasonably reliable estimate of the hydrogen functional group distribution (Table II). Twenty one protonated aryl and alkenyl carbon atoms per 100 carbon atoms require the presence of 21 associated hydrogen atoms (αCH_2 units are assumed to be negligible). Since the carboxyl and phenolic hydrogens were not measured, the remaining 62 hydrogen atoms are aliphatic. Twenty three methylene and methine carbon atoms strongly coupled to protons require the presence of at least 23 hydrogen atoms. Thus, a maximum of 40 hydrogen atoms can be associated with methyl groups and possibly also with highly mobile methine and methylene carbons. Therefore, a maximum of 13 methyl carbon atoms can be present per 100 carbon atoms. This last conclusion is consistent with the presence of approximately 14 quaternary, methyl, and highly mobile methylene and methine carbon atoms per 100 carbon atoms and suggests that the methylene and methine carbon atoms are more abundant than any other type of carbon atoms. While the decay constants of methyl carbon atoms and highly mobile methylene and methine carbon atoms may be similar, the decay constants of quaternary carbon atoms are usually much longer.^{3a,8} With very high S/N and enough data points before the first rotational echo, one might be able to detect in a $\ln I$ vs. t_1 plot a third exponential decay resulting only from the quaternary carbon atoms. This work lacked sufficient S/N to determine the relative amounts of quaternary carbon atoms and of methyl and highly mobile methylene and methine carbon atoms. In short, the sp^3 -hybridized carbon signal intensity can be classified only into the two categories shown in Table II. As the proton types are determined indirectly from the different types of carbon atoms, it is only possible to set upper and lower limits on the various types of aliphatic protons.

The structural information obtained from the analysis of the conventional and dipolar dephasing spectra of the whole coal is summarized in Table II. The information obtained from the analysis of the conventional spectrum is in reasonable accord with the results obtained by other investigators for similar coal samples. The dipolar dephasing spectra provide new insights concerning the distribution of the carbon and hydrogen atoms in this material.

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TABLE I. Decay Constants (μ s) for Structural Units in Wyodak Coal and Simple Organic Compounds

<u>Structural Unit</u>	<u>Wyodak Coal</u>	<u>Literature Values for Simple Organic Compounds</u>
Nonprotonated Sp^2 -hybridized Carbons	381 ± 101	75 - 218
Protonated Sp^2 -hybridized Carbons	21 ± 3	15 - 32
Methine and Methylene Carbons Strongly Coupled to Protons	16 ± 1	12 - 29
Methyl Carbon	50 ± 9	50 - 121

TABLE II. Carbon and Hydrogen Distribution in Wyodak Coal

Structural Unit	Number of Carbon Atoms per 100 Carbon Atoms	Associated Number of Hydrogen Atoms per 100 Carbon Atoms
All	100	84
SP ³ -Hybridized Carbon	37 ± 4	63 ± 3
Quaternary, Methyl, and highly mobile Methylene and Methine	14 ± 3	<40
Other Methylene and Methine	23 ± 3	>23
SP ² -Hybridized Carbon	63 ± 5	21 ± 3
Protonated Aryl and Alkenyl	21 ± 3	21 ± 3
Nonprotonated Aryl and Alkenyl	34 ± 4	0
Carbonyl	8 ± 1	0
Phenolic Hydrocarbon	-	not measured

Figure 1. Pulse sequence used for obtaining dipolar dephasing data.

Figure 2. CP/MAS conventional and dipolar dephasing spectra of Wyodak coal.

Fig. 3. Plot of dipolar dephasing data for aliphatic region of Wyodak Coal.

Fig. 4. Plot of dipolar dephasing data for aromatic region of Wyodak Coal.

Task 5

The Mechanism of Pyrolysis of Bituminous Coal

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

Introduction

In the present state of knowledge concerning the fundamental chemistry of coal liquefaction in the temperature range 375-550°C, the liquefaction reactions are initiated by the thermal rupture of bonds in the bridges joining configurations in the coal, yielding free radicals. The different approaches to liquefaction, except for Fischer-Tropsch variations, represent ways of stabilizing the free radicals to produce liquid-size molecules. The stabilization involving abstraction by the free radicals of hydrogen from the hydroaromatic structures of the coal is believed to be the predominant means of yielding liquid size molecules in the early stages of all coal liquefaction processes, except Fischer-Tropsch variations. The objective of this research is to understand the chemistry of this pyrolytic operation using model compounds which contain structures believed to be prominent in bituminous coals.

Project Status

Gas chromatography/mass spectrometric analysis has been conducted on the 1-BTHIQ's pyrolysis product mixture. The presence of the major products toluene, isoquinoline, 1,2,3,4-tetrahydroisoquinoline and 1-benzylisoquinoline were verified. Two compounds, 3-methylisoindole and 3-methylisoindolizine, apparently resulting from the isomerization of 1,2,3,4-tetrahydroisoquinoline were also observed. Their presence explains the increased yield of 1,2,3,4-tetrahydroisoquinoline.

The pyrolysis of 4-benzylpiperidine (4-BPP) has been conducted at 698, 686 and 648 K (425, 413 and 375°C), and the general results are tabulated in Tables 1-3. The material balances for the pyrolysis of 4-BPP averaged 92.9% for the four temperatures studied, about 3% and 5% lower than those of 9-BTHC and 1-BTHIQ, respectively. The low material balances are probably a result of the high vapor pressures of many of the pyrolysis products (toluene, benzene, piperidine and pyridine). The product distributions for the pyrolysis of 4-BPP at these three temperatures are displayed in Figures 1-3 and Table 4-6. The variation in the yield of 4-benzylpyridine (4-BPY) with temperature is fairly evident albeit less dramatic than those of 9-benzylcarbazole (9-BC) and 1-benzylisoquinoline (1-BIQ) during the pyrolysis of 9-BTHC and 1-BTHIQ, respectively. The apparent lack of piperidine (PIP) in the pyrolysis product mixture is probably due to its high tendency to dehydrogenate to pyridine (PYD).

The overall reaction order for 4-BPP's pyrolysis was determined by both the integral and differential kinetic analysis techniques. The integral analysis data are tabulated in Tables 7-9 and plotted in Figures 4-9. The integral analyses do not make it possible to conclude whether first or second order overall kinetics describe the pyrolysis data more efficiently.

The differential analyses are somewhat disappointing since they do not clarify the situation. The differential analyses are tabulated in Tables 10-12 and graphically displayed in Figures 10-12. The results of these analyses suggest that the pyrolysis mechanism of 4-BPP is too complex to model with simple modeling techniques.

In a manner analogous to the method used with 9-BTHC and 1-BTHIQ, the hydrogen balance was determined and are tabulated in Table 13. The overall hydrogen balance is 92.5% which is somewhat lower than those of 9-BTHC and 1-BTHIQ. The relatively high vapor pressure of many of the products is probably the main reason for the relatively low value.

The chemical equilibrium estimations for 4-BPP and its major pyrolysis products are displayed in Table 14. The relatively low estimated extents of reaction suggest that the thermodynamics (equilibrium) may be the controlling factor for the pyrolysis of 4-BPP.

The collected product distribution data for the pyrolysis of 9-BTHC and 1-BTHIQ were analyzed using 'time-concentration' integral techniques to develop suitable mathematical models for their pyrolyses.^{1,2} This technique utilizes the area under a graph of species concentration and are easily determined from concentration-time data by numerical integration. This modeling technique makes it possible to test the assumed reaction and various aspects of the reaction mechanism. If the experimental data give a linear plot according to an integral equation for a first order reaction, it should not be linear for a similar plot of a second order reaction. Another verification possible with this technique is that experiments conducted with different initial concentrations should give the same value for the rate constant if the correct reaction order and mechanism have been assumed. Obviously with this technique only compounds whose concentrations in the reaction product mixture can be accurately and consistently monitored can be included in the integrated rate equations. The nature of the reaction systems studied necessitated combining several elementary reactions in the integrated equations. The results of this analysis are therefore limited in their direct application to the rates of production of the observed products. The main objective of this analysis is to determine the relative rates of the various pathways.

Five variations of the reaction pathway shown in Figure 13 were tested for the pyrolysis of 9-BTHC and 1-BTHIQ. The pathway modifications examined included all first order reactions, all second order reactions, mixed first and second order reactions with the cumulative reaction of A proceeding to B being first order, all first order reactions with C being converted to D, and all second order reactions with C proceeding to D. The components of the reaction pathway model for 9-BTHC (A) are 9-BC (B), THC (C), CARR (D) and TOL (E). The compounds included in 1-BTHIQ's model are 1-BTHIQ, 1-BIQ, THIQ, ISOQ and TOL as A, B, C, D and E, respectively.

The overall results of the analyses for the pyrolysis of 9-BTHC are tabulated in Tables 15-19 and the similar results for 1-BTHIQ's pyrolysis are presented in Tables 20-24. The all first and all second order reactions pathways seem to model both compounds' pyrolyses most effectively. In comparing the two models for both compounds, the second

order reactions pathway is apparently the better of the two. The relative rate constant k_4 decreases with temperature for the first order reactions model for both compounds. Also the difference in the relative rate constants for the original experiments and the low concentration experiments for 9-BTHC is much less for the second order reactions pathway. The relative sizes of the rate constants for the second order reactions pathways are somewhat confusing. The relative rate constant k_1 is greater than k_2 at the lower temperatures (liquid phase) and approximately equal at the higher temperatures (vapor phase). The product distributions suggest that the dehydrogenation of 9-BTHC or 1-BTHIQ to produce 9-BC or 1-BIQ is slower in the liquid phase relative to the bond scission reaction. The relative rate constants derived from the reaction pathway models are contradictory of this result. It should be remembered that several elementary steps are combined into the pathways for the 'time-concentration' integral analysis and could have a profound effect on the overall results.

Future Work

This work has been completed. The Dissertation has been written and is available through the Marriott Library at the University of Utah.

References

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Table 1. Pyrolysis of 4-Benzylpiperidine (4-BPP).
Temperature: 698 Kelvin (425°C)

<u>Reaction Time, min</u>	<u>Initial Conc'n 4-BPP, mmole/cc</u>	<u>% Material Balance</u>	<u>Conversion of 4-BPP</u>
1.0	0.02866	94.76	0.1107
3.0	0.03107	92.22	0.1922
3.0	0.03269	91.53	0.1835
5.0	0.03159	90.88	0.2563
10.0	0.03138	89.30	0.3925
10.0	0.02933	91.85	0.3665
20.0	0.02972	88.27	0.5291

Notes:

1. % Material Balance = $[(N_A + N_B + N_E + N_H)/N_{A0}] \times 100$
2. Conversion of 4-BPP = $1 - (N_A/N_{A0})$

where, A = 4-BPP

B = 4-Benzylpyridine

E = Toluene

H = Benzene

N_i = millimoles of i at t

N_{i0} = millimoles of i at t=0

$$\bar{C}_{A0} = 0.03063 \pm 0.0014$$

Table 2. Pyrolysis of 4-Benzylpiperdine (4-BPP)
Temperature: 686 Kelvin (413°C)

<u>Reaction Time, min</u>	<u>Initial Conc'n 4-BPP, mmole/cc</u>	<u>% Material Balance</u>	<u>Conversion of 4-BPP</u>
3.0	0.03087	97.76	0.1271
5.0	0.2903	95.98	0.1785
5.0	0.03001	101.16	0.1769
10.0	0.02986	90.57	0.2917
15.0	0.03079	94.29	0.3669
15.0	0.03039	91.69	0.3746
30.0	0.02963	92.22	0.5078

Notes:

1. % Material Balance = $[(N_A + N_B + N_E + N_H)/N_{A0}] \times 100$

2. Conversion of 4-BPP = $1 - (N_A/N_{A0})$

where, N_{i0} = millimoles of i at t=0

N_i = millimoles of i at t

A = 4-BPP

B = 4-Benzylpyridine

E = Toluene

H = Benzene

$$\bar{C}_{A0} = 0.03008 \pm 0.00066$$

Table 3. Pyrolysis of 4-Benzylpiperidine(4BPP)
Temperature: 648 K (375 °C)

Reaction time,min.	Initial Conc'n 4-BPP,mmole/cc	% Material Balance	Conversion of 4BPP
15	.03061	96.69	.1823
30	.03199	90.56	.2516
30	.02958	88.70	.2470
60	.03092	88.04	.2986
120	.03024	89.71	.3186
120	.03092	89.67	.3099
240	.02993	89.99	.4519

where,

$$\text{Conversion} = 1 - [N(4BPP)_t / N(4BPP)_{t=0}]$$

$$\% \text{ Material Balance} = ([N_A + N_B + N_E + N_H] / N_{A0}) \times 100$$

N_i = millimoles of i at t

N_{i0} = millimoles of i at t=0

A = 4BPP

B = 4-Benzylpyridine

E = Toluene

H = Benzene

Table 4. Pyrolysis of 4-Benzylpiperidine(4BPP). Temperature: 648 K (375 °C)
Normalized Product Distribution(%)

Reaction Time,min.	Conversion of 4BPP	%Material Balance	Relative Yields (% , Normalized)						4BPY PYD
			4BPP	4BPY	TOL	PYD	4MPP	4MPY	
15	.1823	96.69	80.90	9.31	5.46	3.96	0	.38	2.35
30	.2493	89.63	79.50	7.63	7.77	4.56	0	.69	1.68
60	.2986	88.04	73.93	6.36	12.50	6.46	.16	.59	.98
120	.3143	89.69	69.87	4.47	17.04	7.67	.16	.79	.58
240	.4519	89.99	51.90	4.30	29.01	13.40	.28	.94	.32

Note: Piperidine = .17 % at 240 min.

Table 5. Pyrolysis of 4-Benzylpiperidine(4BPP). Normalized Product Distribution(%)
 Temperature: 686 K (413 °C)

Reaction Time, min.	Conversion of 4-BPP	% Mat'l Balance	Relative Amounts (% , Normalized)						4BPY/PYD Molar Ratio
			4BPP	4BPY	TOL	PYD	4MPP	4MPY	
3.0	.1271	97.76	84.72	5.23	4.93	4.69	0.3	.42	1.1
5.0	.1777	98.57	77.44	5.39	10.01	6.31	.17	.68	.85
10.0	.2917	90.57	70.84	3.62	16.11	7.72	.65	1.0	.47
15.0	.3707	92.99	59.73	5.28	22.80	9.56	.83	1.8	.55
30.0	.5078	92.22	44.91	4.24	34.99	12.63	1.2	2.0	.34

where,

4BPY = 4-Benzylpyridine

4MPP = 4-Methylpiperidine

4MPY = 4-Methylpyridine

Table 6. Pyrolysis of 4-Benzylpiperidine(4BPP). Normalized Product Distribution(%)
 Temperature: 698 K (425°C)

Reaction Time,min.	Conversion of 4-BPP	% Mat'l Balance	Relative Amounts (% , Normalized)						4BPY/PYD Molar Ratio
			4BPP	4BPY	TOL	PYD	4MPP	4MPY	
1.0	.1107	94.76	90.43	4.21	1.72	3.65	0.0	0.0	1.2
3.0	.1878	91.88	83.40	3.57	7.35	4.94	.25	.48	.73
5.0	.2563	90.88	75.58	3.40	13.38	6.90	.40	.34	.49
10.0	.3795	90.58	60.69	3.75	24.13	9.82	.58	1.0	.38
20.0	.5291	88.27	44.45	1.40	37.47	12.53	1.7	2.45	.11

where,

4BPY = 4 - Benzylpyridine

4MPP = 4 - Methylpiperidine

4MPY = 4 - Methylpyridine

Table 7
 Pyrolysis of 4-Benzylpiperidine. Temperature: 648 K (375 °C)
 Overall Reaction Order Determination-Integral Technique

<u>Reaction Time,min.</u>	<u>Kinetic Plots Ordinates</u>	
	<u>First Order</u> <u>-LN(1-X)</u>	<u>Second Order</u> <u>X/[C₀(1-X)]</u>
15	.2013	7.286
30	.2898	10.51
30	.2837	11.09
60	.3546	13.77
120	.3836	15.46
120	.3709	14.52
240	.6013	27.54

Linear Regression Analysis

<u>Plot</u>	<u>Y-Intercept</u>	<u>Slope</u>	<u>r²</u>
First Order -LN[1-X _A]=k ₁ t	.221	.0015	.9354
Second Order $\frac{X_A}{C_{A0}(1-X_A)} = k_2 t$	7.4	.0787	.9378

where, k₁ [=] min⁻¹ ; k₂ [=] cc(mole-min)⁻¹

X_A = conversion of 4BPP

C_{A0} = initial concentration of 4BPP

Table 8. Pyrolysis of 4-Benzylpiperidine(4-BPP).

Overall Reaction(s) Order Determination-Integral Technique
 Temperature: 686 K (413 °C)

Reaction Time,min.	Kinetic Plot Ordinates	
	First Order -LN(1-X)	Second Order $X/(C_{A0}(1-X))$
3.0	.136	4.72
5.0	.197	7.49
5.0	.195	7.17
10.0	.345	13.8
15.0	.457	18.8
15.0	.469	19.7
30.0	.709	34.8

Linear Regression Analysis

Plot	Y-Intercept	Slope	r^2
First Order $-LN(1-X) = k_1 t$	.104	.021	.9733
Second Order $\frac{X}{C_{A0}(1-X)} = k_2 t$	2.00	1.12	.9964

where, $k_1(=)$ 1/min. ; $k_2(=)$ cc/(mmole-min);

X = conversion of 4BPP; C_{A0} = initial concentration

Table 9 . Pyrolysis of 4-Benzylpiperidine(4BPP).

Overall Reaction(s) Order Determination-Integral Technique

Temperature : 698 K (425 °C)

Reaction Time,min.	Kinetic Plot Ordinates	
	First Order -LN(1-X)	Second Order $X/(C_{A0}(1-X))$
1.0	.117	4.34
3.0	.213	7.66
3.0	.203	6.87
5.0	.296	10.9
10.0	.498	20.6
10.0	.457	19.7
20.0	.753	37.8

Linear Regression Analysis

<u>Plot</u>	<u>Y-Intercept</u>	<u>Slope</u>	<u>r²</u>
First Order -LN(1-X) = k_1t	.114	.033	.9839
Second Order $X/(C_{A0}(1-X)) = k_2t$	2.15	1.79	.9987

where, $k_1(=)$ 1/min.; $k_2(=)$ cc/(mmole-min); X=conversion of 4BPP

C_{A0} = Initial Concentration of 4BPP, mmole/cc

Table 10. Pyrolysis of 4-BPP. Temperature: 648 K (375 °C)
Overall Reaction Order Determination-Differential Technique

<u>Time,min.</u>	<u>C_A, $\frac{\text{mmole}}{\text{cc}}$</u>	<u>-[C_A/ t]</u>	<u>LN[-(C_A/ t)]</u>	<u>LN[$\bar{C}_A$]</u>
15	.02502	1.367x10 ⁻⁴	-8.898	-3.730
30	.02297	5.028x10 ⁻⁵	-9.898	-3.807
60	.02146	8.031x10 ⁻⁶	-11.73	-3.853 *
120	.02098	3.507x10 ⁻⁵	-10.26	-3.970
240	.01677			

Linear Regression Analysis(* point deleted from analysis)

$$\text{LN}[-(C_A / t)] = \text{LN}(k) + n\text{LN}[\bar{C}_A]$$

$$\text{Y-Intercept} = \text{LN}(k) = 9.99$$

$$\text{Slope} = n = 5.1$$

$$r^2 = \text{correlation coefficient} = .7955$$

Table 11. Pyrolysis of 4BPP. Temperature: 686 K (413 °C)
Overall Reaction Order Determination-Differential Technique

<u>Time,min.</u>	<u>C_A, mmole cc</u>	<u>-[ΔC_A/Δt]</u>	<u>LN[-(ΔC_A/Δt)]</u>	<u>LN[C_A]</u>
3.0	.02626	7.61 x 10 ⁻⁴	-7.181	-3.669
5.0	.02474	6.859 x 10 ⁻⁴	-7.285	-3.771
10.0	.02131	4.755 x 10 ⁻⁴	-7.651	-3.906
15.0	.01893	2.749 x 10 ⁻⁴	-8.199	-4.082
30.0	.01481			

Linear Regression Analysis

$$\text{LN}[-(\Delta C_A/\Delta t)] = \text{LN}(k) + n\text{LN}[C_A]$$

$$\text{Y-Intercept} = \text{LN}(k) = 2.21$$

$$\text{Slope} = n = 2.5$$

$$r^2 = \text{correlation coefficient} = .9730$$

Table 12. Pyrolysis of 4-BPP. Temperature: 698 K (425 °C)
Overall Reaction Order Determination-Differential Technique

<u>Time, min.</u>	<u>$C_A, \frac{\text{mmole}}{\text{cc}}$</u>	<u>$-\Delta C_A / \Delta t$</u>	<u>$\text{LN}[-(\Delta C_A / \Delta t)]$</u>	<u>$\text{LN}[\bar{C}_A]$</u>
1.0	.02724	1.182×10^{-3}	-6.741	-3.647
3.0	.02488	1.050×10^{-3}	-6.859	-3.737
5.0	.02278	7.543×10^{-4}	-7.190	-3.868
10.0	.01900	4.583×10^{-4}	-7.688	-4.091
20.0	.01443			

Linear Regression Analysis

$$\text{LN}[-(\Delta C_A / \Delta t)] = \text{LN}(k) + n \text{LN}[\bar{C}_A]$$

$$\text{Y-Intercept} = \text{LN}(k) = 1.3$$

$$\text{Slope} = n = 2.2$$

$$r^2 = \text{correlation coefficient} = .9940$$

Table 13. Hydrogen Balance on the Pyrolysis of 4BPP

<u>Temp., K(°C)</u>	<u>$\sum_H \pm SD$</u>	<u>$[\sum_H / \% \text{ M.B.}] \pm SD$</u>
648 (375)	.8345 $\pm$.05	.9186 $\pm$.04
673 (400)	.9055 $\pm$.06	.9497 $\pm$.05
686 (413)	.8609 $\pm$.08	.9107 $\pm$.06
698 (425)	.8419 $\pm$.08	.9212 $\pm$.07
Averages	.8607 $\pm$.03	.9251 $\pm$.02

where,

$\sum_H$ = Average hydrogen Balance at T

SD = Standard Deviation

$$\sum_H = N(4BPP) + 11/17N(4BPY) + 8/17N(TOL) + 5/17N(PYD) + 7/17N(4MPY) + 12/17N(4MPP) + 11/17N(PIP)$$

4BPY = 4-Benzylpyridine

4MPY = 4-Methylpyridine

4MPP = 4-Methylpiperidine

PYD = Pyridine

PIP = Piperidine

TOL = Toluene

Table 14. Chemical Equilibrium Estimation for the Pyrolysis of 4-BPP

Cumulative Reaction:

$$\begin{aligned} \Delta G_{\text{rxn},T}^{\circ} &= \Delta G_T^{\circ}(4\text{BPY}) + \Delta G_T^{\circ}(\text{PYD}) + \Delta G_T^{\circ}(\text{PIP}) + 2\Delta G_T^{\circ}(\text{TOL}) + 4\Delta G_T^{\circ}(\text{H}_2) - 3\Delta G_T^{\circ}(4\text{BPP}) \\ &= -RT \ln[\text{K}_{\text{eq}}] \end{aligned}$$

<u>Temp., K(°C)</u>	<u>$\Delta G_{\text{rxn},T}^{\circ}$, $\frac{\text{kcal}}{\text{mole}}$</u>	<u>K_{eq}</u>	<u>Estimated Extent of Reaction of 4BPP, %</u>
300 (27)	50.2	2.90×10^{-37}	0.004
648 (375)	20.8	9.4×10^{-8}	11.3
673 (400)	18.9	7.1×10^{-7}	15.5
686 (413)	18.0	1.9×10^{-6}	18.2
698 (425)	17.0	4.6×10^{-6}	21.1
723 (450)	15.2	2.6×10^{-5}	28.2
800 (527)	9.56	1.7×10^{-3}	56.2

Table 15. Relative Reaction Rate Constants for the First Order
Pyrolysis Reaction Pathway Model for 9BTHC

Temp., K	(k_1+k_2)	(k_3+k_4)	k_2	k_3	k_1^a	k_4
633	.0024	.1637	.0010	.0002	.0015	.1635
648	.0112	.0912	.0038	.0007	.0074	.0905
673	.0557	.0518	.0174	.0100	.0383	.0488
683	.0657	.0604	.0361	.0235	.0296	.0369
683 ^b	.0859	.0504	.0370	.0280	.0489	.0224
698	.2199	.0937	.0532	.0514	.1667	.0423
713	.4207	.0998	.0896	.1165	.3311	-.017
Average r^2	.9830	.9520	.9732	.9896		

where, a = calculated from other values
b = low concentration experiments
 k_1 (=) 1/min.

Table 16 Relative Reaction Rate Constants for the Second Order
Pyrolysis Reaction Pathway Model for 9BTHC

Temp., K	(k_1+k_2)	k_2	k_3	k_4	k_1
633	.0055	.0015	.0013	-.006	.0040
648	.0175	.0057	.0053	.0075	.0118
673	.1385	.0392	.0714	.2968	.0993
683	.2048	.1074	.1196	.3250	.0974
683 ^b	.2210	.0899	.1487	.3510	.1311
698	.9798	.1706	.5537	.8720	.8092
713	2.600	.2570	2.156	2.221	2.343
Average r^2	.9883	.9797	.9721	.9203	

where,
a = calculated from other values
b = low concentration experiments
 k_i (=) mole/mole-min

Table 17. 9BTHC Pyrolysis Reaction Pathway Modeling
Mixed First and Second Order Reactions Overall Results

Temp., K	$-(k_3+k_4)$	k_1	k_2	k_3	k_4^a
633	.164	-.022	.054	.0002	.1638
648	.091	-.033	.072	.0007	.090
673	.059	.052	.004	.010	.049
683	.060	.037	.079	.024	.036
683 ^b	.050	.077	.028	.028	.022
698	.094	.109	.180	.051	.043
713	.100	.202	.359	.117	-.017
Average r^2	.9520	.9797	.6990	.9596	

^a = calculated from other values; ^b = low-concentration experiments

Table 18. 9BTHC Pyrolysis Reaction Pathway Modeling. All First Order Reactions with THC being converted to CARB Overall Results.

Temp.,K	(k_1+k_2)	$-(k_3+k_4)$	k_2	k_3	k_5	k_1^a	k_4^a
633	.0024	.164	.0018	.007	.006	.0006	.157
648	.0112	.091	.004	.013	.0008	.0072	.078
673	.056	.059	.012	.078	-.012	.044	-.019
683	.066	.060	.028	.099	.003	.038	-.039
683 ^b	.086	.050	.033	.155	.0023	.053	-.105
698	.220	.094	.059	.326	.016	.161	-.232
713	.421	.100	.102	.755	.022	.319	-.655
Avg. r^2	.9830	.9520	.9955	.9813	.4824		

a = calculated from other values;b=low-concentration experiments

Table 19. 9BTHC Pyrolysis Reaction Pathway Modeling. All Second Order Reactions with THC being converted to CARB Overall Results.

Temp.,K	(k_1+k_2)	$-(k_3+k_4)$	k_2	k_3	k_5	k_1^a	k_4^a
633	.006	.052	.002	-.002	-.008	.004	.052
648	.018	.077	.004	-.013	-.054	.014	.077
673	.139	.208	.014	.091	.084	.125	.117
683	.205	.096	.037	.109	.033	.168	-.013
683 ^b	.221	.048	.031	.130	.018	.190	-.082
698	.980	.467	.069	.308	.152	.911	.159
713	2.60	1.47	.139	1.05	.320	2.46	.427
Avg. r^2	.9883	.9599	.9879	.8754	.7640		

a = calculated from other values;b = low-concentration experiments

Table 20. Relative Reaction Rate Constants for the First Order
Pyrolysis Reaction Pathway Model for 1BTHIQ

Temp., K	(k_1+k_2)	(k_3+k_4)	k_2	k_3	k_1^a	k_4^a
588	.0128	.5244	.0037	.0210	.0091	.5034
598	.0305	.5320	.0073	.0214	.0232	.5106
611	.0620	.3847	.0207	.0334	.0413	.3513
623	.1410	.1639	.0521	.0439	.0889	.1200
638	.3356	.1361	.1386	.0553	.1970	.0080
Average r^2	.9821	.9151	.9874	.9746		

where,

a = calculated from other values
 k_1 (=) 1/min.

Table 21. Relative Reaction Rate Constants for the Second Order
Pyrolysis Reaction Pathway Model for 1BTHIQ

Temp., K	(k_1+k_2)	k_2	k_3	k_4	k_1^a
588	.0256	.0072	.0380	-.147	.0184
598	.0659	.0154	.0503	-.072	.0505
611	.2015	.0586	.1128	.1871	.1429
623	.4090	.1774	.1517	.3392	.2316
638	.8516	.4462	.3162	1.043	.4054
Average r^2	.9794	.9467	.9566	.8975	

where,

a = calculated from other values
 k_1 (=) mole/mole - min.

Table 22. 1BTHIQ Pyrolysis Reaction Pathway Modeling
Mixed First and Second Order Reactions Overall Results

Temp.,K	(k_3+k_4)	k_1	k_2	k_3	k_4^a
588	.524	-.106	.007	.021	.503
598	.532	-.187	.015	.021	.511
611	.385	-.091	.059	.033	.352
623	.164	.046	.177	.044	.120
638	.156	.201	.446	.055	.101
Avg. r^2	.9151	.7121	.9467	.9746	

a = calculated from other values

Table 23. 1BTHIQ Pyrolysis Reaction Pathway Modeling. All First Order
Reactions with THIQ being converted to ISOQ Overall Results.

Temp.,K	(k_1+k_2)	(k_3+k_4)	k_2	k_4	k_5	k_1^a	k_3^a
588	.013	.524	.013	.051	-.032	.0005	.474
598	.031	.532	.029	.063	-.075	.002	.469
611	.062	.385	.047	.089	-.267	.015	.296
623	.141	.164	.054	.083	-.062	.087	.081
638	.336	.156	.138	.176	-.033	.198	-.02
Avg. r^2	.9821	.9151	.9779	.8598	.8800		

a = calculated from other values

Table 24.1BTHIQ Pyrolysis Reaction Pathway Modeling. Mixed First and Second Order Reactions with THIQ being converted to ISOQ Overall Results.

Temp.,K	(k_1+k_2)	(k_3+k_4)	k_2	k_3	k_5	k_1^a	k_4^a
588	.026	.232	.034	.047	.042	-.008	.185
598	.066	.213	.058	.080	.097	.008	.133
611	.202	.134	.102	.188	.238	.100	-.054
623	.409	.062	.127	.162	-.19	.282	-.10
638	.852	.075	.287	.298	-.21	.565	-.22
Avg. r^2	.9794	.8988	.9837	.9831	.7641		

a = calculated from other values.

Figure 1 . Normalized Product Distribution(%). Temperature: 648 K (375°C)

Figure 2.. Normalized Product Distribution(%). Temperature: 686 K(413°C)

Figure 3. Normalized Product Distribution(%).Temperature: 698 K(425°C)

PYROLYSIS OF 4-BENZYLPIPERIDINE (4-BPP)

Figure 4. First Order Integral Kinetics Plot. Temperature: 648 K (375°C)

PYRCLYSIS OF 4-BENZYLPIPERIDINE (4-BPP)

Figure 5. Second Order Integral Kinetics Plot. Temperature: 648 K (375°)

Pyrolysis of 4 - Benzylpiperidine(4BPP)

Figure 6. First Order Integral Kinetics Plot. Temperature: 636 K(413°C)

Figure 7. Second Order Integral Kinetics Plot. Temperature: 686 K (413°C)

PYROLYSIS OF 4-BENZYLPIPERIDINE (4-BPP)

Figure 8. First Order Integral Kinetics Plot. Temperature: 698 K (425°C)

Figure 9. Second Order Integral Kinetics Plot. Temperature: 698 K (425°C)

Figure 10. Differential Kinetics Plot. Temperature: 648 K (375°C)

Figure 11. Differential Kinetics Plot. Temperature: 686 K (413°C)

Figure 12. Differential Kinetics Plot. Temperature: 69E K (425°C)

Figure 13. Reaction Pathway Model

Task 7

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

Faculty Advisor: J. Shabtai
Graduate Student: Y. Shukla

Introduction

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

Project Status

The catalytic HDO reactions of three representative aryl and arylalkyl ethers, i.e., dibenzyl ether, diphenyl ether, anisol, and two furans, i.e., 2,3-benzofuran, dibenzofuran and 2-naphthol as feed are presently being investigated. Infrared and C-13 NMR studies of the products obtained from exhaustive hydrotreatment of the SRC-2 middle distillate indicate that the last 2% of the O-containing compounds are difficult to hydrotreat. These compounds are mainly dibenzofuran types. Results obtained with dibenzofuran (44) as feed are presented in this report. This study observed the change in product composition as a function of experimental conditions, e.g., reaction temperature, hydrogen pressure and catalyst types. The experiments were performed in a shaking autoclave,¹ and the products obtained were identified and quantitatively analyzed by GC-MS.

The reaction of 44 in the presence of sulfided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts² were investigated as a function of reaction temperature in the range of 230-350°C, a hydrogen pressure of 1000 psig and the total reaction time of 1 hour. The results obtained with sulfided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ are summarized in Figures 1 and 2, respectively. As seen in Figure 1, the conversion of 44 increased from 0.5% at 230°C to 9.6% at 350°C. The main intermediate at the lower temperature is 6-phenyl-2,4-cyclohexadienone (78). With an increase in temperature, the concentration of 78 decreased sharply and the concentration of O-phenyl phenol 9 increased. In the middle temperature range, the concentration of 9 decreased while the concentrations of cyclohexane (2), bicyclohexyl (33), cyclohexylbenzene (8) and benzene (3) increased. At higher temperatures the concentration of 33 decreased, and the concentrations of cyclohexane (2) benzene (3) and cyclohexylbenzene (8) increased. Traces of methylcyclopentane (1) and biphenyl (42) were also formed.

Different compositions were observed with the sulfided Ni-Mo/ γ -Al₂O₃ catalyst (Figure 2). The overall conversion varies from 0.5% at 230°C to

7% at 350°C. The main product at the lower temperature is 6-phenyl-2,4-cyclohexadienone (78). With an increase in temperature, the concentration of (78) decreased and the concentrations of biphenyl (42) and cyclohexane (2) increased. In the middle temperature range, the concentration of 42 decreased and the concentrations of 2, benzene (3), bicyclohexyl (33), cyclohexylbenzene (8) and phenol (5) increased. At higher temperatures the concentration of cyclohexane (2) decreased while the concentrations of 3, 5 and 8 increased. Traces of methylcyclopentane (1), bicyclohexanol, cyclohexylphenol was also formed.

The HDO reaction of 44 in the presence of sulfided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts were also investigated as a function of hydrogen pressure in the range of 250-2000 psig at a reaction temperature of 350°C and the total reaction time of 1 hour. The results obtained are summarized in Figures 3 and 4, respectively.

The change in product composition as a function of reaction temperature, hydrogen pressure and catalyst types can be rationalized in terms of the mechanism proposed in Figure 5. With both catalysts at the lower temperature the main intermediate was 6-phenyl-2,4-cyclohexadienone- (78) formed by concerted mechanisms. With Co-Mo, 78 rearranged to O-phenylphenol (9). After hydrogenation followed by C-O hydrogenolysis, it yielded cyclohexylbenzene (8). Compound 8 was hydrogenated to bicyclohexyl (33) and 33 upon C-C bond cleavage formed cyclohexane at the lower temperature. At higher temperatures cyclohexylbenzene (8) on C-C bond cleavage yielded benzene and cyclohexane. With Ni-Mo, 78 yielded biphenyl by either route because Ni was efficient enough to hydrogenate the ketones and remove H₂O to form biphenyl (42). Compound 42 hydrogenated to cyclohexylbenzene (8). Compound (8) further hydrogenated to bicyclohexyl (33), and bicyclohexyl upon C-C bond cleavage formed cyclohexane at the lower temperature. At higher temperatures cyclohexylbenzene on C-C bond cleavage formed benzene and cyclohexane.

Kinetic studies of dibenzyl ether, diphenyl ether and dibenzofuran with commercial catalysts and catalysts synthesized in this laboratory are in progress.

References

1. G. Haider, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1981.
2. U. Weisser and S. Landa, "Sulfide Catalyst Their Properties and Applications," Pergamon, Oxford, 1973.

Figure 1. Change in product composition from hydrodeoxygenation of dibenzofuran (44) c1ccc2c(c1)oc3ccccc32 as a function of reaction temperature [catalyst, sulfided Co-Mo/ γ -Al₂O₃ (Nalco #471); hydrogen pressure, 1000 psig; total reaction time, 1 hr.]

Figure 2. Change in product composition from hydrodeoxygenation of dibenzofuran (44) c1ccccc1-c2ccccc2 as a function of reaction temperature [Catalyst, sulfided Ni-Mo/ γ - Al_2O_3 (Nalco #504); hydrogen pressure, 1000 psig; total reaction time, 1 hr.]

Figure 3. Change in product composition from hydrodeoxygenation of dibenzofuran (44) c1ccc2c(c1)oc3ccccc32 as a function of hydrogen pressure [Catalyst, sulfided Co-Mo/ γ -Al₂O₃ (Nalco #471); reaction temperature, 350°C; total reaction time, 1 hr.]

Figure 4. Change in product composition from hydrodeoxygenation of dibenzofuran (44) c1ccc2c(c1)oc3ccccc32 as a function of hydrogen pressure. [catalyst, sulfided Ni-Mo/ γ -Al₂O₃ (Nalco #504); reaction temperature, 350°C; total reaction time, 1 hr].

Figure 5. Indicated different pathways of dibenzofuran (44) HDO reaction.
 (A) Sulfided Co-Mo/ γ -Al₂O₃ catalyst
 (B) Sulfided Ni-Mo/ γ -Al₂O₃ catalyst

Task 7

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

Hydrodenitrogenation of Coal-Derived Liquids and Related N-Containing Compounds

Faculty Advisor: J. Shabtai
Graduate Student: J. Yeh

Introduction

The main objective of this research project is to develop effective catalyst systems and processing conditions for hydrodenitrogenation (HDN) of coal-derived liquids (CDL) in a wide range of nitrogen contents and structural type composition. This is of particular importance in view of the higher concentration of nitrogen-containing compounds in CDL as compared to that in petroleum feedstocks. For a better understanding of denitrogenation processes, the project includes systematic denitrogenation studies not only of CDL but also of related model N-containing compounds found in such liquids, e.g., phenanthridine, 1,10-phenanthroline, carbazoles, acridines, etc., as a function of catalyst type and experimental rate, mechanism and stereochemistry of HDN of structurally distinct N-containing aromatic systems in the presence of sulfided catalysts.

Project Status

Coal-derived liquids are highly aromatic and have high nitrogen and oxygen contents. Thus, hydrogenation of condensed aromatic materials and removal of heteroatoms present in coal-liquids are important steps for conversion of the latter into suitable feedstocks for further processing.

In this study, the effect of temperature and different catalyst types on the hydrogenation and HDN of a coal-derived liquid is being investigated. The feedstock, SRC-II, was vacuum distilled to obtain a cut that would boil below 430°C under atmospheric pressure. Sulfided Co-Mo/Al₂O₃ and sulfided Ni-Mo/Al₂O₃ were the catalysts. They were prepared by stepwise impregnation. The reactions were performed in an autoclave. The samples were analyzed using a Perkin Elmer CHN instrument. Since the CHN determination of nitrogen is unreliable below 0.5% and the SRC-II distillate has about 1% nitrogen, some 1,10-phenanthroline was added to the SRC-II distillate to increase the nitrogen in the reactor feed to about 2%. Hydrogen consumption was measured by monitoring the hydrogen pressure needed to maintain the reaction pressure.

Figure 1 summarizes the observed hydrogen and nitrogen wt % in the product from the hydrogenation of SRC-II as a function of reaction time at 300°C, using a sulfided Co-Mo/Al₂O₃ catalyst. Initially, a rapid increase of hydrogen wt % was observed. However, for longer reaction times, the hydrogen wt % increased more slowly. The nitrogen wt % continued to decrease at a constant rate as the reaction proceeded. Since the heterocyclic ring structures required hydrogenation before carbon-nitrogen

bond scission could occur, a high hydrogen consumption may have occurred at low degrees of nitrogen removal. At high degrees of nitrogen removal, differential hydrogen consumption may have been low because most of the aromatic compounds were saturated. Figures 2, 3 and 4 summarize the hydrogen and nitrogen wt % in the product from the hydrogenation of SRC-II as a function of reaction time at 325°C, 350°C and 375°C, respectively. The trends of the curve are similar to those seen in Figure 1. Since the nitrogen removal rate was nearly constant, a zero order reaction has been assumed. Table 1 and Figure 5 summarize this zero-order rate constant as a function of temperature. Linearity in Figure 5 suggests that the zero order reaction rate assumption is a useful model for nitrogen removal from these complex mixtures. From Figure 5 there is an apparent activation energy of 13.3 K cal/mol for the HDN of the SRC-II distillate over the sulfided Co-Mo/Al₂O₃ catalyst.

Reference

1. G. Muralidhar, F.E. Massoth and J. Shabtai, submitted for publication in J. Catal.

Table 1. Zero order rate constants for nitrogen removal as a function of reaction temperature for sulfided Co-Mo/Al₂O₃ catalyst.

<u>Temperature</u>	<u>k x 10³, Rate Constant (Wt %/min).</u>
300°C	0.938
325°C	1.39
350°C	3.00
375°C	3.24

Figure 1. Change in hydrogen and nitrogen contents of the product from hydrogenation of SRC-II as a function of reaction time. Feed: 100 cc of SRC-II distillate and 5 g 1,10-phenanthroline.¹ Pressure: 2500 psig, Catalyst: 5 g of sulfided 3% Co 8% Mo/Al₂O₃ (prepared by stepwise impregnation), Temperature: 300°C. Five drops of CS₂ is added.

Figure 2. Change in hydrogen and nitrogen contents of the product from hydrogenation of SRC-II as a function of reaction time for reaction temperature, 325°C. Other conditions are the same as in Figure 1.

Figure 3. Change in hydrogen and nitrogen contents of the products from hydrogenation of SRC-II as a function of reaction time, for temperature, 350°C. Other conditions are the same as in Figure 1.

Figure 4. Change in hydrogen and nitrogen contents of the product from hydrogenation of SRC-II as a function of reaction time for temperature, 375°C. Other conditions are the same as in Figure 1.

Figure 5. Temperature dependency of the nitrogen removal rate.
Catalyst: Sulfided Co-Mo/ Al_2O_3 .

Task 13

Catalyst Research and Development

Synthesis of Light Hydrocarbons from CO and H₂

Faculty Advisor: F.V. Hanson

Graduate Student: Y.S. Tsai

Introduction

The production of low molecular weight olefins (C₂-C₄) from the hydrogenation of carbon monoxide over unsupported iron-manganese catalysts has been investigated. The results from the preliminary tests which were performed in a bench-scale fixed-bed reactor system showed that the unsupported iron-manganese catalysts were very selective in the production of C₂-C₄ olefins. Data from the screening tests of the sixteen iron-manganese catalysts indicated that a catalyst composed of 2 parts of manganese per 100 parts of iron was the most selective. The effects of the process variables were also studied. The results essentially agreed with those reported in the literature.

The influence of catalyst pretreatment on the product yield and selectivity has been examined. Hydrogen, carbon monoxide and synthesis gases with ratios of H₂/CO, 2H₂/CO and 3H₂/CO were used. The preliminary results indicated that the pretreatment by the synthesis gas with a ratio of 2H₂/CO led to a higher production of C₂-C₄ olefins after 12 hours on stream. However, the long-term effects on the catalyst activity and selectivity with this pretreatment has still not been determined. The experiment was carried out for 45 hours at the same conditions as were described in the previous report. The data indicates that the yield of... and selectivity for C₂-C₄ olefins is reproducible, but the selectivities of CH₄ and CO₂ are generally higher than the selectivities obtained in the previous study.

Project Status

The experiments for the study of pretreatment effects were performed over the YST-2 catalyst (3.6 Mn/100 Fe atomic ratio). The operating conditions were a synthesis gas with a ratio of 2H₂/CO, a 200 psig pressure and a 1.0 cm³g⁻¹sec⁻¹ space velocity. The temperature was adjusted to maintain a constant CO conversion of 7-9%. The product yield and selectivity for the five pretreatment methods are listed in Table 1. The pretreatment time was 8 hours and the catalyst was on stream for 12 hours. The catalyst activity with hydrogen reduction was lower (i.e., 7.2% CO conversion at 226°C) than the catalyst activity with other methods (i.e., 7.1% CO conversion at 210°C with a 2H₂/CO pretreatment). However, hydrogen reduction generally led to the higher production of C₂-C₄ hydrocarbons (i.e., 46.7%) and lower total selectivities of CH₄ and CO₂ (i.e., 29.4%) than the selectivities obtained with other methods (i.e., 44.6% C₂-C₄ production and 37.5% of CH₄ and CO₂ with a 2H₂/CO pretreatment). Most of the methods except for the CO pretreatment had an O/P ratio of 2.50+ for the C₂-C₄ hydrocarbons.

Because an impressive O/P ratio of 4.09 for the C₂-C₄ hydrocarbons was obtained with the 2H₂/CO pretreatment, a long-term study was initiated to determine the trend for the product yield and selectivity for 45 hours on stream. Table 2 indicates the product yield and selectivity versus time at the same conditions as those shown in Table 1. The data indicates that at 14 hours on stream, the catalyst activity and selectivity reached a constant level. However, the CO conversion decreased from 7.9% to 7.3% at 44 hours on stream. The C₂-C₄ production and the O/P ratio (i.e., at 14 hours) were generally reproducible, but the total selectivities of CO₂ and CH₄ were higher (i.e., 40.9%) than the selectivities obtained in the previous case (i.e., 37.5%). Therefore, hydrogen reduction is considered to be more suitable for the production of C₂-C₄ olefins because (1) hydrogen reduction leads to a higher production of C₂-C₄ hydrocarbons (i.e., 46.7%), (2) the selectivities of CO₂ and CH₄ are lower than those obtained from the other methods (i.e., 30.4% and 35% or more for other cases) and (3) the catalyst activity and selectivity are more stable without a decreasing trend for up to 45 hours.

Future Work

A catalyst characterization study will be conducted. A literature survey on CO hydrogenation as well as heat and mass transfer for the fixed-bed reactor will be continued.

Table 1. Effects of pretreatment on the product yield and selectivity.

<u>Pretreatment^a</u>		<u>H₂</u>	<u>CO</u>	<u>H₂/CO</u>	<u>2H₂/CO</u>	<u>3H₂/CO</u>
<u>Temperature, °C</u>		226	210	210	210	210
<u>CO Conversion, %^b</u>		7.2	8.4	9.2	7.1	6.6
Selectivity, %	CO ₂	12.1	9.3	12.8	9.7	9.8
	C ₁	18.3	23.8	27.1	27.8	28.6
	C ₂ -C ₄	46.7	42.1	42.9	44.6	44.3
	C ₅ ⁺	18.1	22.3	14.9	15.8	15.4
	ROH	4.1	2.5	2.3	2.2	1.9
<u>O/P in C₂-C₄</u>		2.70	1.68	3.84	4.09	3.81

^aPretreatment time: 8 hours.

^bTime on stream: 12 hours.

^cCatalyst: YST-2 (3.6 Mn/100 Fe).

^dOperating Conditions: H₂/CO = 2/1, 200 psig, 1.0 cm³g⁻¹sec⁻¹ space velocity.

Table 2. Product yield and selectivity versus time for YST-2 catalyst, $2\text{H}_2/\text{CO}$ pretreatment for 8 hours, $\text{H}_2/\text{CO} = 2/1$, 200 psig, $1.0 \text{ cm}^3\text{g}^{-1}\text{sec}^{-1}$ space velocity.

<u>Time on Stream, hr</u>	2.5	11.0	14.0	24.0	35.0	40.5	44.0
<u>Temperature, °C</u>	210	210	210	210	210	210	210
<u>CO Conversion, %</u>	23.7	9.7	7.9	7.7	6.8	7.7	7.3
Selectivity, %	CO_2	12.7	14.7	14.1	14.4	14.5	14.8
	C_1	31.0	27.4	26.8	26.8	25.9	25.6
	$\text{C}_2\text{-C}_4$	43.2	44.5	45.9	45.7	46.3	45.6
	C_5^+	10.6	10.7	11.2	11.0	11.2	11.2
	ROH	2.5	2.7	2.0	2.1	2.1	2.8
<u>O/P in $\text{C}_2\text{-C}_4$</u>	2.31	3.68	4.09	4.30	4.65	3.95	4.44

IV. Conclusions

Detailed conclusions are included in the reports for each task. Tasks 3, 6, 8, 9, 10, and 11 have been completed. Tasks 12 and 14 are inactive. Task 4 is no longer funded and has been discontinued. No work was done under Task 15.