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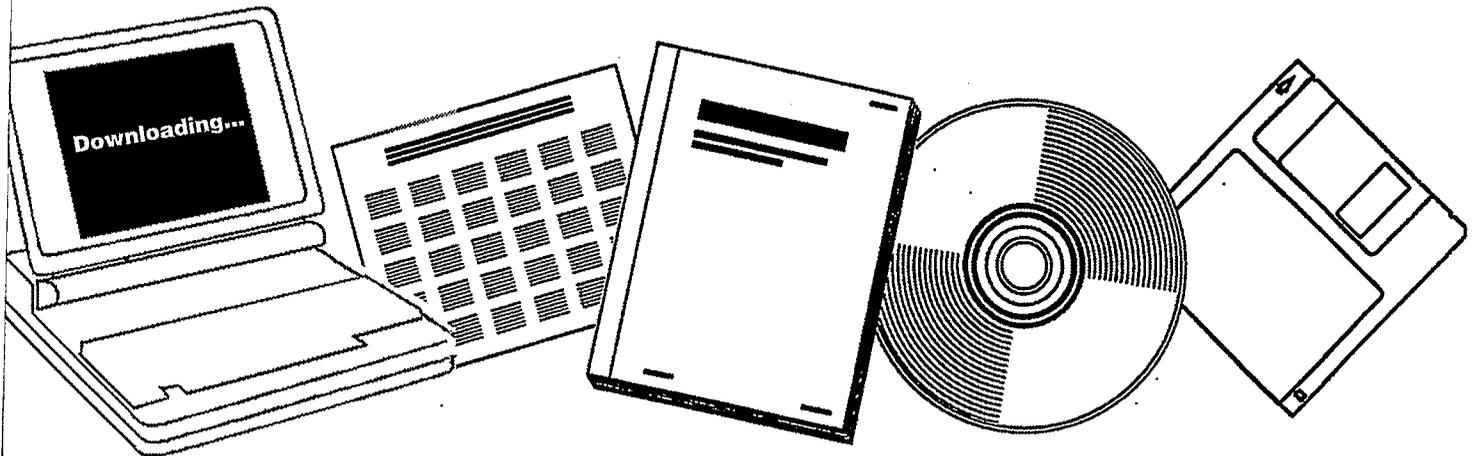
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**CHEMISTRY AND CATALYSIS OF COAL
LIQUEFACTION: CATALYTIC AND THERMAL
UPGRADING OF COAL LIQUID AND HYDROGENATION
OF CO TO PRODUCE FUELS. QUARTERLY PROGRESS
REPORT, OCTOBER-DECEMBER 1981**

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

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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 1981

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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 or extent of hydrogenation will be the subject of study in subsequent tasks in which crackability and hydrolysis 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.

III Highlights to Date

Additional oxygen chemisorption data in conjunction with ESCA measurements on various supported cobalt molybdena catalysts have shown that the O_2 chemisorption technique is related to the state of dispersion of the active molybdena phase rather than specific hydrodesulfurization or hydrogenation sites.

Papers and Presentations

"The Effect of H_2S on the Hydrogenation and Cracking of Hexene over a CoMo Catalyst," R. Ramachandran and F.E. Massoth, J. Catal., 67, 248 (1981).

"Effect of Catalyst Deactivation on the Kinetics of Benzothiophene over a CoMo/ Al_2O_3 Catalyst," R. Ramachandran and F.E. Massoth, presented at the 7th North American Meeting of the Catalysis Society, Boston, Massachusetts, October 1981.

"Effect of the Support on the Catalytic Functions of Cobalt-Molybdena Catalysts," G. Muralidhar, F.E. Massoth and J. Shabtai, ibid.

Task 1

Chemical-Catalytic Studies of Coal Liquefaction

Faculty Advisor: J. Shabtai

Graduate Student: R. Jensen

Introduction

This project is concerned with the development of suitable processing conditions and catalyst-solvent systems for coal liquefaction under mild temperature (<350°C) and pressure (<2000 psi).

Project Status

One of the main conditions for effective use of catalyst-solvent systems in liquefaction below the coal softening point is the necessity of increasing the micropore volume of the solid coal. Previous studies in this department show that pretreatment of coal with metal halides, e.g., ZnCl₂, at relatively mild temperatures (200-350°C) causes considerable increase in surface area and microporosity. Elucidation of the nature of chemical reactions between metal halides and coal has attracted recently considerable interest. In the framework of our work on homogeneously catalyzed liquefaction, it was considered of importance to develop a better understanding of such reactions. Therefore, systematic studies of metal halide-catalyzed reactions were undertaken, using the following types of model compounds:

- (a) Alkylbenzenes with branched alkyl groups;
- (b) Alkylbenzenes with n-alkyl groups; and
- (c) Diarylalkanes.

These studies were intended to provide information on (1) the mode of catalytic activity of metal halides in a wide range of experimental conditions; and (2) the direction and rate of metal halide-catalyzed dealkylation and hydrodealkylation processes, as related to cleavage reactions of inter-cluster linkages in the coal structure.

The previous reports (DE/ET/14700-6, 14700-7 and 14700-8) described the results obtained in a systematic study of hydrodealkylation reactions of representative monoalkylbenzenes of type (a), i.e., isopropylbenzene (2), sec-butylbenzene (3) and tert-butylbenzene (1), and of type (b), i.e., n-propylbenzene, n-butylbenzene, and n-hexylbenzene. All of these studies were performed using a silica-gel supported ZnCl₂ catalyst.

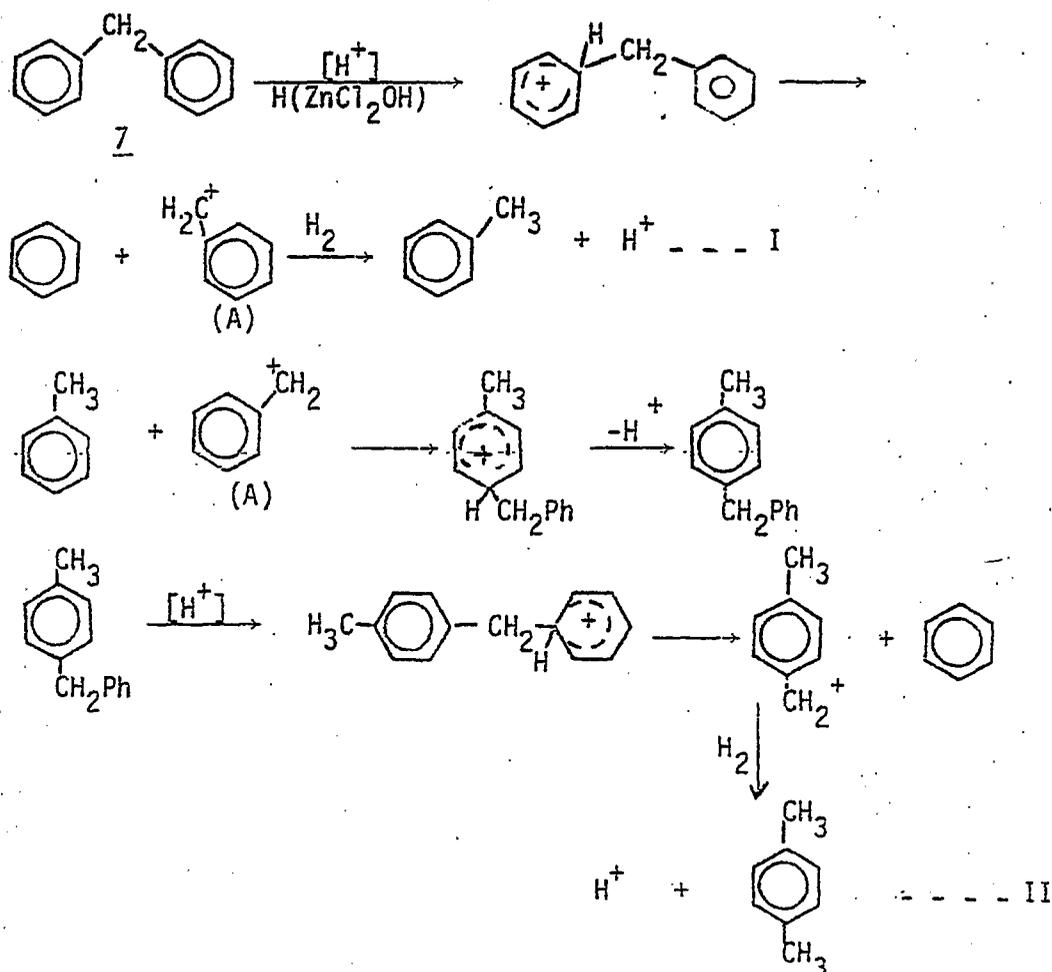
The present report describes the results obtained in a hydrodealkylation study of a compound of type (c), i.e., diphenylmethane (7), using the same supported ZnCl₂ catalyst. Reactions were carried out at 350°C and 450°C, under a hydrogen pressure of 850 psig, using the same micro-reactor employed previously.¹ The total reaction time in each run was

kept constant at 90 seconds. Products obtained were identified and quantitatively analyzed by a combination of gas chromatography and mass spectrometry.

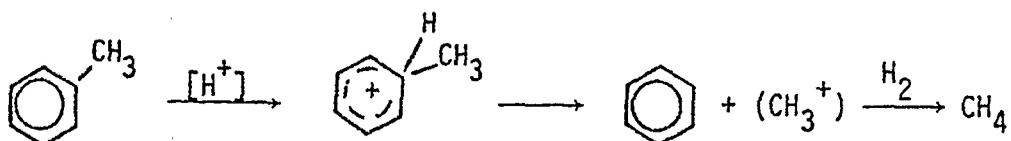
Table I summarizes the product composition observed at the above two temperatures. As seen, the conversion of 7 increases as temperature is increased (from 22.7 at 350°C to 60.1% at 450°C). The main liquid product formed is benzene. The selectivity of formation of this compound increases with temperature (from 83.1% at 350°C to 96.2% at 450°C). This indicates that the depth of hydrodealkylation of 7 increases markedly with increase in temperature. At the lower temperature (350°C) the liquid product contains also toluene, xylenes, and polymethylated benzenes (total yield, 16.9%). The latter are probably derived by transalkylation reactions of initially formed hydrodealkylation products, e.g., toluene (see below, mechanistic studies). With increase in temp to 450°C, the yield of toluene and xylenes decreases, and polymethylated benzenes are not formed. The gaseous products in both experiments (No. 218 and 223) consist mostly (84-85.5%) of methane, together with small amounts of C₂, C₃ and C₄ hydrocarbons.

The product composition from diphenylmethane, and its change with temperature can be rationalized by the following mechanistic scheme:

The first step in the proton-catalyzed hydrodealkylation of compound 7 should yield benzene and an equimolar amount of a resonance-stabilized benzylic carbonium ion (A). The latter could form toluene by reaction with hydrogen (reaction I), or could become involved in transalkylation reactions, e.g., reaction II, yielding *p*-xylene.



Transalkylation of toluene with (A) at the ortho position, in a manner analogous to reaction II, yields o-xylene, while subsequent transalkylation of o- and p-xylenes with (A) produces trimethyl- and higher polymethylated benzenes (Table I, experiment 218). Transalkylation reactions, e.g., reaction II, yield one mol of benzene per mol of (A) consumed. This provides a pathway for benzene formation, in addition to the main hydrodealkylation reaction I. Benzene, which is the predominant liquid product, could be derived also by direct hydrodealkylation of toluene:



Although such a reaction requires the intermediate formation of an unstable primary carbenium ion, it apparently increases in importance at high temperature, e.g., $>450^\circ\text{C}$. It is also possible that the hydrodealkylation of toluene does not involve the thermodynamically unfavorable formation of a bona fide methyl carbonium ion, but instead proceeds by a concerted hydrogenolysis mechanism leading directly to benzene and methane as stable products.

Transalkylation reactions, e.g., reaction II, decrease in importance at 450°C (Table 10, experiment 223), since alkylation-dealkylation equilibria are displaced in the direction of dealkylation with increase in temperature.

Future Work

The hydrodealkylation studies of diarylkanes will be continued. A newly built coal liquefaction unit designed for performance of homogeneously catalyzed reactions at low temperature and pressure will be put in operation by Mr. Peter Rose, a new Ph.D. student who was assigned to work on Task I of the program.

Reference

1. Richard Jensen, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1981.

TABLE 1

Change in Product Composition from $ZnCl_2$ -Catalyzed Hydrodealkylation of Diphenylmethane (7) as a Function of Reaction Temperature

Experiment No.	218	223
Reaction temperature, °C	350	450
Conversion of <u>7</u> , mole %	22.7	60.1
Catalyst	$ZnCl_2$	$ZnCl_2$
Catalyst wt. %	7.4	8.0
Gaseous Product Component, mole %		
CH ₄	85.5	84.0
C ₂ H ₆	} 14.5	8.0
C ₂ H ₄		1.0
C ₃ H ₈		3.9
C ₃ H ₆		0.4
<u>i</u> -C ₄ H ₁₀		1.9
<u>i</u> -Butene		0.4
Liquid Product Component, mole %		
Benzene	83.1	96.2
Toluene	3.2	2.2
Xylenes	5.7	1.6
Polymethylated benzenes ^c	8.0	----

^aIn each run were used 0.15g (.001 mole) of 7 and 0.05g of 5% $ZnCl_2/SiO_2$ catalyst. ^bHydrogen pressure, 850 psig. ^cTrimethyl- and higher polymethylated benzenes.

Task 2

Carbon-13 NMR Investigation of CDL and Coal

Faculty Advisor: R.J. Pugmire
Post-Doctoral Associate: D.K. Dalling

Introduction

This task is concerned with the use of ^{13}C NMR spectroscopy in the analysis of coal, coal-derived liquids and coal-derived residues.

Project Status

Recent work on this task has been performed in support of Task 7. Carbon-13 NMR spectra have been obtained for a series of liquids derived from experimental catalytic upgrading of an SRC-II distillate with a boiling point of 230-455°C. The sulfided catalysts were Co-Mo and Ni-W on alumina. The details of the autoclave reactor, elemental analyses and infrared spectra are reported elsewhere.

Figure 1 presents the ^{13}C NMR spectrum of the SRC-II liquid feedstock. A Bruker WM500 spectrometer was used to obtain spectra for some of the samples in this series. Figure 1 represents carbon NMR at a very high field (69kG or 125 MHz). Only a few features of interest will be discussed here. In the aliphatic region, the resonance lines near 14, 23, 32, 29 and 29.5 ppm indicate the presence of n-alkanes or n-alkyl fragments, as they are produced by carbons one to four and five and up, respectively, of a straight chain saturate. The size of the ϵ peak relative to the others indicates that average alkyl chain lengths are in the range of 10-12 carbons. The resonance signals in the range of 18-25 ppm are characteristic of methyls attached to aromatic or hydroaromatic rings, while the peaks from 10-15 ppm generally result from methyls in branched alkyls. In the aromatic region the signals in the range of 150-160 ppm establish the presence of aryl ethers and phenols or anilines. Unsubstituted carbons adjacent or para to oxygen or nitrogen substituents produce peaks in the region of 114-122 ppm. These are also evident in this spectrum.

The liquid depicted in Figure 1 was hydrodeoxygenated at temperatures from 200-370°C. In Figure 2 the aliphatic portion of the feedstock SRC-II liquid spectrum is compared with that which is obtained after the liquid has been subjected to hydrogen at 350°C for one hour at 1750 psig in the presence of sulfided Co-Mo/ Al_2O_3 catalyst. One may note that after reaction there is an increase in intensity and/or the number of resonance lines in the 12, 23.5, 27 and 35 ppm areas, indicating increased alkyl branching, perhaps as a result of ring dealkylation followed by isomerization. In Figure 3, the aromatic portion of the same samples are compared. For the hydrotreated compound, many of the lines from 150-160 and 110-120 ppm are absent, while additional signals are observed from 125-130 ppm. These results are consistent with the removal of aryl heteroatoms (O, N, S) from the sample, which is also in agreement with the elemental analyses.

The carbon aromaticity (f_a) of the hydrodeoxygenated products was measured at each reaction temperature. The results are presented in Tables 1 and 2 for Co-Mo and Ni-W catalysts, respectively. The experimental C/H atomic ratios are also given in those tables. The f_a 's and C/H ratios of Tables 1 and 2 are compared graphically in Figures 4 and 5, respectively. It is seen in Figures 4 and 5 that there is general agreement between the f_a and C/H curves, and there is also general agreement between the two catalysts: the f_a and C/H values decrease monotonically to about 320-350°C, at which point they again begin to increase. This upturn is believed to result from a shift in the hydrogenation-dehydrogenation equilibrium toward dehydrogenation. The differences which may be noted between Figures 4 and 5 are thought to result from the fact that the hydrogenation activity of the Ni-W catalyst is somewhat higher, producing a more rapid disappearance of aryl ethers.

The new generation of Bruker spectrometers capable of performing some recently designed experiments which allow one to glean multiplicity in formation from complex spectra such as that given in Figure 1. In general the number of lines in a multiplet is one greater than the number of attached protons. These new techniques involve refocusing of carbon and/or proton magnetization during a data acquisition cycle by use of appropriate pulsing schemes. The two techniques illustrated here are termed INEPT and J-resolved 2-D spectroscopy. The requisite pulse sequences are depicted in Figures 6 and 7.

Some results using the INEPT technique are shown in Figures 8 and 9. In Figure 8, the pulsing intervals have been arranged so that resonance signals from methyls and methines are positive, while those from methylenes are negative. The positive lines around 15 ppm are produced by methyls in alkanes or alkyl chains, while those in the region from 18 to 22 ppm result from methyls on aromatic or hydroaromatic rings, as discussed above. The CH peaks are not strongly enhanced in this spectrum and tend to be obscured by the negative methylene lines. In Figure 9, the methine resonances are brought out more clearly by use of a different set of delays.

Another method of determining line multiplicities, J-resolved 2-dimensional Fourier Transform NMR, is illustrated in Figures 10-12. By performing the experiment noted in Figure 7 numerous times with varying delay sequences, followed by Fourier transformation along both time axes, results like those of Figures 10-12 may be produced. The bottom part of the figures is an expansion of the traditional spectrum as given in Figure 1. The top part of those figures is like that of a topographical map from a direct overhead view. The density plotted lines result from rapidly changing contours, corresponding to the multiplet peaks associated with the lines in the trace directly below them. Hence in Figure 10 the resonance lines around 21 ppm are associated with quartets, i.e., they result from CH₃ carbons, while those around 23 ppm, being triplets, are for the most part due to CH₂'s. One may note that there is one prominent doublet, corresponding to a CH, near 23.8 ppm. In Figure 11 one views an aromatic area of the spectrum. Most of the lines here are associated with doublets, indicating protonated aromatic carbons. The line near 130.3 ppm is really two resonances, one a singlet, the other a doublet. Figure 12 was extracted from the area of unprotonated aromatic carbons. The item of interest here is that these peaks show small multiplets, resulting from long-range coupling to protons attached to other carbons, which provides even more information about their environment.

Future Work

Installation of a CXP-200 spectrometer is currently underway in our laboratory. This new instrument will be capable of performing the experiments described above. Thus access will be gained to powerful new tools for use in the analysis of coal-derived liquids.

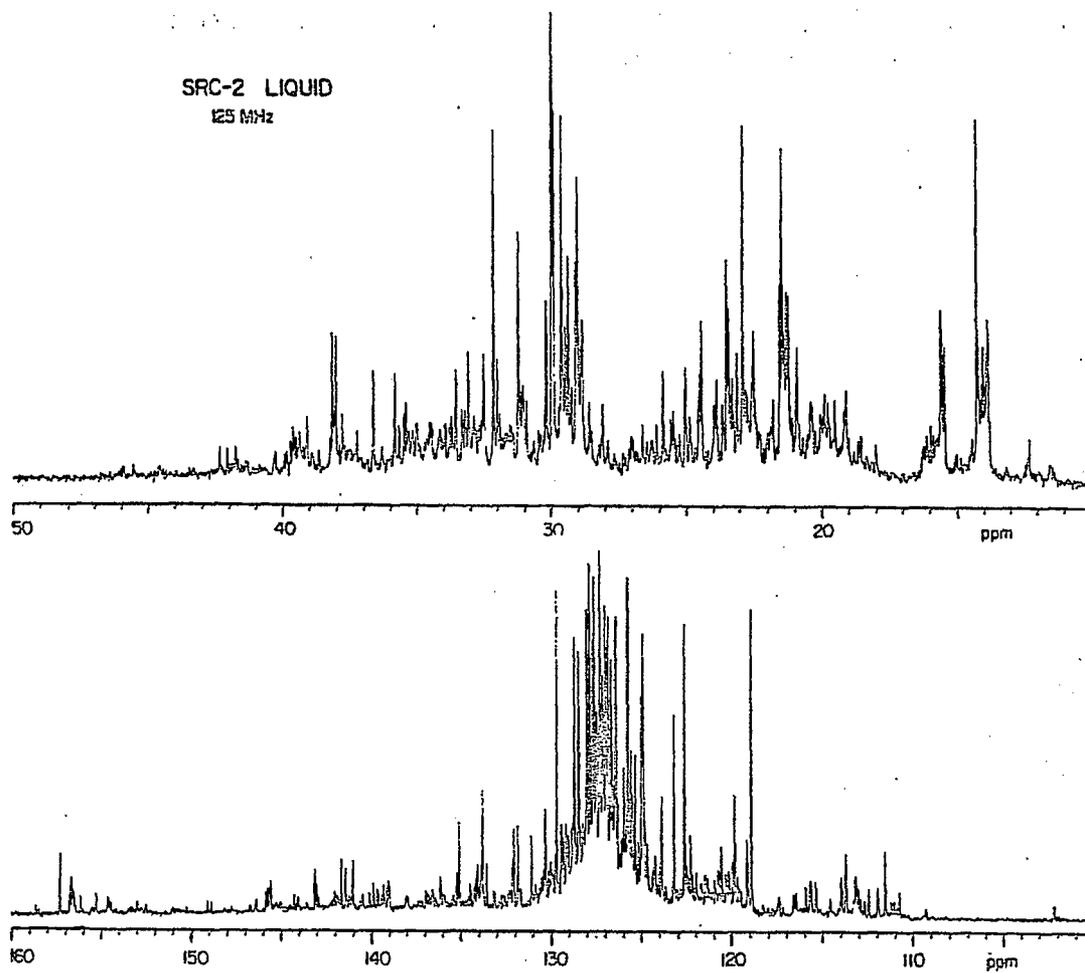


Figure 1. High field ¹³C NMR spectrum of an SRC-II distillate (b.p. 230-455°C). Top, aliphatic region; bottom, aromatic region.

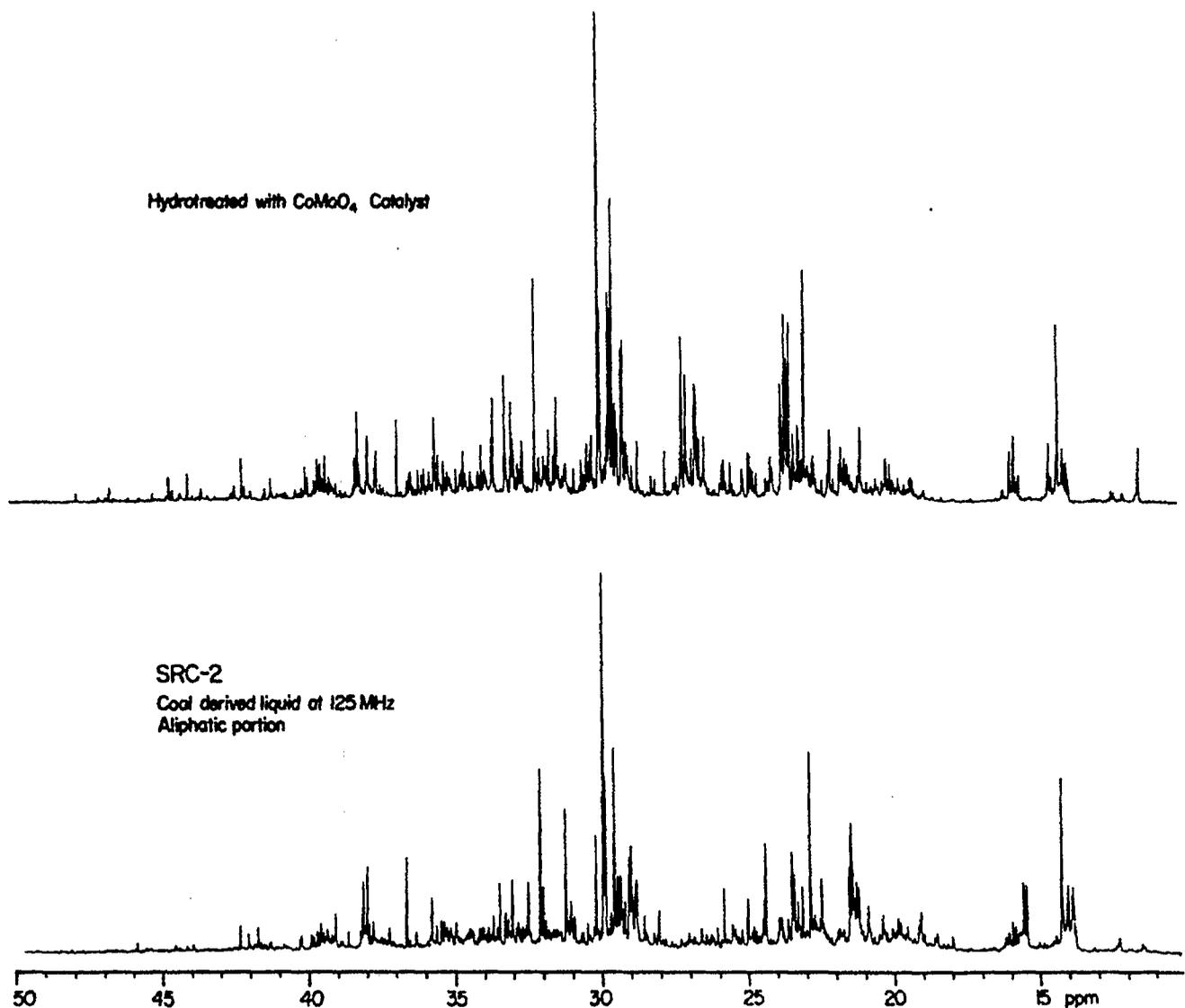
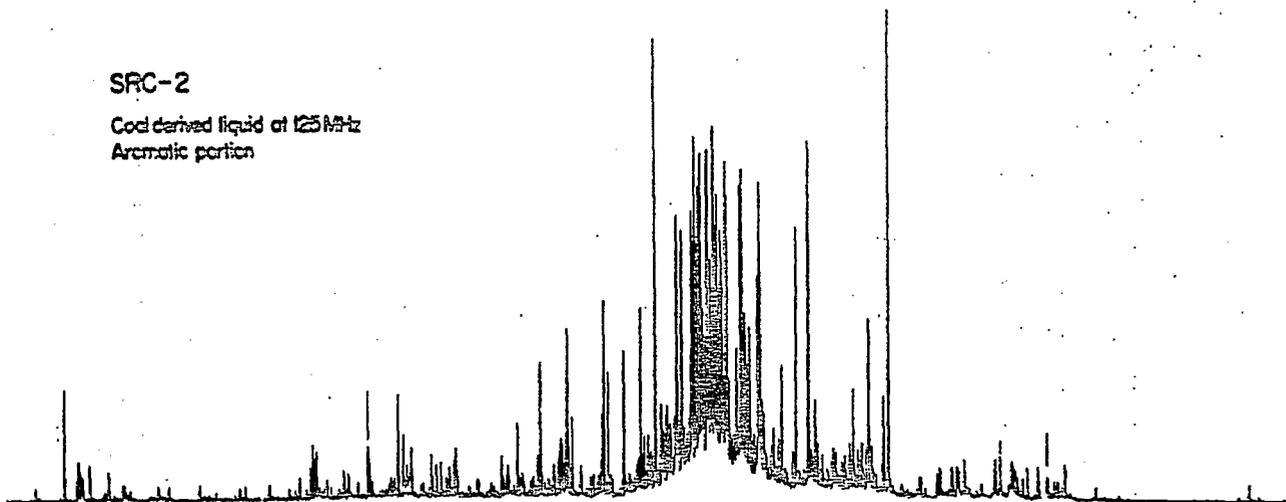


Figure 2. Comparison of the aliphatic regions of the ^{13}C NMR spectra of an SRC-II coal-derived liquid feedstock and the product resulting from hydrodeoxygenation of same at 350°C for one hour, hydrogen pressure 1750 psig, with sulfided Co-Mo/ Al_2O_3 catalyst.

SRC-2

Coal derived liquid at 125 MHz
Aromatic portion



Hydrotreated with CoMoQ₃ Catalyst

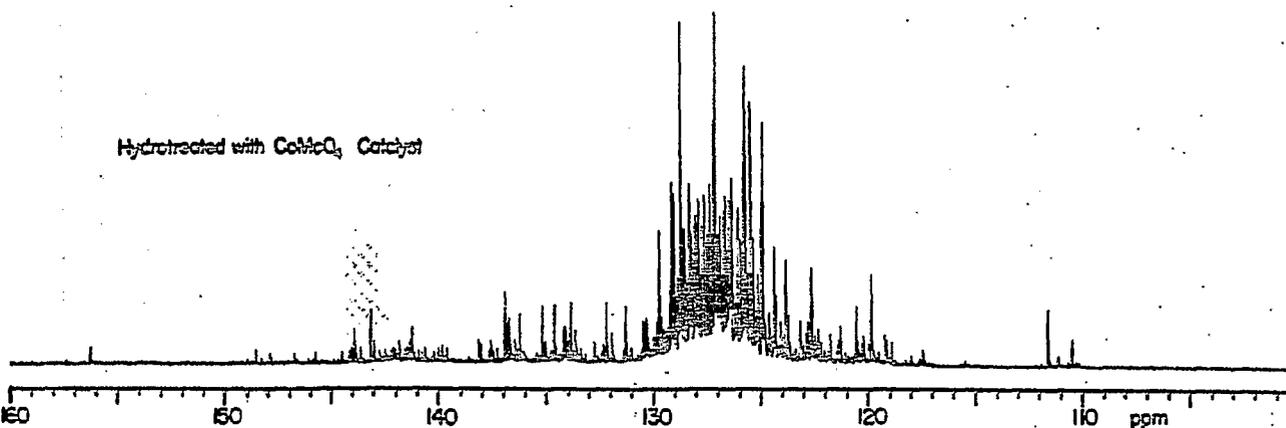


Figure 3. Comparison of the aromatic spectral regions of the ¹³C NMR spectra of an SRC-II coal-derived liquid feedstock and the product resulting from hydrodeoxygenation of same at 350°C for one hour, hydrogen pressure 1750 psig, with sulfided Co-Mo/Al₂O₃ catalyst.

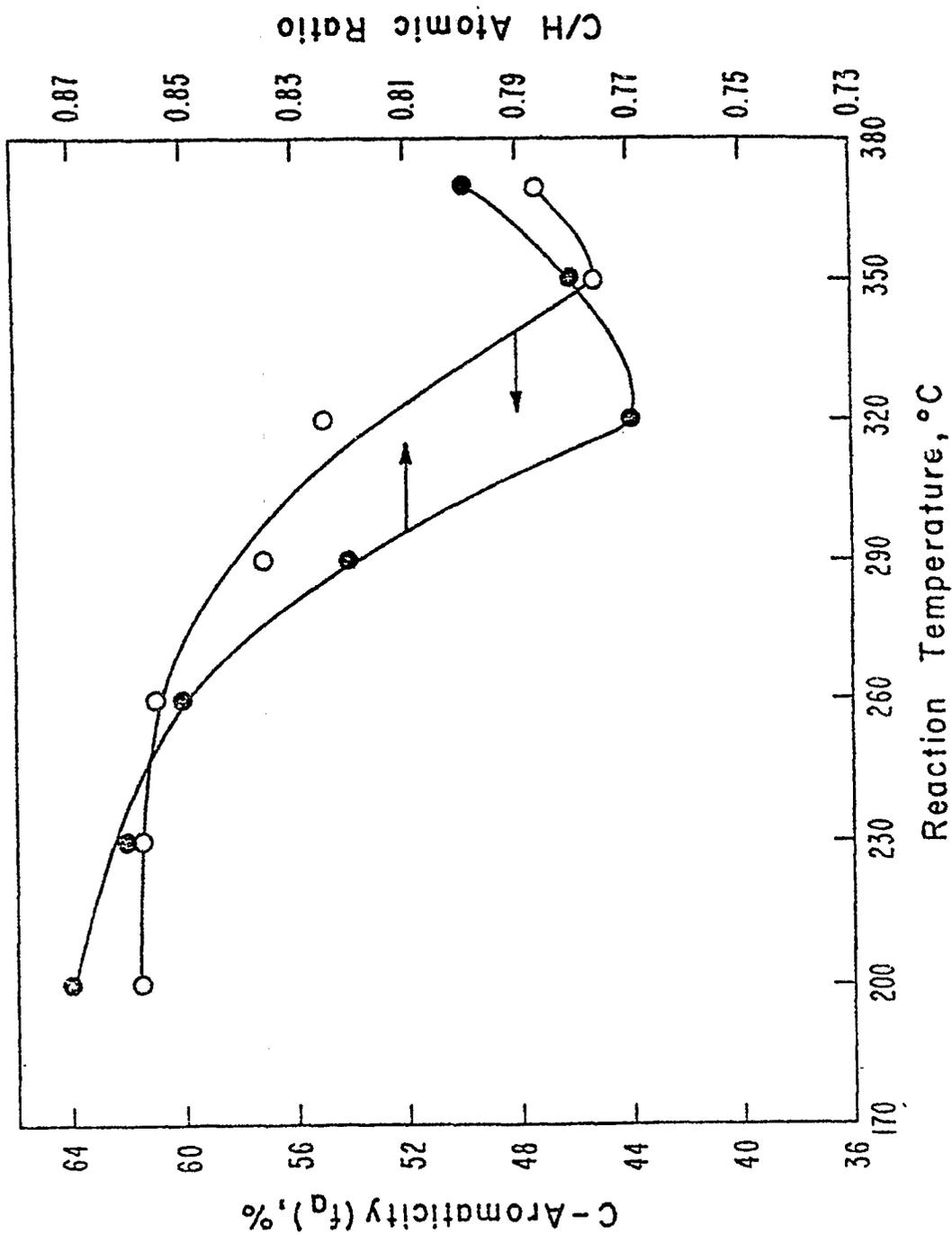


Figure 4. Change in C-Aromaticity (f_d) and C/H Atomic Ratio of Product from Hydrodeoxygenation of SRC-II Distillate (b.p. 230-455°C) as a Function of Reaction Temperature (Hydrogen Pressure: 1750 psig; Reaction Time: 1 hr.; Catalyst: Sulfided Co-Mo/Al₂O₃).

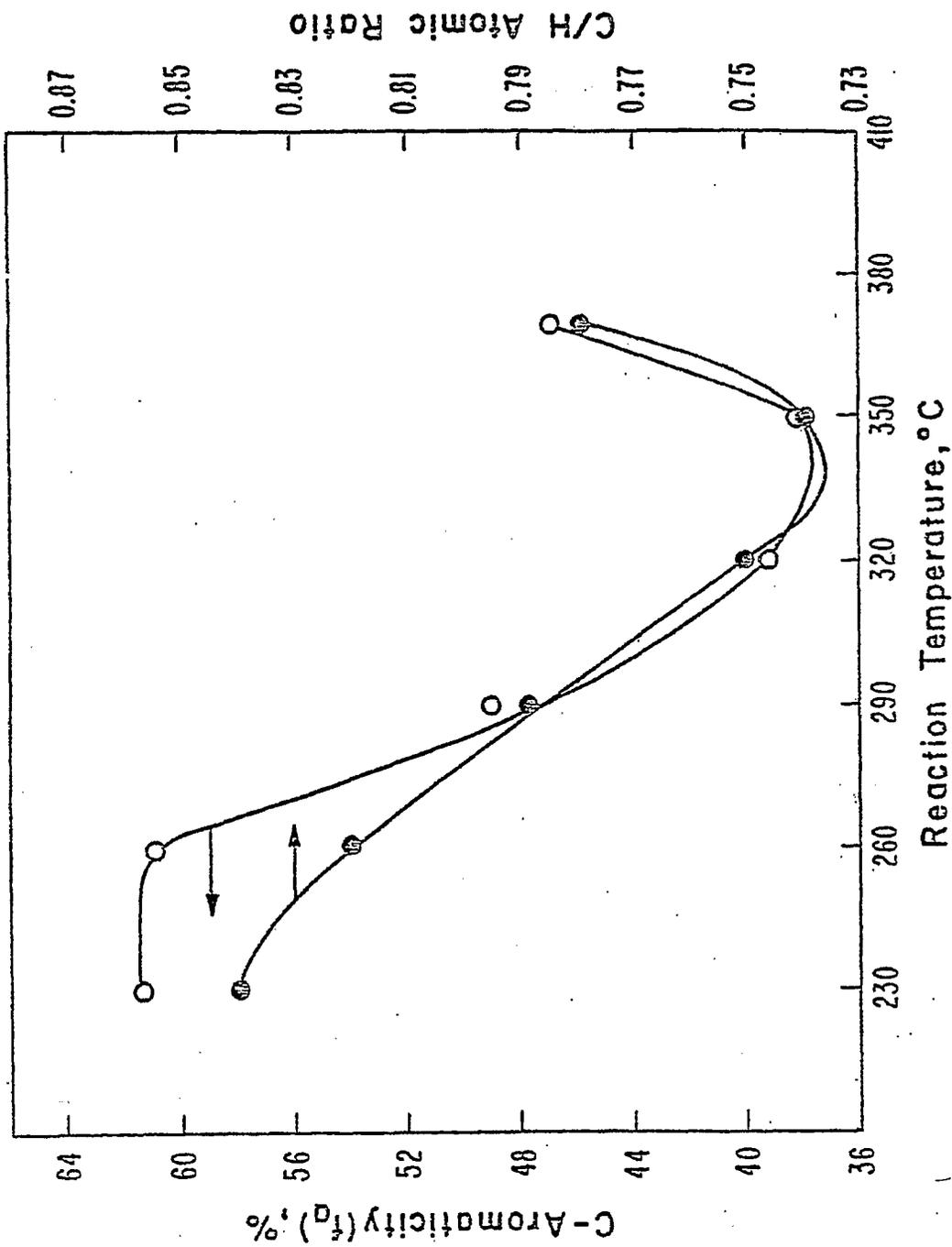


Figure 5. Change in C-Aromaticity (f_a) and C/H Atomic Ratio of Products from Hydrodeoxygenation of SRC-II Distillate (b.p. 230-455°C) as a Function of Reaction Temperature (Hydrogen Pressure: 1750 psig; Reaction Time: 1 hr.; Catalyst: Sulfided Ni-W/Al₂O₃).

INEPT

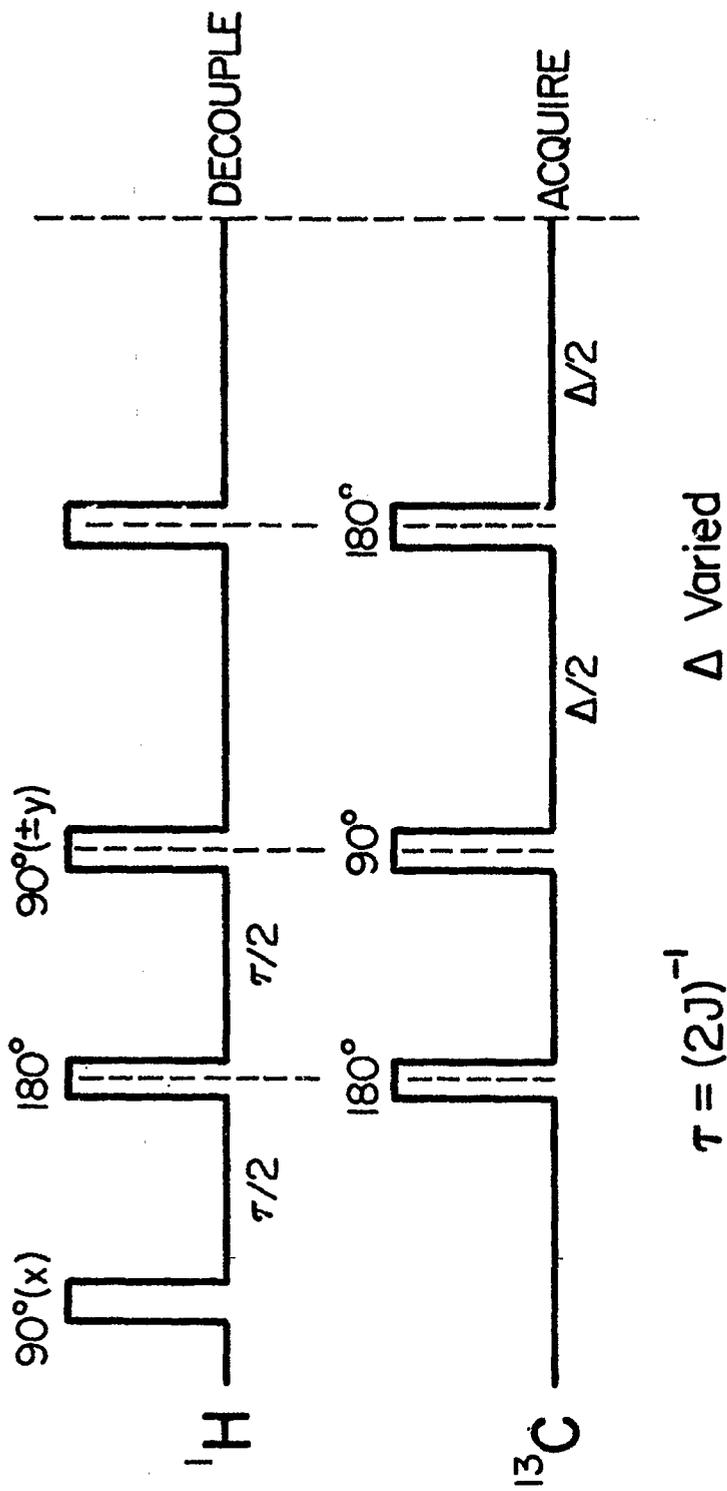


Figure 6. The $^{13}\text{C}/^1\text{H}$ pulse sequence, entitled INEPT, necessary to produce J-refocused ^{13}C NMR spectra. Δ is varied to enhance selectivity, zero, or negate resonance lines corresponding to various multiplicities in the coupled spectrum.

J-Resolved 2-D

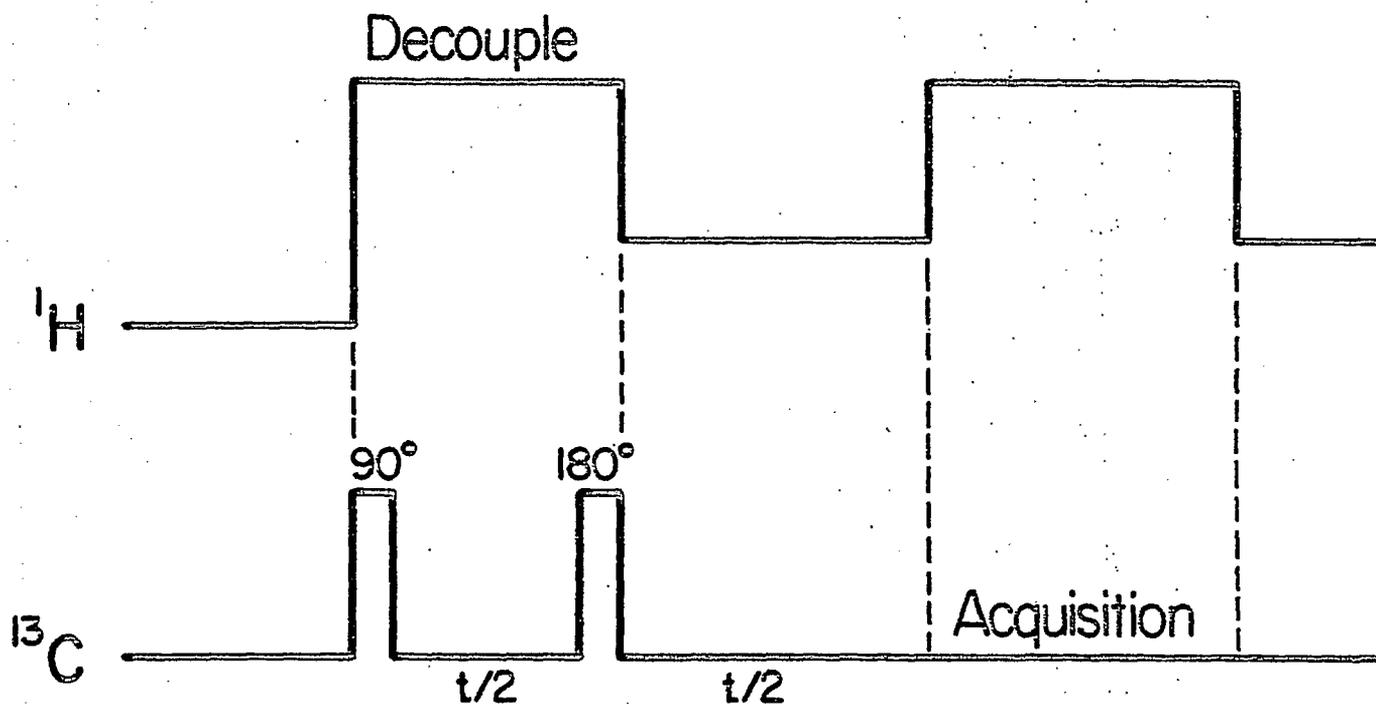


Figure 7. The $^{13}\text{C}/^1\text{H}$ pulse sequence which is used for generation of J-resolved spectra. The experiment is repeated at varying values of t , and the resulting data is Fourier transformed in two dimensions, along both time axes.

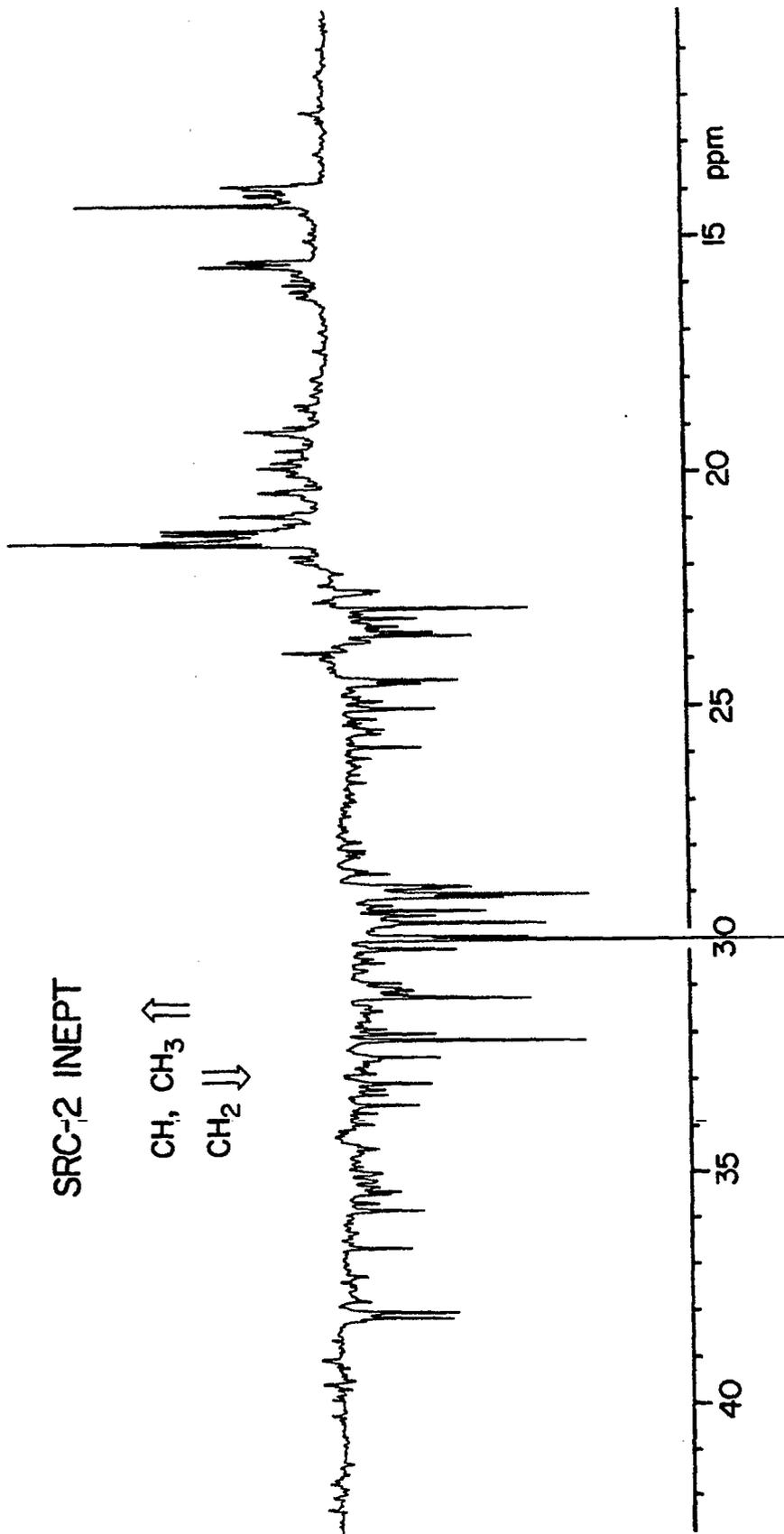


Figure 8. The aliphatic portion of the ¹³C NMR spectrum of an SRC-II derived distillate (b.p. 230-455°C) where an INEPT pulse sequence has been used to negate resonance lines due to methylenes, leaving those due to CH₃ and CH positive.

SRC-2 INEPT

CH only

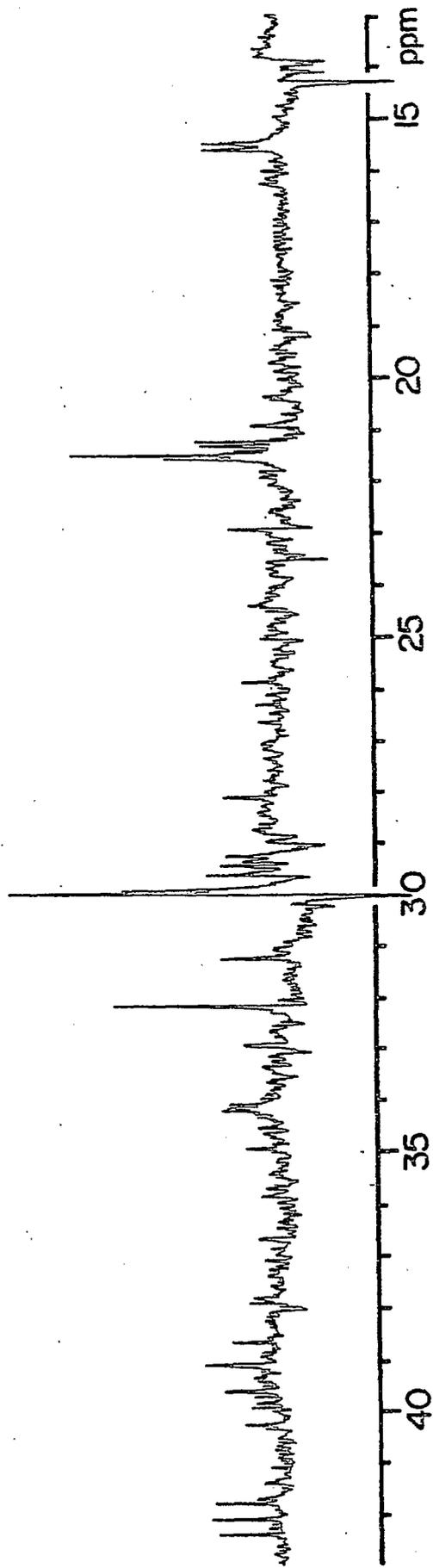


Figure 9. Same as Figure 8, except only CH signals are preserved; those due to other types of carbons (CH₂, CH₃) are nulled or inverted (but not perfectly).

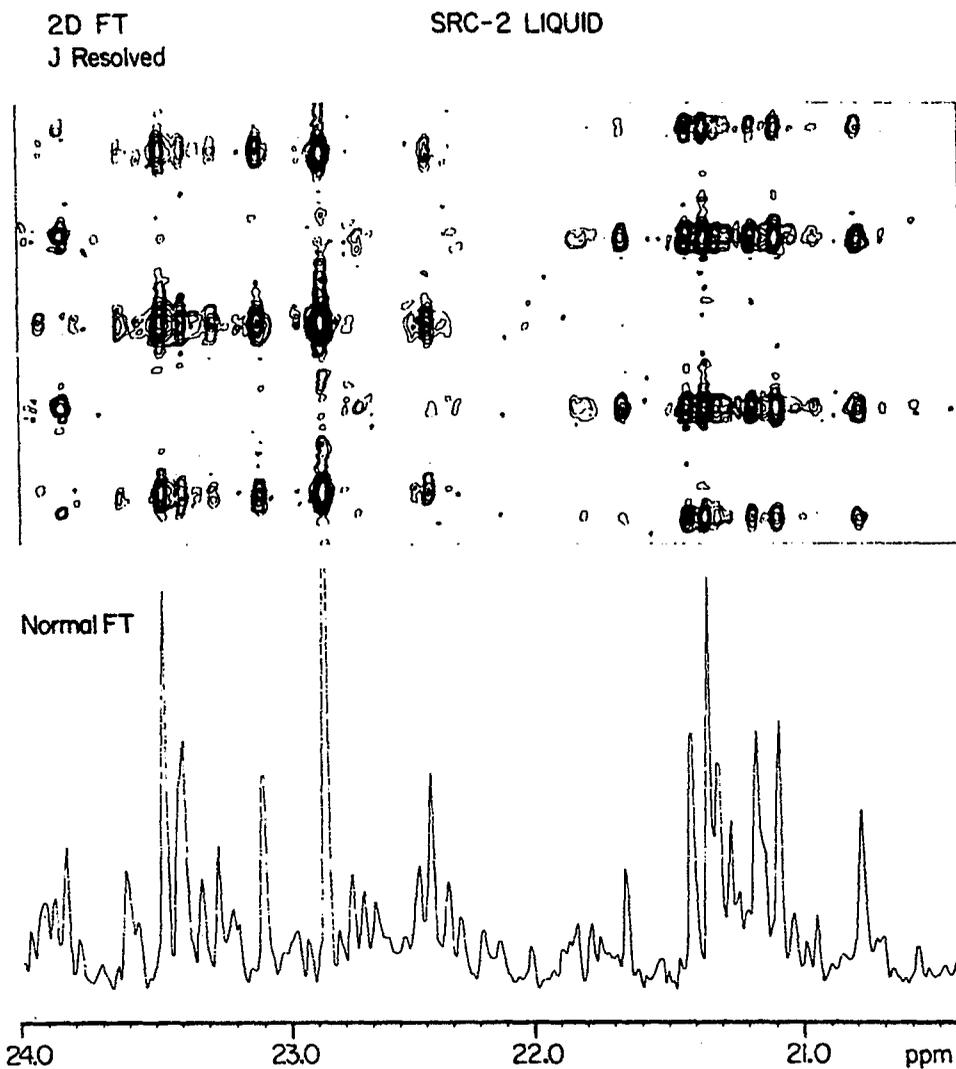


Figure 10. A spectrum of the aliphatic region of the ^{13}C NMR spectrum of an SRC-II coal-derived liquid which has been analyzed using the J-resolved 2-D pulse sequence. The bottom trace is that of the traditional spectrum, while the top trace is a topographical plot, as if viewed from directly overhead, of the multiplets associated with each signal. Note the presence of quartets (fold), triplets and doublets.

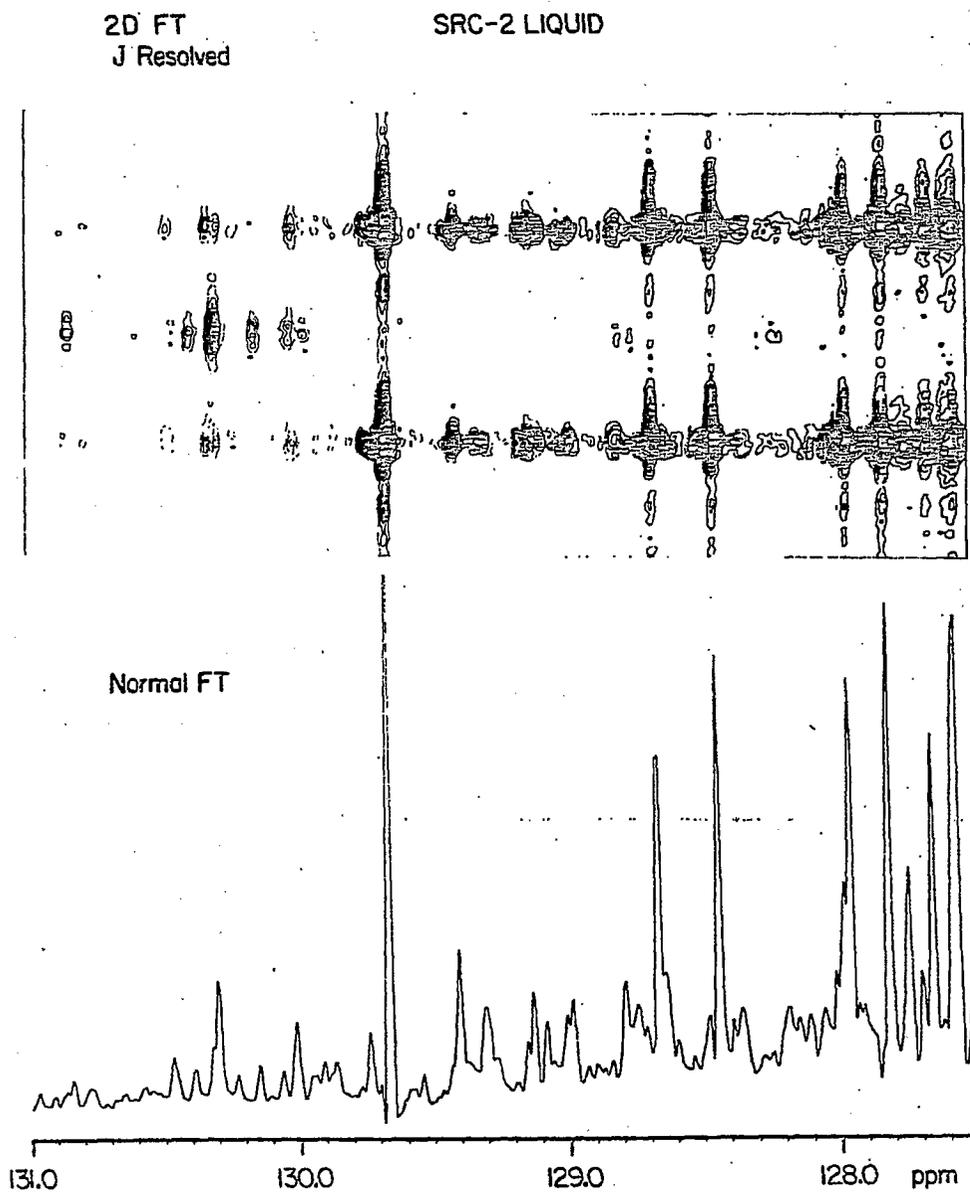


Figure 11. A portion of the aromatic spectral region of the ^{13}C NMR spectrum of an SRC-II coal-derived liquid which has been analyzed using the J-resolved 2-D pulse sequence. Most lines are associated with doublets. Note a triplet and doublet degeneracy at 130.3 ppm.

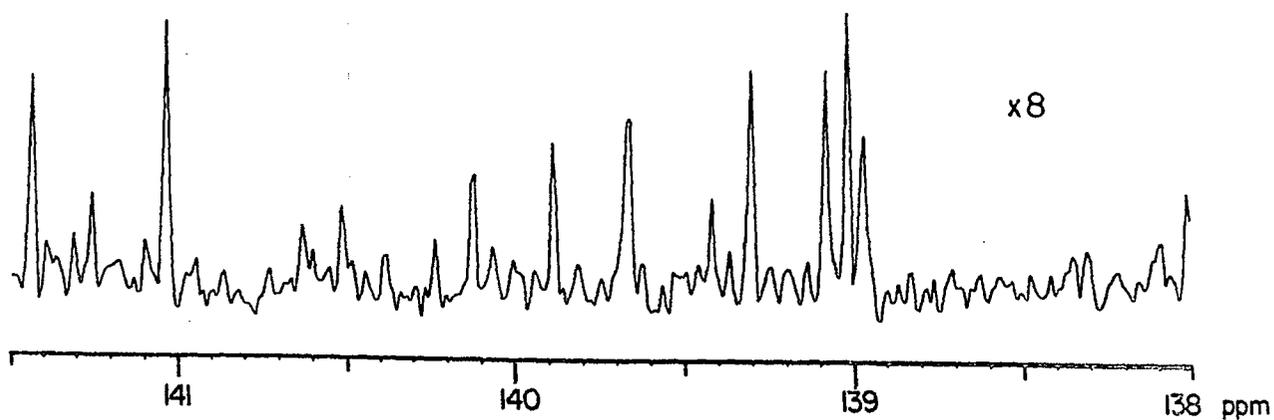
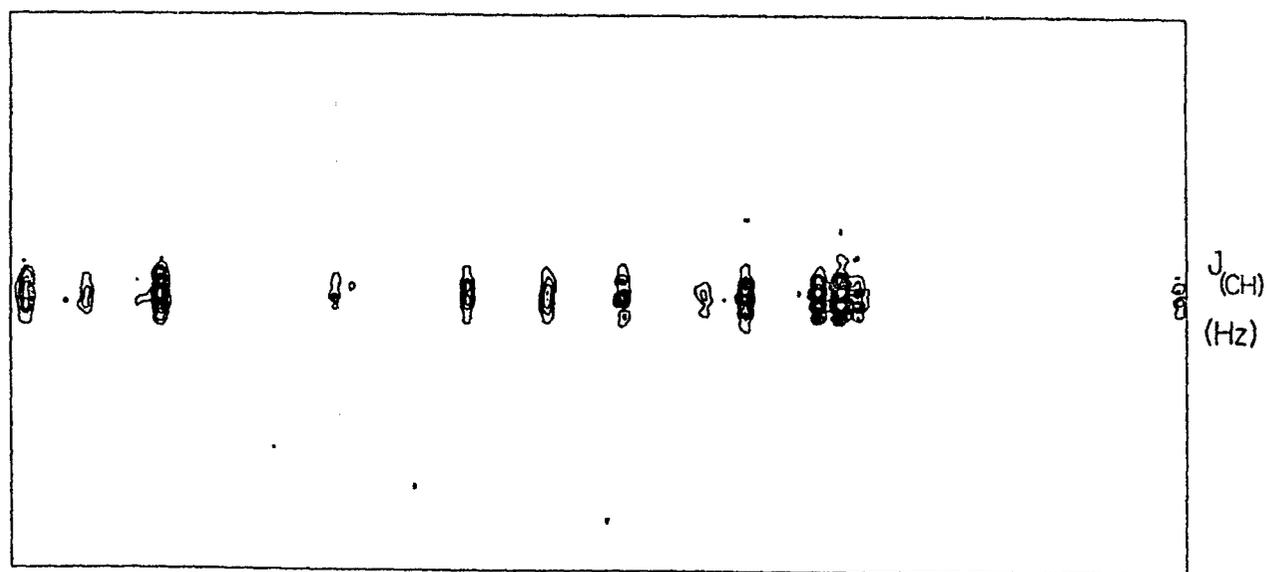


Figure 12. A portion (further downfield) of the aromatic spectral region of the ^{13}C NMR spectrum of an SRC-II coal-derived liquid which has been analyzed using the J-resolved 2-D pulse sequence. The primary multiplicity of all lines is singlet. However, long range multiplet splittings are in evidence.

Table 1. Change in C-aromaticity and C/H atomic ratio of products from hydrodeoxygenation of SRC-II middle-heavy distillate (b.p. 230-455°C) as a function of reaction temperature.^{a-e} (Co-Mo/Al₂O₃)

<u>Reaction Temp., °C</u>	<u>C-Aromaticity^e, f_a</u>	<u>C/H Atomic Ratio</u>
Feed	62.0	0.87
200	61.4	0.87
230	61.4	0.86
260	61.0	0.85
290	57.2	0.82
320	55.1	0.77
350	45.3	0.78
370	47.4	0.80

^aIn each experiment were used 10 g of SRC-II distillate and 2 g of catalyst.

^bCatalyst, Co-Mo/Al₂O₃ (Nalco 471); the catalyst was sulfided prior to use.

^cPressure, 1750 psig.

^dTotal reaction time, 1 hr.

^eDefined as aromatic carbon ÷ (aromatic carbon + aliphatic carbon) x 100.

Table 2. Change in C-aromaticity and C/H atomic ratio of products from hydrodeoxygenation of SRC-II (middle-heavy distillate b.p. 230-455°C) as a function of reaction temperature.^{a-e} (Ni-W/Al₂O₃)

<u>Reaction Temp, °C</u>	<u>C-Aromaticity^e, f_a</u>	<u>C/H Atomic Ratio</u>
Feed	62.0	0.87
230	61.2	0.84
260	61.2	0.82
290	49.0	0.79
320	39.2	0.75
350	38.7	0.74
370	46.8	0.78

^aIn each experiment were used 10 g of SRC-II distillate and 2 g of catalyst.

^bCatalyst, Ni-W/Al₂O₃ (Sphericat 550); the catalyst was sulfided prior to use.

^cPressure, 1750 psig.

^dTotal reaction time, 1 hr.

^eDefined as aromatic carbon ÷ (aromatic carbon + aliphatic carbon) x 100.

Task 3

Catalysis and Mechanism of Coal Liquefaction

Faculty Advisor: D.M. Bodily
Graduate Student: Jason Miller

Introduction

The hydroliquefaction of coal may be characterized by a mechanism which involves the initial rupture of covalent bonds to form reactive intermediates. These intermediates may be stabilized by hydrogen transfer to form lower molecular weight products or they may polymerize to form insoluble char or coke. Metal halides such as zinc chloride have been shown to be active in the bond scission stage of the reaction where as many catalysts are active only in stabilizing the intermediates, often by regenerating a hydrogen donor. The combination of thermal and catalytic reactions occurring simultaneously results in a complicated reaction mechanism. The chemistry of $ZnCl_2$ will be studied with model compounds and coal by such reactions as hydrogen transfers, cleavage of specific bonds and interaction with π electron systems.

A high performance liquid chromatograph, HPLC, will be used to analyze liquid products of the reactions under study. Further characterization of the products will be by nuclear magnetic resonance, NMR, structural analysis and vapor pressure osmometry.

Project Status

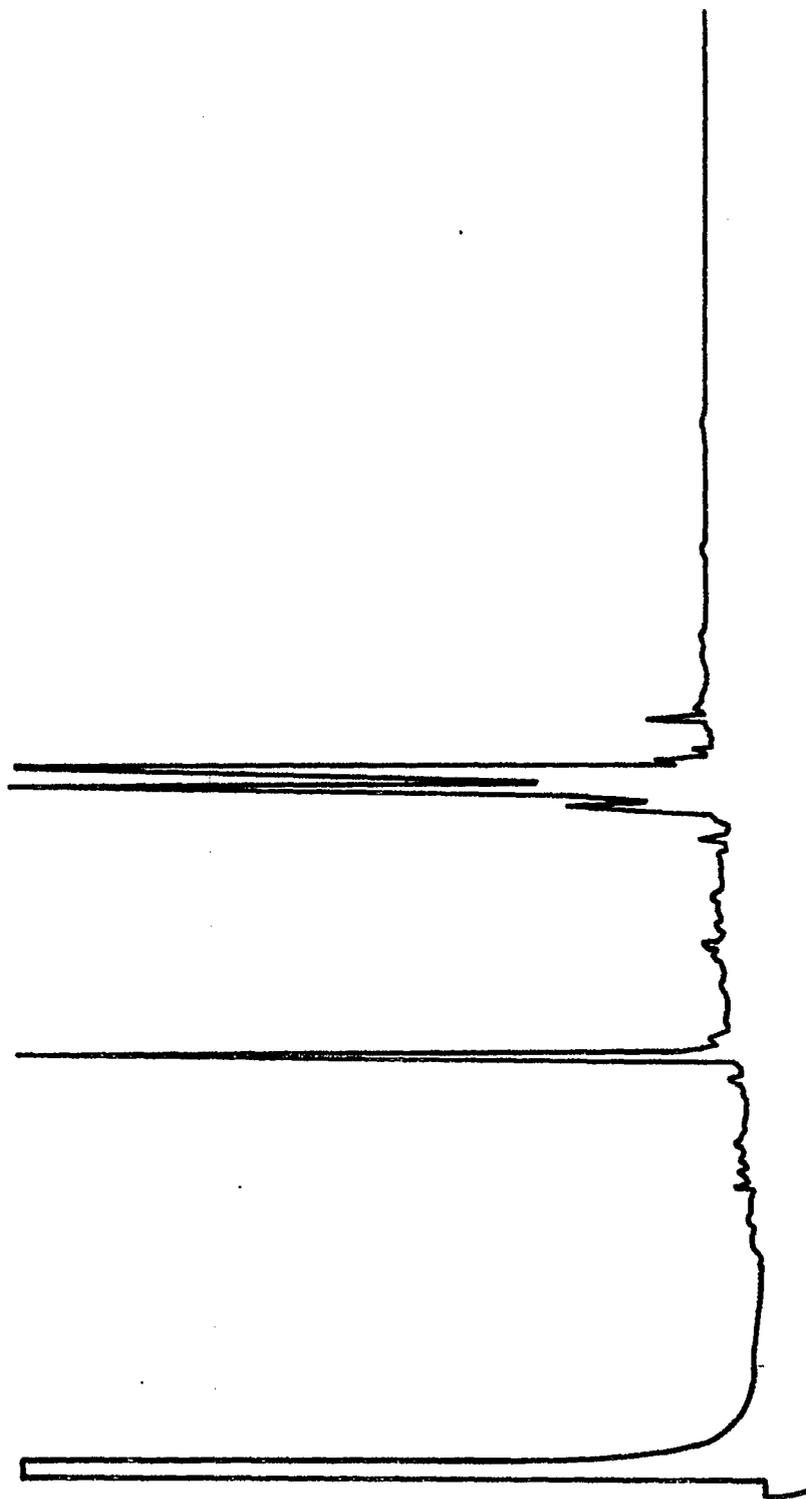
Further analysis was performed on fractions collected in HPLC work previously reported. Figures 1-3 are gas chromatograms of fractions obtained from a single HPLC separation. The gas chromatography, GC, conditions are listed on the figures. The HPLC separation was on a phenyl μ -Bondapack column. Dominant peaks are observed in each spectrum at 8.8 and 14-15 minutes retention time. Figure 4 is a gas chromatogram of the initial fraction from HPLC separation using a NH_2 μ -Bondapack column under conditions previously reported. The GC conditions for Figure 4 are different from those of Figures 1-3, but there is no indication of dominant peaks such as in Figures 1-3. Figure 4 has the appearance of the spectra of a homologous series.

Infrared spectra and other analysis of standard compounds and fraction 1 from the phenyl μ -Bondapack separation indicate that the fraction contains a large amount of alkyl substituted one-ring aromatic compounds. The OH group is also observed to be present in this fraction.

Future Work

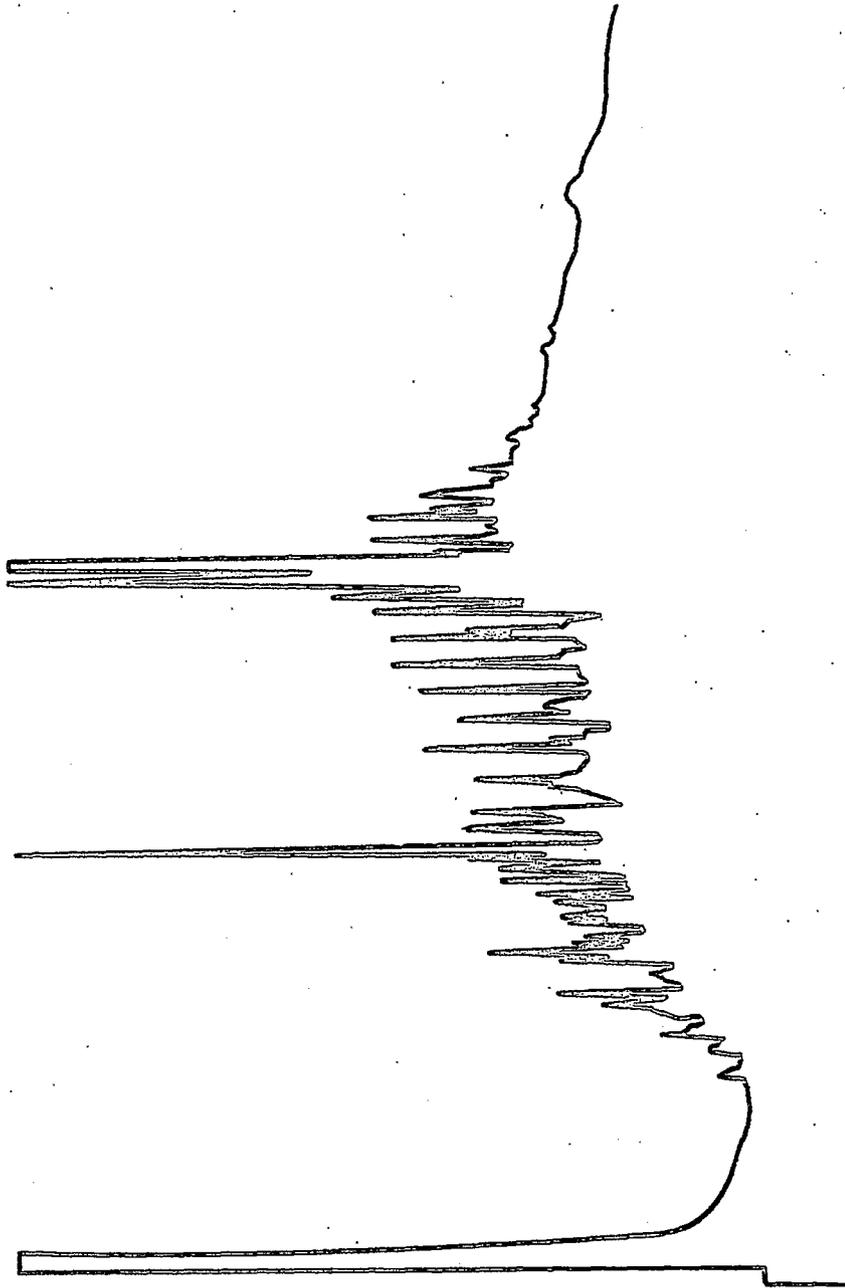
A thesis is being written summarizing the procedures, results and conclusions of research into HPLC coal derived liquids.

Figure 1. Gas Chromatogram of Fraction 1 (FR-1) phenyl- μ Bondapak Separation of Hiawatha Coal-Derived Liquid.



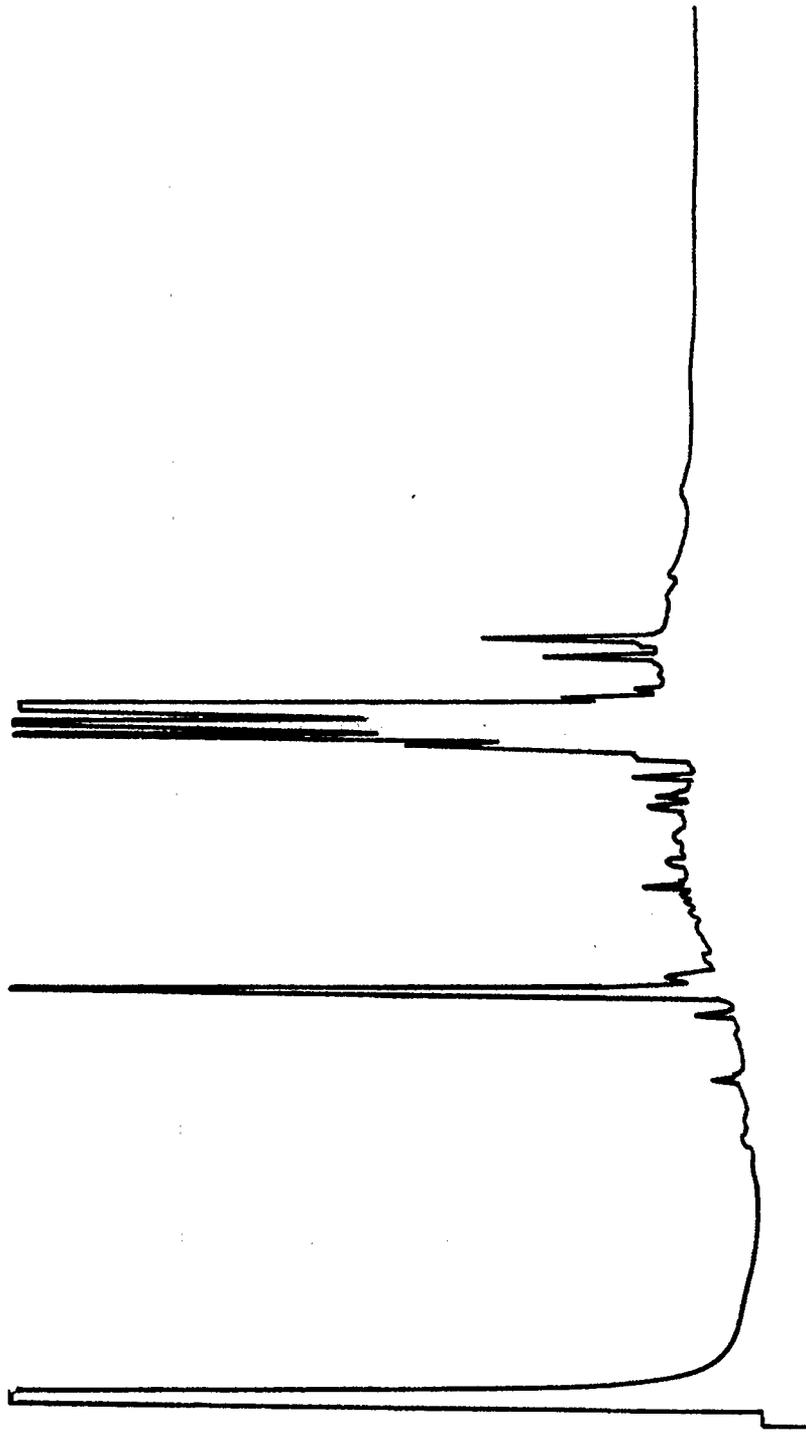
Injection Size: 1.5 μ l
Temp 1: 750C
Time Hold: 0.5 min
Program Rate: 150C/min
Final Temp: 3000C

Figure 2. Gas Chromatogram of Fraction 2 (FR-2) phenyl- μ Bondapak separation of Hiawatha Coal-Derived Liquid.



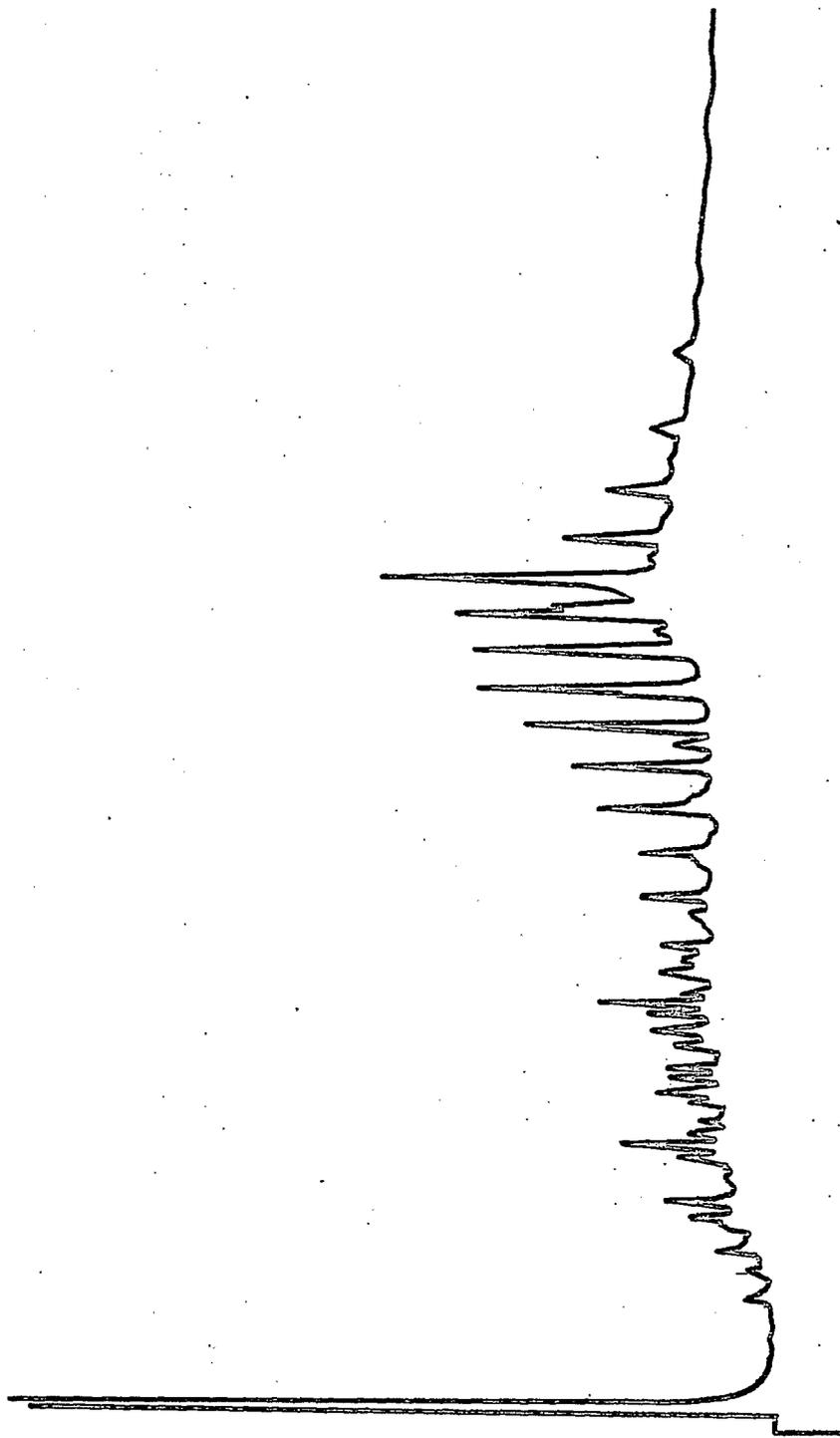
Injection Size: 2.0 μ l
Temp 1: 50°C
Program Rate: 10°C/min
Final Temp: 300°C
Final Time: 20 min

Figure 3. Gas Chromatogram of Fraction 3 (FR-3) phenyl- μ Bondapak Separation of Hiawatha Coal-Derived Liquid.



Injection Vol: 1.75 μ l
Temp 1: 500C
Program Rate: 100C/min
Final Temp: 300C
Final Time: 20 min

Figure 4. Gas Chromatogram of Fraction 1 (FR-1) NH₂- μ Bondapak Separation of Hiawatha Coal-Derived Liquid.



Injection Vol: 1.0 μ l
Initial Temp: 50°C
Temp Prog: 10°/min
Final Temp: 270°C
Final Time: 20 min

Task 3

Catalysis and Mechanism of Coal Liquefaction

Faculty Advisor: D.M. Bodily
Graduate Student: Tsejung Ray

Introduction

Metal halides such as $ZnCl_2$ are well-known to be active catalysts for coal hydrogenation. Zinc chloride has been shown to be a very effective catalyst for coal hydrogenation in the entrained-flow reactor developed at the University of Utah.^{1,2} Bell and co-workers³⁻⁵ have studied the reactions of model compounds with $ZnCl_2$ under conditions similar to those employed in coal hydrogenation. They observed cleavage of C-O and C-C bonds in the model compound and proposed that the active catalytic species is a Bronsted acid formed from $ZnCl_2$.

Shibaoka, Russell and Bodily⁶ proposed a model to explain the liquefaction of coal, based on microscopic examination of the solid products from metal halide catalyzed coal hydrogenation. The model involves a competition between hydrogenation and carbonization reactions. The hydrogenation process starts at the surface of vitrinite particles and progresses toward the center. The vitrinite is converted to a plastic material of lower reflectance, which is the source of oils, asphaltenes and preasphaltenes. Concurrently, carbonization occurs in the center of the particles, resulting in vesiculation and a higher reflectance material. The partially carbonized material can be hydrogenated at later stages, but at a lower rate than the original coal.

Thermal and/or catalytic bond rupture occurs during the liquefaction process. The initial products of the bond cleavage reactions may be stabilized by hydrogen addition, resulting in cleavage of bridges between aromatic ring systems and in dealkylation of aromatic rings. If the initial products of the reaction are not stabilized, they may polymerize to form semicoke-like material. This primary semicoke may be isotropic or exhibit a fine-grained anisotropic mosaic texture, depending on the rank of the coal. The plastic material formed by stabilization of the initial products may be further hydrogenated or, under hydrogen deficient conditions, may form secondary semicoke. The secondary semicoke is of medium to coarse-grained anisotropic mosaic texture. Bodily and Shibaoka⁷ used this model to explain the nature of the residues from hydrogenation in the short-residence, entrained-flow hydrogenation reactor. The role of the $ZnCl_2$ catalyst is examined in this study.

Project Status

Problems with the heating elements of the fluidized sand bath prevented testing of the hydrogenation reactor. Clear Creek, Utah coal (hvb, 45.4% VM) will be used in these studies. This coal has shown good reactivity at short reaction times with $ZnCl_2$ catalyst.⁸ The $ZnCl_2$ catalyst will be impregnated on the coal surface from aqueous solution. Experimental work this quarter has involved grinding, preparing and characterizing the coal samples,

developing techniques for catalyst impregnation and preparation of grain mounts.

Future Work

The short residence time reactor will be tested and heat-up rates determined. Experiments to determine the softening temperature of the coal and catalyst-impregnated coal will be initiated.

References

1. R.E. Wood and W.H. Wiser, Ind. Eng. Chem., Proc. Design Devel., 15, 144 (1976).
2. J.M. Lytle, R.E. Wood and W.H. Wiser, Fuel, 59, 471 (1980).
3. D.P. Mobley and A.T. Bell, Fuel, 58, 661 (1979).
4. N.D. Taylor and A.T. Bell, Fuel, 59, 499 (1980).
5. D.P. Mobley and A.T. Bell, Fuel, 59, 507 (1980).
6. M. Shibaoka, N.J. Russell and D.M. Bodily, Fuel, submitted.
7. D.M. Bodily and M. Shibaoka, Fuel, submitted.
8. R. Yoshida and D.M. Bodily, Preprints, Fuel Chem. Div., Am. Chem. Soc., 24 (2), 371 (1979).

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 thermal rupture of bonds in the bridges joining configurations in the coal, yielding free radicals. The different approaches of liquefaction, except for Fischer-Tropsch variations, represent ways of stabilizing the free radicals to produce molecules. The stabilization involving abstraction by the free radicals of hydrogen from the hydro-aromatic 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

The pyrolysis apparatus¹ has been reconfigured, Figure 1, so as to hopefully eliminate the injection problems. The 4-port Valco switching valve is used to change the helium carrier gas source during an injection. Just prior to tube breakage, the valve is switched so that the helium flowing through the pyrolyzers is utilized as the carrier gas for the gas chromatograph. After injection is complete (approximately 30 sec), the helium flow is switched back to the gas chromatographic helium source. Both carrier gas streams are purified by similar means to maintain consistency. As shown in Figure 1, thermocouples are located in strategic positions so that the injection pulse can be maintained at high enough temperatures to prevent product condensation. The remote switch for starting the integrator/recorder should prove very helpful in maintaining consistency in analysis from experiment to experiment.

Work has been continued in an attempt to improve analytical procedures and analyses. A 1/4" 10% OV-17 on 100/120 mesh Chromasorb WHP column has been the best column for the separation of reaction products from 9-benzyl-1,2,3,4-tetrahydrocarbazole. Problems have been encountered with the upper detection limits of the gas chromatographic detectors with respect to the desired pyrolysis sample size. This has been dealt with by the use of a column outlet splitter, utilizing a split ratio of approximately 10:1 to reduce the sample size proceeding to the detectors.

Problems have also been encountered with what appears to be limitations of the oven in the gas chromatograph. It has been found that with the 1/4" columns it appears that the oven is incapable of heating at a rate of 40°C/min because of the bulk of material (12' long 1/4" diameter column) to be heated.

Future Work

The problems encountered with the gas chromatograph's oven heating rates will be studied further to determine if a problem exists or if it is a limitation of the instrument.

Upon solving or at least understanding this problem, the outlet splitter will be calibrated with standard mixtures representative of possible pyrolysis products mixtures.

Test runs will be made with carbazole and toluene to determine if the problems with material balances have been solved by system reconfiguration. These test runs will also be used to refine experimental technique before beginning actual kinetic runs.

Reference

1. W.H. Wiser, J.K. Shigley, DOE Contract No. DE-AC22-79ET14700, Quarterly Progress Report, Salt Lake City, Utah, April - June 1981.

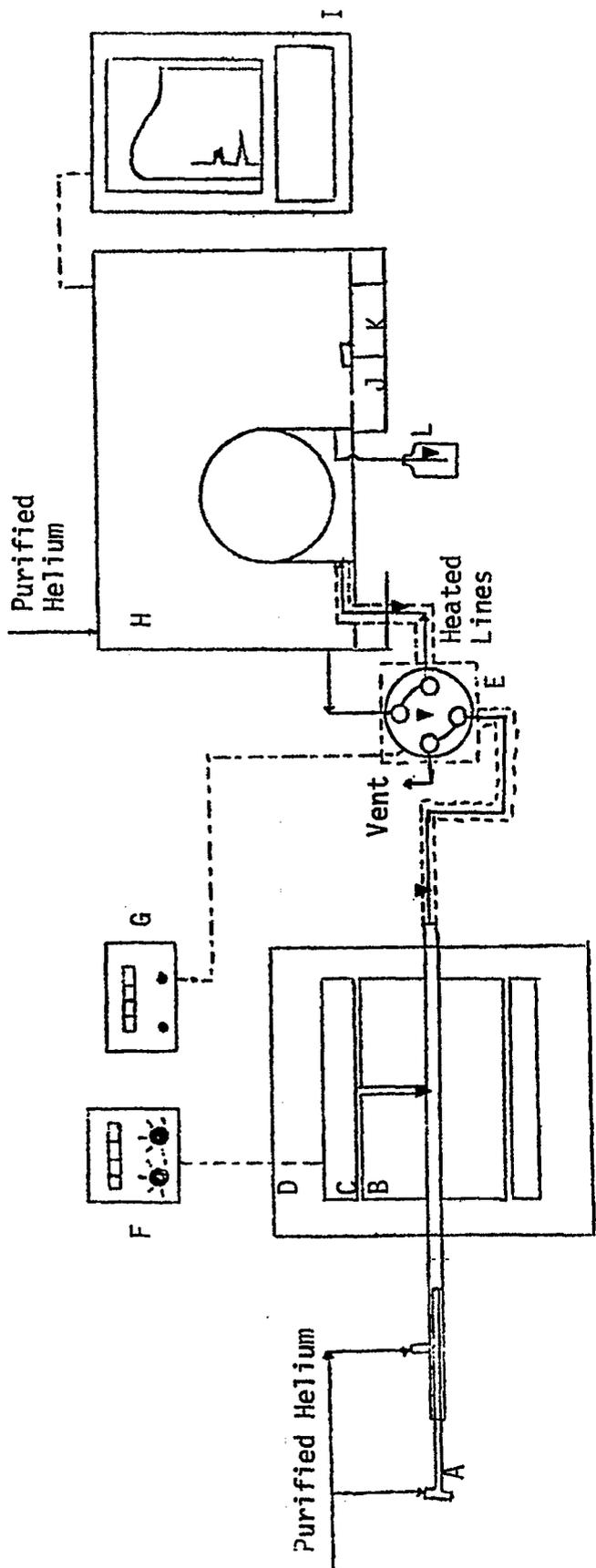


Figure 1. Pyrolysis Assembly

- A. Plunger
 - B. Pyrolyzer Assembly
 - C. Lindberg Resistance Heaters
 - D. Insulation
 - E. Valco 4-Port Switching Valve
 - F. Heater Temperature Controller
 - G. Valve Heater Temperature Controller
 - H. Gas Chromatographic Analyzer
 - I. Gas Chromatograph Printer/Plotter-Integrator
 - J. Hot Wire Detector
 - K. Flame Ionization Detector
 - L. Cold Trap
- ▼ Thermocouple Locations

Catalytic Hydrogenation of CD Liquids and Related
Polycyclic Aromatic Hydrocarbons

Faculty Advisor: J. Shabtai
Research Associate: C. Russell

Introduction

The main objective of this research project is to develop a versatile process for controllable hydrotreating of highly aromatic coal liquids, viz., a process permitting production of naphthenic-aromatic feedstocks containing variable relative concentrations of hydroaromatic vs. aromatic ring structures. Such feedstocks, including the extreme case of a fully hydrogenated coal liquid, are suitable starting materials for catalytic cracking, as applied for preferential production of light liquid fuels. The overall objective of this project and of a parallel catalytic cracking study is, therefore, to develop and optimize a hydrotreating-catalytic cracking process sequence for conversion of coal liquids into conventional fuels.

The present project includes also a study of metal sulfide-catalyzed hydrogenation of model polycyclic arenes present in coal liquids, e.g., phenanthrene, pyrene, anthracene and triphenylene, as a function of catalyst type and experimental variables. This part of the study provides basic information on the rate, mechanism and stereochemistry of hydrogenation of structurally distinct aromatic systems in the presence of sulfided catalysts.

Project Status

This report provides results obtained in a kinetic study of the hydrogenation of anthracene (1) in the presence of a sulfided Ni-W/Al₂O₃ catalyst (precursor: Nalco Sphericat 550). Hydrogenation reactions were carried out in an autoclave system described elsewhere,¹ and modified to allow for collection of samples during reaction. Products were identified by a combination of gas chromatography and mass spectrometry, and by comparison with pure reference compounds.

Kinetic rate constants were obtained for a hydrogen pressure of 2500 psig at the two low reaction temperatures of 220° and 250°C. Figure 1 summarizes the kinetic rate constants obtained and the proposed reaction network for hydrogenation of anthracene (1).

As seen, there are two alternative initial products formed in the stepwise hydrogenation of 1, i.e., 1,2,3,4-tetrahydroanthracene (2) and 9,10-dihydroanthracene (3). Subsequent hydrogenation of 2 yields two isomeric octahydroanthracene products, i.e., 1,2,3,4,5,6,7,8-octahydroanthracene (4) and 1,2,3,4,9,10,11,12-octahydroanthracene (5). On the other hand, 9,10-dihydroanthracene (3) undergoes a hydrogenation-rearrangement reaction to form only 1,2,3,4-tetrahydroanthracene (2) as

a product. Kinetic analysis showed that there was no measurable reaction of 3 to form the octahydro intermediate 5. Perhydroanthracene (6) is formed as final product by hydrogenation of the octahydro intermediates 4 and 5.

The rate constants indicated in Figure 1 show that in the low temperature range of 220-250°C compound 3 is the preferred initial product, i.e., $k_1 > k_2$. However, as above indicated, compound 3 slowly reacts to form only compound 2 and, therefore, any subsequent hydrogenation products, having two or three hydroaromatic rings are formed via intermediate 2. At the low temperatures used (220-250°C) k_7 and k_8 are extremely low. Therefore, the relative rates of conversion of intermediates 4 and 5 into the final product 6 will be determined with more certainty at higher temperatures. Preliminary studies in the range of 310-345°C indicate that k_7 is consistently higher than k_8 , apparently as a result of steric factors.²

Future Work

The kinetic study of anthracene hydrogenation will be extended to the 250-380°C temperature range, and completed. Kinetic studies of the hydrogenation of chrysene and naphthacene will be initiated. Kinetic studies using SRC-II distillate fractions as hydrogenation feeds will also be carried out.

References

1. L. Veluswamy, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1977.
2. J. Shabtai and C. Russell, to be published.

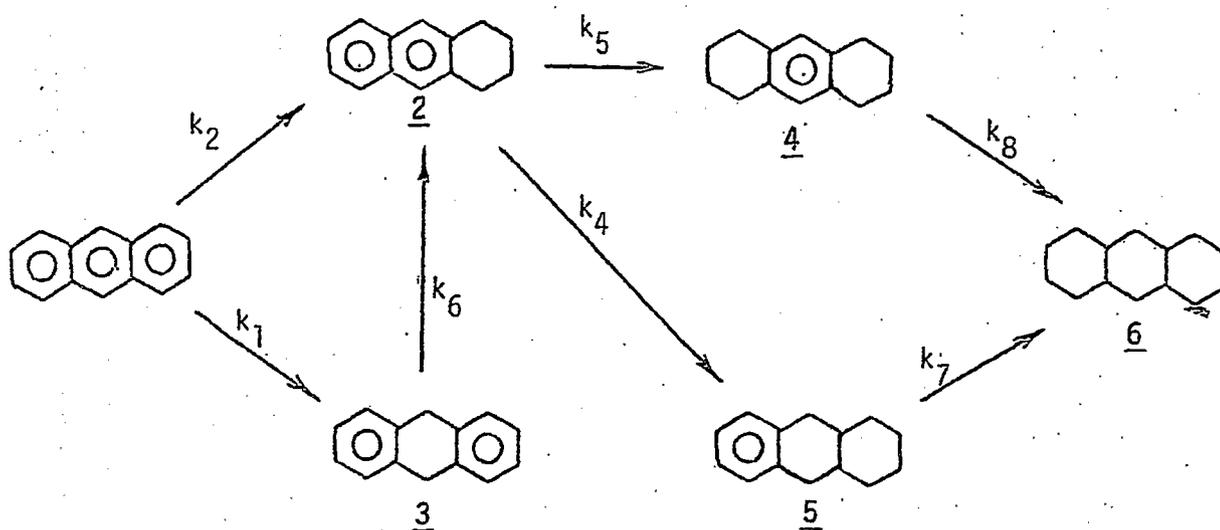


Figure 1. Indicated Reaction Network of Anthracene Hydrogenation over a Sulfided Ni-W/Al₂O₃ Catalyst.

T, °C	Rate Constants, ^a min ⁻¹						
	<u>k₁</u>	<u>k₂</u>	<u>k₄</u>	<u>k₅</u>	<u>k₆</u>	<u>k₇</u>	<u>k₈</u>
220	0.015	0.003	--	0.0013	0.00007	--	--
250	0.027	0.010	0.0103	0.0116	0.00085	<0.0001	0.0001

^aHydrogen pressure, 2500 psig; catalyst, sulfided Ni-W/Al₂O₃ (precursor: Nalco Sphericat 550).

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 variables. A part of the study is concerned with determination of the rate, mechanism and stereochemistry of HDN of structurally distinct N-containing aromatic systems in the presence of sulfided catalysts.

Project Status

This report provides partial results obtained in an ongoing kinetic study of the hydrodenitrogenation of 5,6-benzoquinoline (1) in the presence of sulfided Ni-W, Ni-Mo and Co-Mo catalysts (precursors: Ni-W/Al₂O₃, Nalco Sphericat 550; Ni-Mo/Al₂O₃, Nalco NM 504; and Co-Mo/Al₂O₃). Kinetic experiments were performed with an autoclave system described elsewhere, and modified to allow for withdrawing of samples during the reaction. Products were identified by a combination of high resolution gas chromatography-mass spectrometry and by comparison with reference compounds. Quantitative analyses were performed by gas chromatography. Results obtained at 300°C (hydrogen pressure, 2500 psig) with the above three catalysts are summarized on Figure 1 and the accompanying table of kinetic rate constants. As seen, with all catalysts hydrogenation of the pyridine ring in 1 as indicated by k_1 is a very fast reaction. This is consistent with a steric hindrance-free edgewise adsorption of 1 on the catalyst surface by means of the aromatic nitrogen. The 5,6-benzo group does not interfere with such adsorption and consequent polarization of the pyridine moiety in 1. Such polarization is probably one of the major factors determining the value of k_1 . (It should be noted that in the case of 7,8-benzoquinoline, the 7,8-benzo group prevents edgewise adsorption of the molecule via the aromatic nitrogen with consequent sharp decrease in the rate of the initial hydrogenation step). It is further seen in Figure 1 that $k_3 > k_2$ with all catalysts, viz., the 1,2,3,4-tetrahydro-5,6-benzoquinoline (2) formed in the initial hydrogenation step undergoes fast further hydrogenation to yield the two isomeric octahydrobenzoquinolines (3), and only to a negligible extent hydrodenitrogenation to 1-propylnaphthalene (5). It is also found that $k_6 > k_5$ with the sulfided Ni-W catalyst, while with the sulfided Co-Mo catalyst $k_5 > k_6$. This indicates the higher C-N hydrogenolysis activity vs.

lower ring hydrogenation activity of the Co-Mo catalyst as compared with the Ni-W catalyst at this stage of the process. In general, C-N hydrogenolysis becomes important only after at least two or all of the three aromatic rings in 1 have been hydrogenated to yield compounds 3 and 4 as intermediates. Sulfided catalysts having augmented C-N hydrogenolysis activity² are being presently prepared in the framework of Task 10, and their activity for HDN of polycyclic N-containing aromatics will be investigated.

Future Work

The kinetic study of the hydrogenation of 5,6-benzoquinoline with the above indicated catalysts will be extended to higher temperatures.

References

1. L. Veluswamy, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1977.
2. G. Muralidhar, F.E. Massoth and J. Shabtai, Proc. 7th North American Meeting of the Catalysis Society, Boston, Massachusetts, 1981.

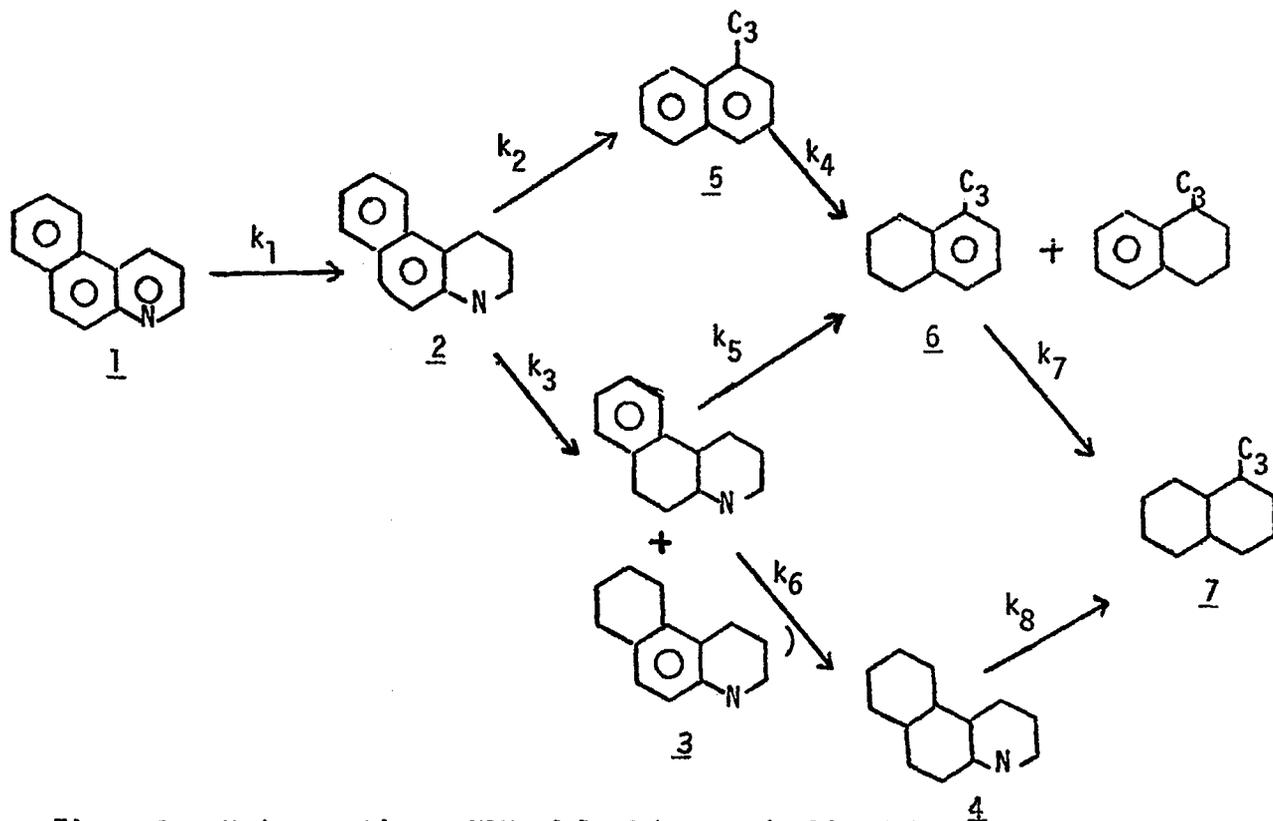


Figure 1. Hydrogenation - HDN of 5, 6-benzoquinoline (1)
Rate constants, hr⁻¹ (hydrogen pressure, 2500 psig; temperature, 300°C)^a

Catalysts	Temperature	k_1	k_2	k_3	k_4	k_5	k_6	k_7^b	k_8^b
Sulfided Ni-W/Al ₂ O ₃	300°C	3.390	<0.0005	0.762	--	0.015	0.087	<0.002	<0.002
Sulfided Co-Mo/Al ₂ O ₃	300°C	3.672	0.0007	0.346	--	0.041	0.021	<0.002	<0.002
Sulfided Ni-Mo/Al ₂ O ₃	300°C	5.130	0.0046	0.672	--	0.036	0.041	<0.002	<0.002

^aThe reactions were carried out on the presence of tetradecane as a solvent; solvent/1 wt ratio = 20:1.

^bThe values of k_7 and k_8 were too low for accurate determination at this temperature. Determinations at higher temperatures are presently underway.

Task 7

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

Catalytic Hydrodeoxygenation of Coal-Derived Liquids and Related Oxygen-Containing 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. The study provides information not only on the mechanism of HDO as related to the subject of catalytic upgrading of coal 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 aralkyl ethers, i.e., dibenzyl ether (7), diphenyl ether (6) and anisole (25), are presently being investigated. Results obtained with dibenzyl ether (7) as feed are presented in this report. This study involved determination of the change in product composition as function of experimental conditions, e.g., reaction temperature, hydrogen pressure and catalyst type. Experiments were performed in a shaken autoclave reactor,¹ and products obtained were identified and quantitatively analyzed by a combination of gas chromatography and mass spectrometry.

The reactions of 7 in the presence of sulfided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts were first investigated as a function of reaction temperature in the range of 110 - 260°C, keeping other experimental conditions identical in each run (hydrogen pressure, 1000 psig; total reaction time, 0.5 hr; amount of reactant 7, 5.0 g; and amount of catalyst, 1.0 g). Results obtained with the sulfided Co-Mo/ γ -Al₂O₃ and Ni-Mo/ γ -Al₂O₃ catalysts are summarized in Figures 1 and 2, respectively. As seen in Figure 1, the conversion of 7 increases rapidly between 140 - 200°C (from 4.7% at 140°C to 81.7% at 200°C) and then moderately from 200°C to 260°C. The main products formed at all temperatures were toluene (4) and benzyl alcohol (17), which are the anticipated primary C-O hydrogenolysis products from 7. As seen, benzyl alcohol (17) gradually decreases in concentration with increase in temperature, while the concentration of toluene (4) correspondingly increases. Small amounts of other products, i.e., cyclohexane (2), benzene (3), 1,2-diphenylethane (20) and 1,1-diphenylethane (21), are also formed.

Different compositional trends are observed with the sulfided Ni-Mo/ γ -Al₂O₃ catalyst (Figure 2). As seen, with this catalyst, the main product from 7 at

lower temperature (i.e., 110°C) is 1,2-diphenylethane (21). With increase in temperature, however, the concentration of the latter decreases sharply (from 70% at 110°C to ca. 7% at 170°C), while the concentration of toluene (4) rapidly increases (i.e., from ca. 20% at 110°C to ca. 90% at 260°C). Small amounts of other products, i.e., benzyl alcohol (17), phenyl p-tolylmethane (20), methylcyclopentane (1), diphenylmethane (19), and unidentified components (M.W. 272) are also formed.

The reactions of 7 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 - 1500 psig (total reaction time, 0.5 hr; amount of reactant, 5 g; amount of catalyst, 1.0 g; reaction temperature with the Co-Mo catalyst, 155°C and with the Ni-W catalyst, 170°C). Results obtained are summarized in Figures 3 and 4, respectively.

As seen in Figure 3, with the Co-Mo catalyst the concentrations of toluene (4) only slowly increases, while that of benzyl alcohol (17) slowly decreases with increase in pressure from 250 to 1500 psig. Small amounts of 1,1-diphenylethane (21) and 1,2-diphenylethane (20) are also formed.

With the Ni-Mo catalyst (Figure 4) there is a much more pronounced pressure effect as the concentration of toluene (4) increases from ca. 60% at 250 psig to 82% at 1500 psig, while the concentration of 1,2-diphenylethane (21) decreases from 30% at 250 psig to 5% at 1500 psig.

The change in product compositions with the two catalysts as a function of temperature and hydrogen pressure can be rationalized in terms of the mechanism proposed in Figure 5. With sulfided Co-Mo as catalyst the HDO reaction of 7 is apparently a two-step process involving equimolar formation of toluene and benzyl alcohol, followed by hydrogenolysis of the latter to yield toluene as the only final product. On the other hand, with sulfided Ni-Mo the first reaction step involves direct oxygen removal from 7 to form 1,2-diphenylethane, followed by hydrogenolysis of the latter to yield toluene.

Future Work

A semi-batch autoclave for kinetic studies was constructed and put in operation. Kinetic HDO studies of coal-derived liquids and representative ethers, e.g., dibenzyl ether (1), diphenyl ether (6) and anisole (25) will be carried out.

Reference

1. G. Haider, Ph.D. Thesis, University of Utah, Salt Lake City, Utah 1981.

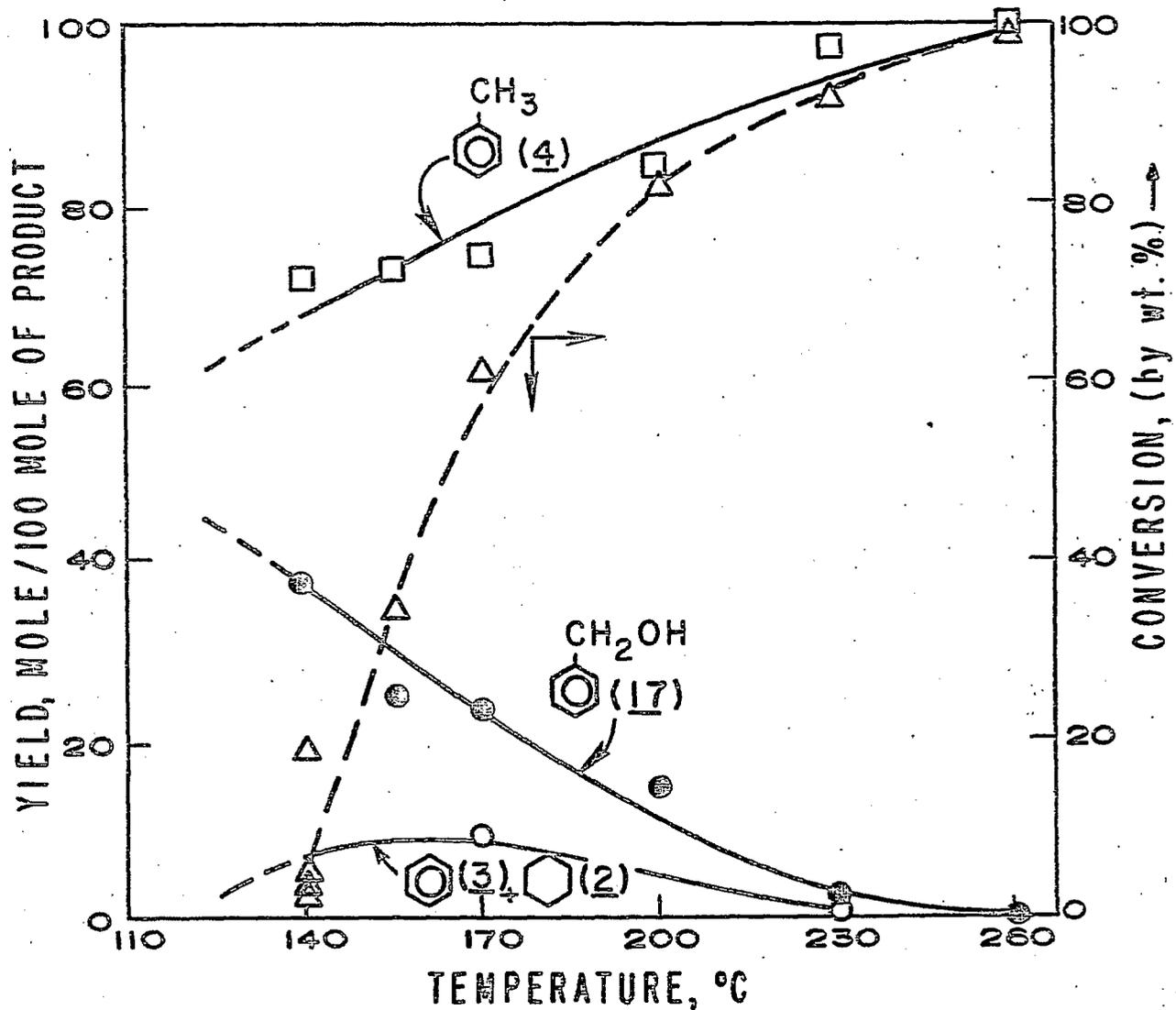


Figure 1. Change in product composition from hydrodeoxygenation of dibenzyl ether (7) as a function of reaction temperature [catalyst, sulfided Co-Mo/ γ -Al₂O₃ (Nalco #471); hydrogen pressure, 1000 psig; total reaction time, 0.5 hr].

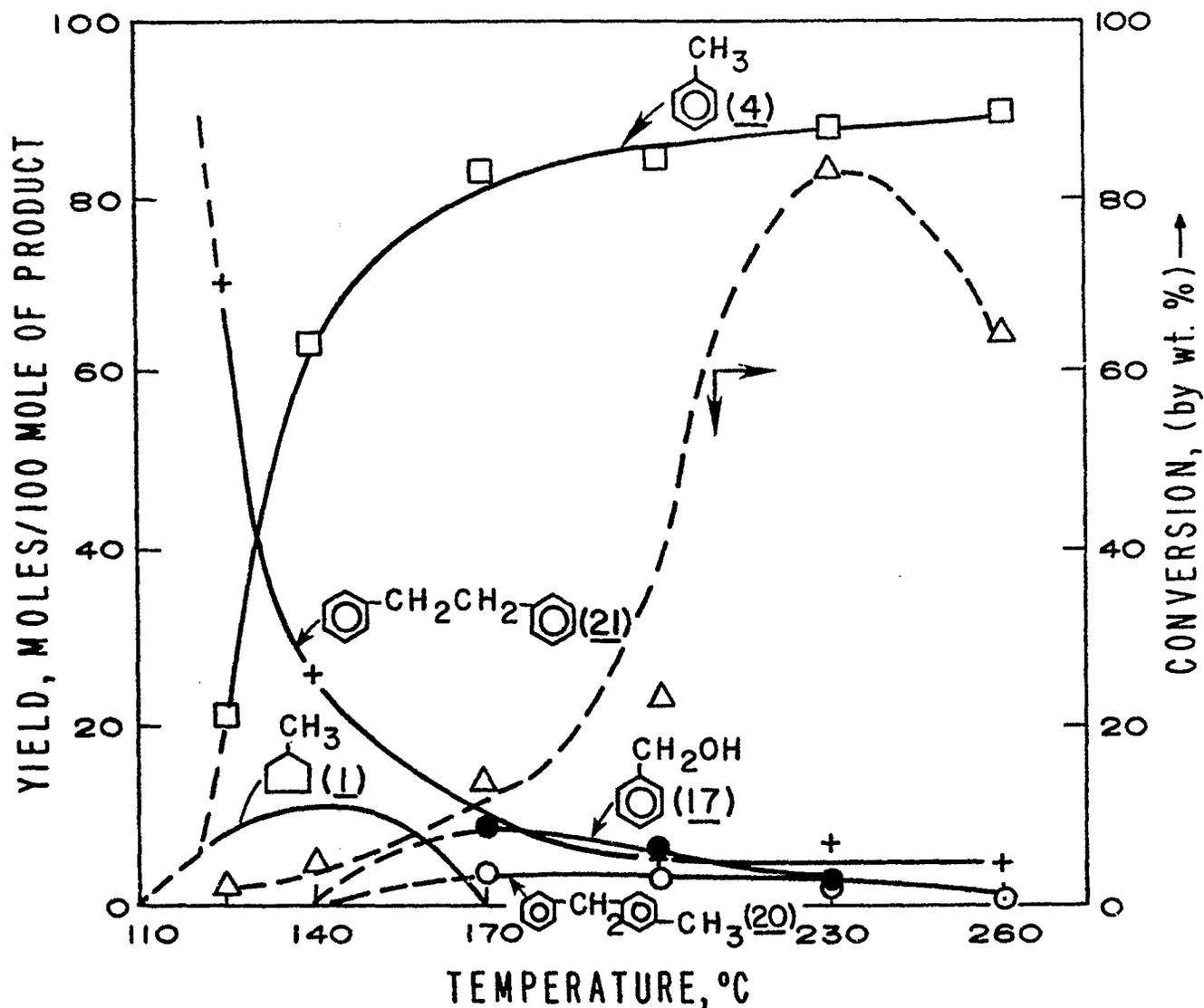


Figure 2. Change in product composition from hydrodeoxygenation of dibenzyl ether (7) as a function of reaction-temperature [catalyst, sulfided Ni-Mo/ γ -Al₂O₃ (Nalco #504); hydrogen pressure, 1000 psig; total reaction time, 0.5 hr].

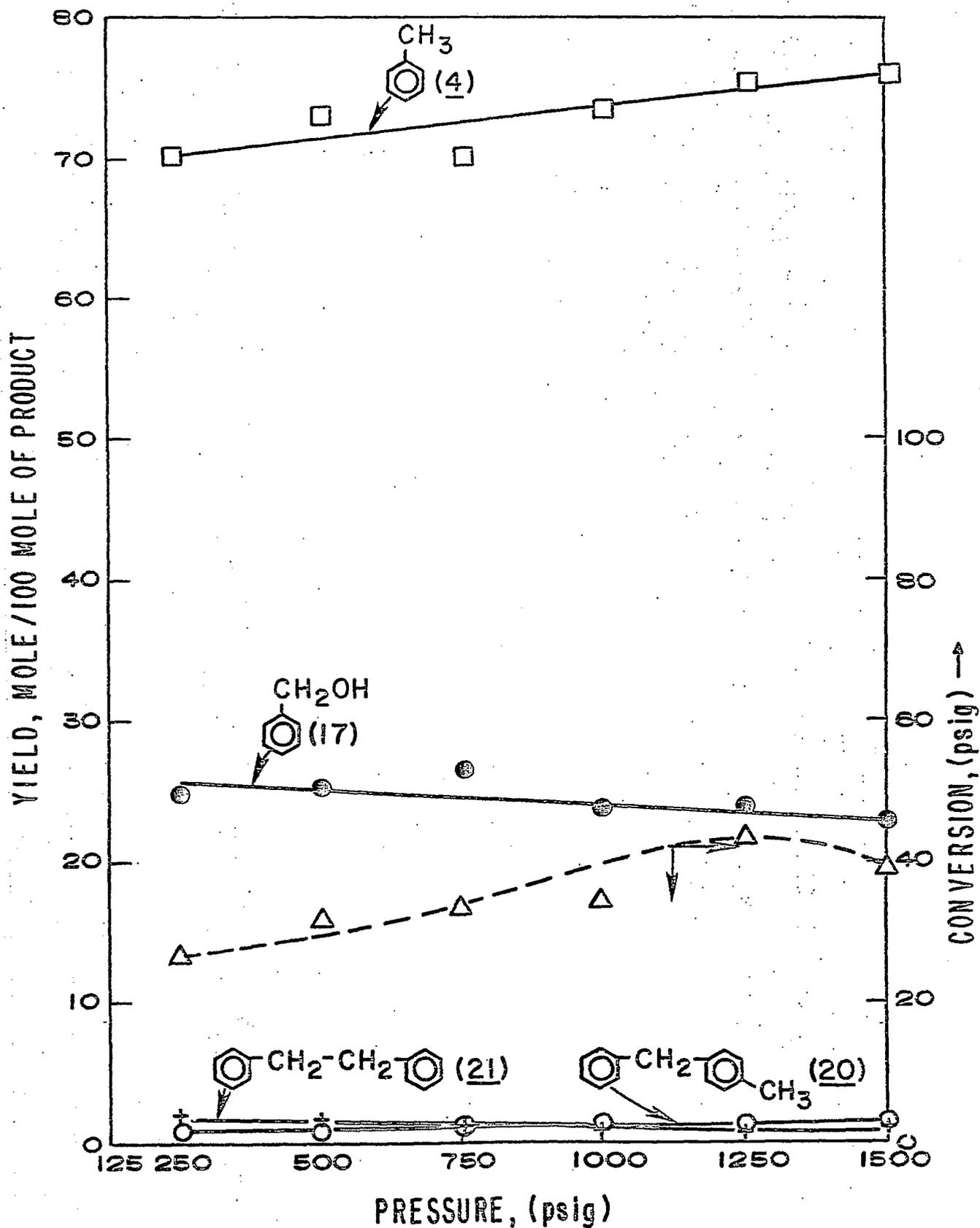


Figure 3. Change in product composition from hydrodeoxygenation of dibenzyl ether (7) as a function of hydrogen pressure [catalyst, sulfided Co-Mo/ γ -Al₂O₃ (Nalco #471); reaction temperature, 155°C; total reaction time, 0.5 hr].

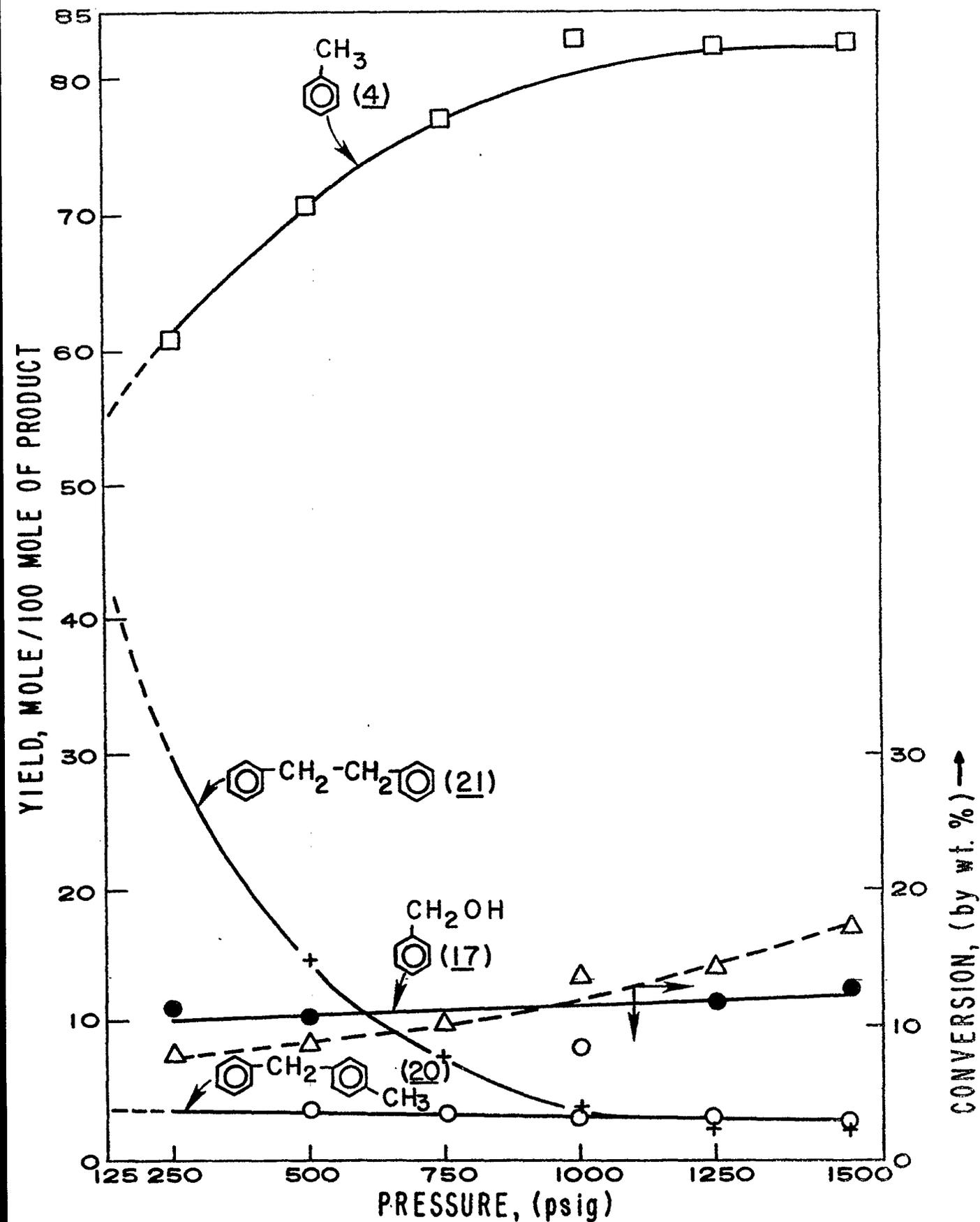


Figure 4. Change in product composition hydrodeoxygenation of dibenzyl ether (7) as a function of hydrogen pressure [catalyst, sulfided Ni-Mo/ γ -Al₂O₃ (Nalco #504); reaction temperature, 170°C; total reaction time, 0.5 hr].

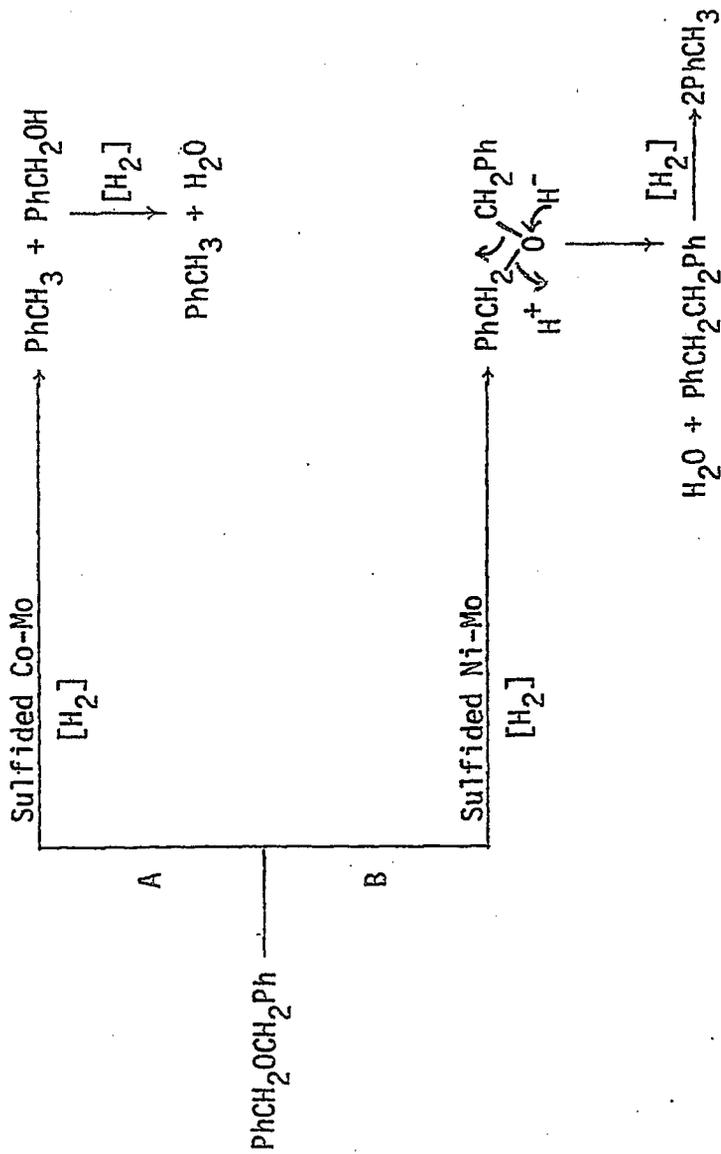


Figure 5. Indicated different pathways of dibenzylether hydrodeoxygenation to toluene with sulfided Co-Mo/Al₂O₃ vs Ni-Mo/Al₂O₃ catalysts:
 (A) two-step HDO process via benzyl alcohol as intermediate (Co-Mo catalyst);
 (B) concerted single-step HDO reaction yielding 1,2-diphenylethane as intermediate (Ni-Mo catalyst).

Task 8

Catalytic Cracking of Hydrogenated Coal-Derived Liquids and Related Compounds

Faculty Advisor: J. Shabtai
Graduate Student: John McCauley

Introduction

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

The present project is concerned with the following interrelated subjects: (1) systematic catalytic cracking studies of polycyclic naphthenes and naphthenoaromatics found in hydrogenated coal liquids and (2) systematic catalytic cracking studies of hydrotreated coal-derived liquids.

Project Status

Newly synthesized cross-linked smectite catalysts, ^{1,2} in particular RE³⁺-exchanged cross-linked montmorillonites and hectorites (designated as RE-Al-CLM and RE-Al-CLH, respectively), are being tested in the framework of this task for catalytic cracking activity. These types of molecular sieve catalysts are characterized by large critical pore sizes (range, 12-40 Å) suitable for intrasorption and cracking of bulky hydrocarbon molecules (kinetic diameters > 10 Å) present in coal-derived liquids. Testing is being performed in a pulse reactor, using cumene, 1-isopropylnaphthalene, perhydrophenanthrene, dodecahydrotriphenylene, and perhydropyrene as model feed compounds. Initial results will be presented in the next report.

Parallel to this work, studies are being carried out in a conventional catalytic cracking flow system,³ using partially hydrogenated coal liquids and polycyclic naphthenoaromatic hydrocarbons as feeds.

Future Work

The above indicated studies will be continued.

References

1. J. Shabtai, U.S. Patent 4,238,364 (1980).
2. J. Shabtai, R. Lazar and A.G. Oblad, Proc. 7th International Congress on Catalysis, Tokyo, Japan, 1980, pp 828-840.
3. S. Sunder, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1980.

Task 9

Hydropyrolysis (Thermal Hydrocracking) of CD Liquids

Faculty Advisors: J. Shabtai

A.G. Oblad

Graduate Student: Y. Wen

Introduction

This project is concerned with a systematic investigation of hydro-pyrolysis (thermal hydrocracking) as an alternative processing concept for upgrading of heavy coal-derived liquids into light liquid products. The high efficiency and versatility of hydro-pyrolysis has been indicated in previous studies with heavy CDL feedstocks and with model compounds.¹⁻³ The present project is an extension of this previous work for the purpose of (a) further developing and enlarging the scope of the hydro-pyrolytic reaction, and (b) optimizing the operating conditions for different types of feedstocks, e.g., coal liquids from different liquefaction processes, partially hydrotreated coal liquids, and relevant model compounds. The project includes systematic studies of reaction kinetics, product composition, and coking tendencies, as a function of operating variables. The work with model compounds provides necessary data for further elucidation of mechanistic aspects of the hydro-pyrolysis process.

Project Status

The debugging of the new hydro-pyrolysis unit (see preceding reports) was completed and a systematic hydro-pyrolysis (HP) study of a representative naphthenoaromatic compound, i.e., tetralin, has been initiated. The HP reactions of this compound are being investigated as a function of experimental variables, i.e., hydrogen pressure (in the range of 250-3000 psig), temperature (in the range of 450-600°C), and LHSV (in the range of 0.5 to 10 hr⁻¹).

Future Work

The HP study of tetralin will be continued, and studies of higher naphthenoaromatic hydrocarbons, e.g., 9,10-dihydroanthracene, and of partially hydrogenated N-containing polycyclic compounds, e.g., 1,2,3,4-tetrahydroquinoline, will be initiated. The purpose of the latter study will be to determine the efficiency of hydro-pyrolysis as a denitrogenation reaction.

References

1. J. Shabtai, R. Ramakrishnan, and A.G. Oblad, *Advances in Chemistry*, No. 183, Thermal Hydrocarbon Chemistry, Amer. Chem. Soc., 1979, pp 297-328.
2. R. Ramakrishnan, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1978.
3. A.G. Oblad, J. Shabtai and R. Ramakrishnan, U.S. Patent 4,298,457 (1981).

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

Faculty Advisors: F.E. Massoth
J. Shabtai
Post-Doctoral Fellows: G. Muralidhar
Y. Liu

Introduction

The objective of this research is to develop an insight into the basic properties of supported sulfide catalysts and to determine how these relate to coal liquids upgrading. The proposed program involves a fundamental study of the relationship between the surface-structural properties of various supported sulfide catalysts and their catalytic activities for various types of reactions. Thus, there are two clearly defined and closely related areas of investigation, viz., (1) catalyst characterization, especially of the sulfided and reaction states and (2) elucidation of the mode of interaction between catalyst surfaces and organic substrates of different types. The study of subject (1) will provide basic data on sulfided catalyst structure and functionality, and would allow the development of catalyst surface models. Subject (2), on the other hand, involves systematic studies of model reactions on sulfide catalysts, and the utilization of data obtained for development of molecular level surface reaction models correlating the geometry (and topography) of catalyst surfaces with the steric-conformational structure of adsorbed organic reactants. The overall objective of the project is to provide fundamental data needed for design of specific and more effective catalysts for upgrading of coal liquids.

Atmospheric activity tests using model compounds representative of hydrodesulfurization (thiophene), hydrogenation (hexene) and cracking (isooctene) have been developed. These were employed to assay changes in the catalytic functions of various supported CoMo catalysts. It was found that hydrodesulfurization (HDS) and hydrogenation activities were generally unaffected by the type of alumina used or by the cobalt salt used in the preparation; whereas, cracking activity varied considerably, being highest for γ -Al₂O₃ and cobalt sulfate addition. Addition of acidic, basic or neutral ions to the standard γ -alumina catalyst at 0.5 wt % level showed interesting changes in catalytic activities for various functions. In a series of catalysts employing silica-alumina as the support, the HDS and hydrogenation functions decreased with increasing silica content, while cracking went through a maximum in activity. Catalysts prepared by supporting CoMo on TiO₂, SiO₂·MgO and carbon showed low activities, except for high cracking activity for the two former catalysts.

Oxide precursors of CoMo and Mo catalysts supported on various silica-aluminas evaluated by ESCA showed that support active component interaction decreased with increase of silica in the support. It was also found that cobalt did not influence the Mo dispersion.

Project Status

During this quarter, Mo-containing catalysts supported on titania and silica-magnesia were evaluated for HDS and hydrogenation, and examined by ESCA. CoMo catalysts containing 5 wt % additives were prepared and the activities for the three catalytic functions HDS, hydrogenation and cracking were evaluated.

Results for the TiO₂ and SiO₂·MgO catalysts are summarized in Table 1. Because of lower activity of the Mo catalysts compared to the CoMo catalysts, the activities of the Mo catalysts were evaluated at 400°C instead of 350°C. The activities of these catalysts are low compared to Al₂O₃ supported catalysts and more comparable with silica or 75% silica alumina supported catalysts. The Mo dispersion determined by ESCA for the SiO₂·MgO catalysts also fall between the SiO₂ and 75% SiO₂·Al₂O₃ catalysts. However, the Mo dispersion for the TiO₂ catalysts are unusually high compared with their catalytic activities and O₂ chemisorption (see below). This may be an artifact caused by the low surface area of the TiO₂ support. Thus, compared to the other high area supports, the Mo can cover more TiO₂ support area, giving an apparent high Mo dispersion. Evidence that the Mo dispersion is not as high as observed comes from the half width values of the Mo ESCA peaks. The low values in Table 1 indicate a relatively low degree of dispersion when compared to previous values for the silica-alumina series.²

Correlations of Mo dispersion with O₂ chemisorption data obtained under Task II are shown in Figure 1. Reasonably linear correlations for both Mo and CoMo catalysts are obtained for the silica-alumina supports and the silica-magnesia support. The Mo dispersion for the titania supported catalyst is anomalously high for reasons discussed above. It should be noted that O₂ chemisorption was measured on the sulfided catalysts whereas the ESCA measurements were made on the calcined (oxidized) catalysts. Other investigators^{3,4} have shown that sulfiding does not alter the Mo dispersion from that on the calcined catalyst. Therefore, the linear relationships shown in Figure 1 indicate that O₂ chemisorption reflects the Mo dispersion, provided the support has sufficient surface area.

The effect of additives on the catalytic activities of CoMo/Al₂O₃ catalysts was further investigated. Prior studies had been at 1/2% level; the new studies were at 5% level. The additives were all impregnated on the calcined CoMo/Al₂O₃ catalyst, then recalcined at 540°C. Catalytic activities for thiophene HDS, hexene hydrogenation and isooctene cracking were determined as previously reported. The results of these tests together with earlier results for 1/2% additives are given in Table 2 in terms of activity for each reaction relative to the standard CoMo/Al₂O₃ catalyst (3% Co, 8% Mo on γ -Al₂O₃).

In general, the HDS activity was considerably suppressed at the 5% additives level as compared with the 1/2% level, although the order of deactivation was essentially the same. HDS deactivation appeared to relate to the acidity of the additive, increasing in the order: acidic < neutral < basic. However, B was a notable exception, being acidic as noted by its high cracking and yet causing the highest deactivation. Hydrogenation was also depressed with 5% additives, but not as markedly as the HDS activity. The order of deactivation did not generally follow that of the 1/2% additives. Noteworthy in this respect was the lack of any effect with Zn and the total deactivation with Na between the 1/2 and 5% additives. Evidently, hydrogenation activity is less directly related to the acidic nature of the additive. Cracking activity seemed to relate most closely with additive acidity.

B and F additions were especially active, giving complete cracking of the isooctene. The neutral additives and P showed no effect, while basic additives decreased cracking.

These results are very informative with respect to the nature of the active sites present on CoMo/Al₂O₃ catalysts. Evidently, the additives are incorporated into or cover some of the active CoMo phase in the oxide catalyst to give the effects observed. It is not known at present, however, whether they influence the Mo dispersion during sulfiding or simply cover active sites. Further research is needed to resolve this project.

The high pressure flow reactor for evaluating the various catalysts under more realistic conditions than employed in the current atmospheric tests has been put in operation. Preliminary tests with a commercial CoMo/Al₂O₃ catalyst have been made to determine appropriate model compounds and reaction conditions for comparative tests on the various catalysts. Dibenzothiophene has been chosen for HDS, naphthalene for aromatic hydrogenation and indole for HDN. Considerable effort has been expended in developing analysis of reaction products. Catalyst tests will begin shortly.

Future Work

Additional ESCA studies will be undertaken on some other oxide catalysts and some in sulfided form using a new dry box facility for transfer of samples without exposure to air. Work will begin on a series of NiMo supported catalysts to compare with the CoMo series. Some catalysts containing different levels of Co and Mo will be prepared and tested. High pressure activity tests on catalysts previously run at low pressure will be undertaken.

References

1. W.H. Wiser, F.E. Massoth, J. Shabtai and G. Muralidhar, DOE Contract No. DE-AC01-79ET14700, Quarterly Progress Report, Salt Lake City, Utah, April - June 1981.
2. ibid., July - Sept 1981.
3. B. Delmon, Third International Congress on the Chemistry and Uses of Molybdenum, Ann Arbor, Michigan, 1979.
4. S. Clausen, H. Topsie, R. Candia, J. Velladsen, B. Lengeler, J. Als-Nielsen and F. Christensen, J. Phys. Chem., 85, 3868 (1981).

Table 1. Activities and Mo dispersions for silica-magnesia and titania supports.

Catalyst ^a	Rate Constants		δ_{Mo} ^c	FWHM ^d Mo
	k_T ^b	k_H ^b		
Mo/SiO ₂ ·MgO ^e	1.1	28.4	0.07	2.1
Mo/TiO ₂	2.7	39.9	0.27	1.6
CoMo/SiO ₂ ·MgO ^e	11.9	29.9	0.06	2.3
CoMo/TiO ₂	6.9	18.5	0.15	1.4

^a8% Mo or 3% Co 8% Mo.

^b k_T , rate constant for HDS (cm³/g min atm); k_H , rate constant for hydro-
genation (cm³/g min); at 400°C for Mo and 350°C for CoMo catalyst.

^cMo dispersion as determined in Ref. 2.

^dFull width at half maximum height for major Mo peak (eV).

^e27% MgO.

Table 2. Effect of additives on relative activities of CoMo catalysts.

Level, % Additive ^c	Relative Activity ^a					
	HDS		HYD		CKG ^b	
	1/2	5	1/2	5	1/2	5
F	1.22	0.30	1.14	0.71	1.37	C
Cl	1.16	--	0.95	--	1.27	--
Ti	--	0.24	--	0.82	--	3.25
P	1.06	0.18	0.98	0.44	0.96	0.36
Zn	1.02	0.19	0.89	0.85	0.98	0.93
Mg	1.00	0.06	0.95	0.52	0.98	0.98
Na	0.60	0	0.96	0	0.67	0
Ca	0.54	0	0.89	0.39	--	0.23
B	0.46	0	0.82	0.21	1.90	C

^aActivities relative to standard catalyst (3% Co 8% Mo/Al₂O₃).

^bC denotes complete conversion.

^cAdditive at indicated level added to standard catalyst.

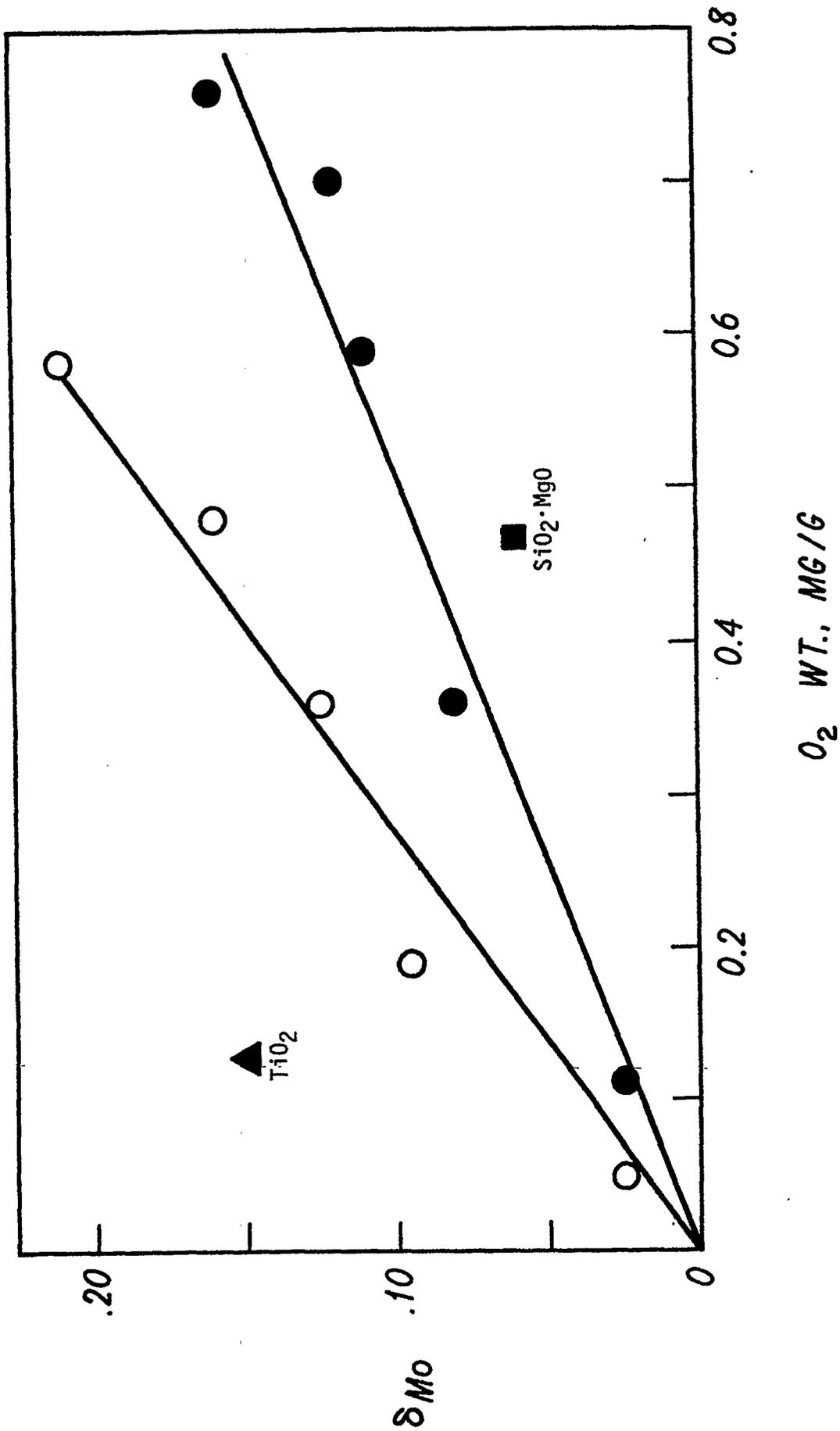


Figure 1. Mo dispersion vs. O_2 chemisorption of Mo (○) and CoMo (●) catalysts for $SiO_2 \cdot Al_2O_3$ series plus $SiO_2 \cdot MgO$ (■) and TiO_2 (▲) catalysts.

Basic Study of the Effects of Poisons on the
Activity of Upgrading Catalysts

Faculty Advisor: F.E. Maßoth
Post-Doctoral Fellow: W. Zmierczak

Introduction

The importance of cobalt-molybdena catalysts for hydrotreating and hydrodesulfurization of petroleum feedstocks is well-known. These catalysts are also being studied for hydrodesulfurization and liquefaction of coal slurries and coal-derived liquids. However, such complex feedstocks result in rapid deactivation of the catalysts. To gain an insight into the deactivation mechanism, the detailed kinetics of reactions of model compounds representative of heteroatom hydrogenolysis and hydrogenation 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 and activity. Supplementary studies are made to gain additional insight into the effect of poisons on the active catalyst sites. Finally, catalysts aged in an actual coal pilot plant run are studied to compare with laboratory studies.

Previous work on this project has shown that catalyst poisoning by pyridine or coke results in loss of active HDS sites, but that the remaining unpoisoned sites retain their original activity. Pyridine appeared to be site selective in poisoning effect whereas coke was non-specific. Furthermore, a distribution of HDS site strengths was observed with pyridine poisoning.

Investigation of the use of oxygen chemisorption for quantitatively assessing the number of active sites on sulfided HDS catalysts showed that oxygen uptake at -78°C best represented true chemisorption. For oxygen chemisorption performed on a limited number of catalysts at -78°C : (1) Mo/ Al_2O_3 and CoMo/ Al_2O_3 catalysts showed essentially the same values; (2) oxygen chemisorption on CoMo catalysts showed a rough correlation with HDS and hydrogenation activity; (3) preadsorbed pyridine reduced the oxygen adsorption of the catalyst in an almost linear manner; (4) on coked catalysts, oxygen uptake was higher than on freshly sulfided catalysts.

Project Status

During this period work on O_2 chemisorption was completed. Additional CoMo catalysts were tested to check earlier activity correlations. A series of Mo catalysts was also tested to clarify the effect of Co on the O_2 uptake-activity correlations. Details of the O_2 chemisorption procedure used were given previously.^{1,2} All measurements were made at -78°C . Catalyst activity data were obtained under Task 10.

Table 1 presents the chemisorption data obtained on all catalysts to date. These included Mo and CoMo catalysts on a variety of different supports, as well as several commercial catalysts. Generally, the Co-containing catalysts gave marginally higher O₂ chemisorption. Figure 1 shows relationships of O₂ uptake versus thiophene HDS and hexene hydrogenation activities for the CoMo catalysts. Considerable scatter is evidenced in both cases, showing that neither accurately reflects a direct correlation. In addition, the HDS correlation is not linear and does not go through the origin.

With the thought that perhaps the scatter may be due to different promotional effects of the Co on the catalytic activity, a number of catalysts containing only Mo were tested for O₂ chemisorption (Table 1). Since the catalytic activity for HDS was low, these catalysts were run at 400°C instead of 350°C used for the CoMo catalysts. Figure 2 shows the correlations obtained for the Mo catalysts. Again, considerable scatter was obtained for the HDS correlation, although the relationship appeared roughly linear, in contrast to the one obtained for the CoMo catalysts. The hydrogenation correlation for the Mo catalysts showed appreciable curvature in contrast to the linear correlation with the CoMo catalysts.

It is concluded that no clear evidence comes from these results which establishes a direct relationship between O₂ chemisorption and either HDS or hydrogenation sites, invalidating this technique for measuring active sites on sulfided catalysts. It is more probable the O₂ chemisorption is generally related to the state of dispersion of the active phase, which is only indirectly related to active sites. Preliminary results have shown a direct relationship between O₂ chemisorption and Mo dispersion as determined by ESCA measurements (see Task 10 of current report).

Future Work

A stirred microbalance reactor will be used for the simulated poisoning experiments to quantitatively assess poisoning effects on intrinsic activity functions of the CoMo catalyst. The catalyst will be subjected to various levels N-containing bases of different strengths to determine strengths and numbers of active HDS and hydrogenation sites.

References

1. W.H. Wiser, F.E. Massoth and W. Zmierczak, DOE Contract No. DE-AC01-79ET14700, April- June 1981.
2. ibid., July-Sept 1981.

Table 1

Oxygen Chemisorption on Different Catalysts

No.	Catalyst Support	O ₂ Chemisorption, mg/g	
		Mo ^a	CoMo ^b
1	γ -Al ₂ O ₃	0.58	0.76
2	10% SiO ₂ -Al ₂ O ₃	0.48	0.70
3	25% SiO ₂ -Al ₂ O ₃	0.36	0.59
4	75% SiO ₂ -Al ₂ O ₃	0.19	0.36
5	SiO ₂	0.05	0.11
6	73% SiO ₂ -MgO	--	0.47
7	TiO ₂	--	0.13
13	5% Ti-Al ₂ O ₃ ^c	1.32	--
14	5% Mg-Al ₂ O ₃ ^c	0.78	--
15	5% Ca-Al ₂ O ₃ ^c	0.02	--
8	5% Zn-Al ₂ O ₃ ^c	--	0.64
9	γ -Al ₂ O ₃ (+5% Zn) ^d	--	0.63
10	American Cyanamid	--	0.87
11	Topsoe	0.97	0.94
12	Ketjenfine	--	0.64

^a8% Mo^b3% Co 8% Mo^c5% Me impregnated on γ -Al₂O₃^d5% Zn impregnated on catalyst 1

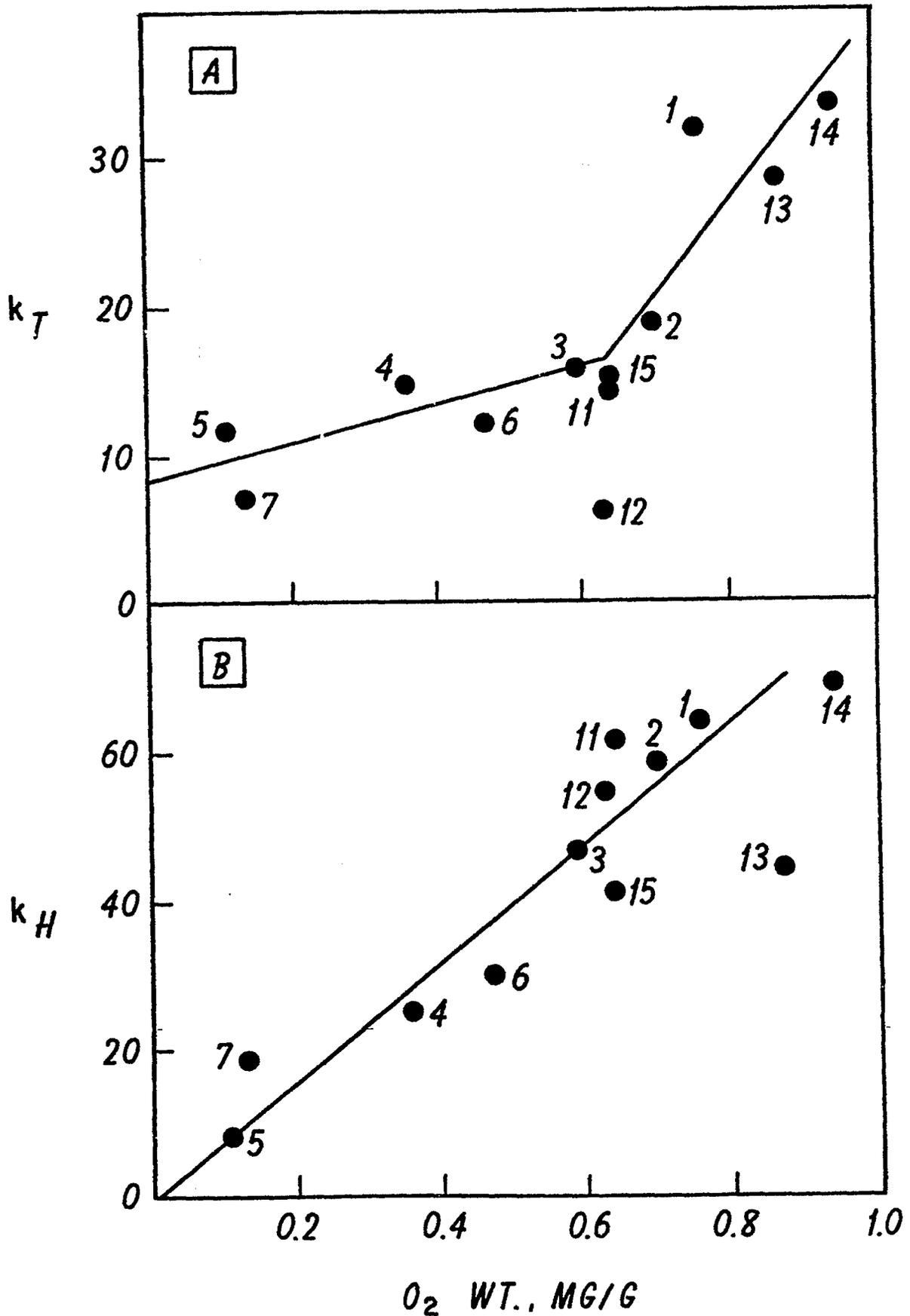


Figure 1. Catalytic activity at 350°C of different CoMo catalysts vs. O_2 chemisorption. (A) k_T , rate constant for HDS, cm³/g min atm; (B) k_H , rate constant for hydrogenation, cm³/g min. Numbers refer to catalysts listed in Table 1.

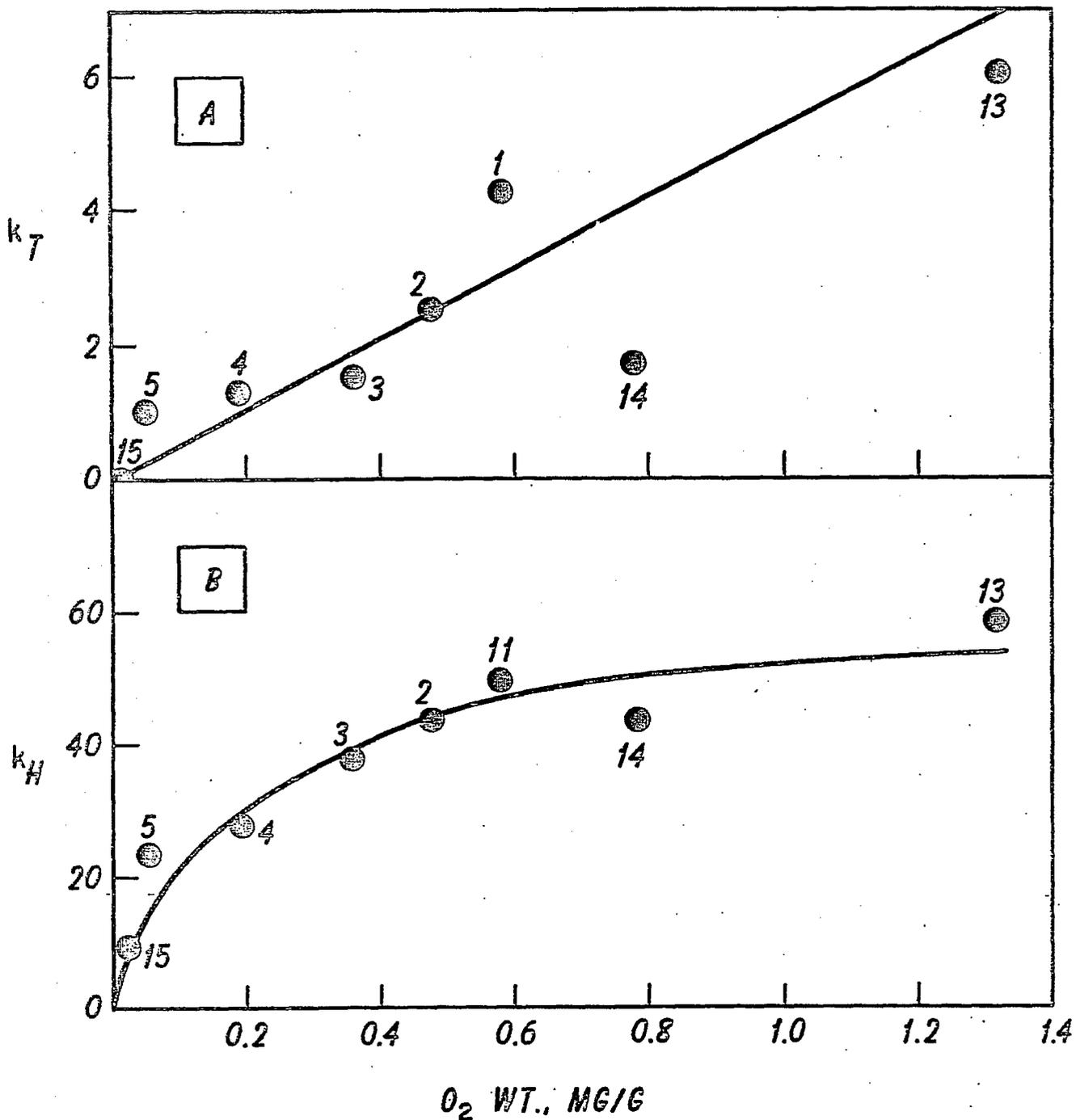


Figure 2. Catalytic activity at 400°C of different Mo catalysts vs. O₂ chemisorption. (A) k_T , rate constant for HDS, cm³/g min atm; (B) k_H , rate constant for hydrogenation, cm³/g min. Numbers refer to catalysts listed in Table 1.

Task 13

Catalyst Research and Development

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

Introduction

The objectives of this project are to develop a preparation technique for a Raney type catalyst (particularly Raney iron-manganese catalyst) and to determine the optimum process variables for the maximum production of gasoline boiling range hydrocarbons, low molecular weight olefins and BTX via the hydrogenation of carbon monoxide. A detailed discussion of the objectives were presented in a previous report.¹

An electrical heating furnace was built to prepare Al-Fe and Al-Fe-Mn alloys. Several samples of alloys were prepared and the optimum preparation conditions were determined. A stirred tank reactor was fabricated to activate the alloys in an aqueous solution of sodium hydroxide at different activation conditions. A fixed-bed reactor system was built in which catalyst screening tests are being carried out to determine the catalyst composition and activation variables which will optimize the catalyst activity and selectivity. The same reactor system will be used for the process variable investigation. Two types of Raney iron catalysts were prepared at different activation conditions. These catalysts were tested in the fixed bed reactor to determine the proper range of process variables (temp, pressure, space velocity) to carry out a standard catalyst screen test. The Raney iron catalysts were found to be more active, in terms of CO conversion even at an unreduced state, compared to a precipitated iron catalyst reduced at 500°C.

Project Status

A series of tests have been carried out with a gas chromatograph to determine the response factors of each gas product from CO hydrogenation. (A poor mass balance of the reaction had mainly originated from incorrect response values used in the gas product analysis with the GC.) Different quantities of each pure gas sample were injected into the GC and the absolute response area of each gas was obtained using a TCD or FID detector. There were good linear relations between the response area vs. the volume of gas injected for all the gases tested. There was no indication of a sample overloading problem. The response factor values were calculated from the response area obtained. Table 1 shows the response factors determined along with the values reported by Dietz.² Generally there is good agreement between the two sets of values except for CO₂ and methane. The higher value of CO₂ may be explained by the CO₂ which was detected by a TCD detector at a higher temperature (65°C) than the CO and N₂ (0°C). The GC was temperature programmed from 0° to 200°C. The low value of methane could not be explained, and repeated tests showed the same results.

The hydrocarbons from C₅ to C₇ always showed lower values than Dietz's data. It was speculated that the discrepancies originated from a loss of sample during the taking of samples and injecting them into the GC. The response factors of Dietz were used for the C₅-C₇ compounds.

The three possible methods used to obtain a quantitative analysis with the GC³ are: (1) direct calibration, (2) correction factor method and (3) internal standard method. A modification of the correction factor method has been chosen. The direct calibration method is time-consuming and inconvenient. The internal standard method is reliable and convenient, but it is not possible to apply it to this reactor system.

A computer program was rewritten in BASIC based on the old program.⁴ Carbon monoxide conversion, carbon mass balance, product carbon % of each product, etc. can be calculated by giving the input values of the CH₄ and CO response area. These were obtained from the GC just prior to each analysis of the CO hydrogenation products from a fixed bed reactor run. (The BASIC program and an example of printout is included in this report.)

The CO conversion was defined in two ways.

(1) CO conversion on an output basis

$$\text{CO conv \%} = \{1 - N(\text{CO}) / [\Sigma N(\text{CO}) + N(\text{HC})]\} \times 100$$

(2) CO conversion based on input and output

$$\text{CO conv \%} = \left(1 - \frac{k * F_2}{C_1 * F_1}\right) \times 100$$

In the first definition, the denominator is the sum of the total carbon number of moles in the product, which must be equal to the total carbon number of moles of CO in the reactants at steady state. The numerator is the carbon number of moles of CO in the product. This conversion represents the actual CO conversion within experimental limits of product analysis (including liquid and solid high hydrocarbons). In the second definition, the denominator is the total carbon number of moles input, that is, mole fraction of CO (C₁) multiplied by input gas flowrate (F₁). The numerator is the output gas flowrate (F₂) multiplied by the total carbon mole fraction in the product (K). The two conversion values should agree within experimental error if all the products can be collected and counted at a steady state reaction condition. An excellent review on mass balance problems has been published by H.H. Nijs and P.A. Jacobs.⁵

A simple glass unit was used to transfer the Raney catalyst from the storage bottle to the catalyst bed of the reactor without exposing the catalyst to air is shown in Figure 1. An appropriate amount of catalyst, wet with absolute ethanol, was transferred into the flask. The glass unit was connected to a vacuum pump and the ethanol was pumped out until the whole glass unit gave constant weight. It took about 1.5 hr for this procedure. Then the top vacuum stopcock was opened and deionized water was introduced into the bottom flask through the vacuum stopcock. The water slurry of the catalyst was transferred to the catalyst bed. The water was then evaporated in flowing hydrogen for about 2 hr at room temperature. The reactor was then heated slowly to the reduction temperature of the catalyst.

To determine a proper range of process variables (particularly temp) for the catalyst screening tests, a fixed bed reactor run was made (Table 2). The CO conversion increased with increasing temperatures up to 493^oK, then it decreased. The carbon mass balance error percent was higher at higher conversions. From 453^o to 473^oK, the methane yield decreased, C₅⁺ yield increased and the O/P (olefin/paraffin carbon ratio in C₂-C₄ fraction) decreased, while C₂-C₄ selectivity remained essentially constant. At 483^oK the O/P ratio and C₅⁺ yield decreased and the methane yield increased abruptly. This change in catalyst selectivity may have been due to catalyst deactivation via coke formation. At 503^oK the catalyst activity in terms of CO conversion was lower than that at 493^oK.

Another run was made with the same catalyst at a much lower temperature (423^oK) to minimize deactivation. In Table 3 the catalyst selectivity and CO conversion were determined at different total reaction times of catalyst on stream. From Table 3, the product carbon percent of each fraction (or component) remained essentially constant except for the first 0.4 hours.

In Figure 2 the product carbon percent is plotted as a function of the reaction time. In Figure 3 the carbon mass balance error percent is plotted. In the initial period the error was about 17%, then it dropped to the 9% range. However, the conversion on an output basis remained quite constant at 2.7% except for the first initial period.

Since there were no liquid products collected in the cold trap of the reactor, the possible sources of mass balance error are an inaccurate measurement of gas flowrate or a loss of CO through formation of carbide, carbonyl or coke during the synthesis reaction.

Another fixed bed run was made with the same catalyst pretreated at the same conditions but carburized after reduction. The extent of this experiment was to assess carburization as a possible explanation for the error in the carbon balance. The conditions of carburization were determined according to W.D. Johnston et al.,⁶ who reported almost 100% transformation of fine particles of Raney iron catalyst into an ϵ -Fe₂C phase at the following conditions: temperature = 240^oC, H₂/CO = 3, pressure = 1 atm and carburization time = 6 hr. The results with the carbided catalysts are presented in Table 4.

The carbon mass balance error percent (Table 4), which is roughly equal to the difference between the two conversions defined previously, with the carbided catalyst at 423^oK is better than the carbon mass balance just reduced as shown in Figure 2. The dark points are the data at 473^oK, SV = 4.1 still show considerable errors. From the above run it could not be confirmed that carbide formation is a source of error. Additional experiments will be performed to resolve the mass balance errors and to determine a proper region of process variables for the catalyst screening tests.

Future Work

A study will be done to minimize the carbon mass balance error, i.e., measurement of gas flowrate for a long period, etc. Several samples of Raney iron and Raney iron-manganese catalysts will be prepared at different activation conditions (leaching temp, leaching time, NaOH concentration, etc).

These catalysts will be subjected to standard catalyst screening tests at a fixed condition of process variables in a fixed bed reactor.

Several catalyst characterization techniques, such as XPD, BET surface area, TGA reduction study and chemisorption, will be utilized to better understand the differences in catalyst activities and selectivities between catalysts prepared at different conditions.

References

1. W.H. Wiser, F.V. Hanson and C.S. Kim, DOE Contract No. DE-AC01-79ET 14700, Quarterly Progress Report, Salt Lake City, Utah, Oct - Dec 1979.
2. W.A. Dietz, Journal of Gas Chromatography, 68 (1967)
3. Quantitative Gas Chromatography, Supelco Bulletin 770.
4. Y.S. Tsai, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1980.
5. H.H. Nijs and P.A. Jacobs, Journal of Chromatographic Science, 19, 40 (1981).
6. W.D. Johnston, R.R. Heikes and J. Petrolo, J. Phys. Chem., 64, 1720 (1960).

Table 1. Response factors of products from CO hydrogenation.

TCD Detector		FID Detector			
N ₂	42 (42)	CH ₄	0.76 (0.97)	C ₅ H ₁₂	-- (1.04)
<u>CO</u>	<u>42 (42)^a</u>	C ₂ H ₆	-- (0.97)	C ₅ H ₁₀	-- (1.04) ^b
CO ₂	62 (48)	<u>C₂H₄</u>	<u>1.02 (1.02)^a</u>	C ₆ H ₁₄	-- (1.03)
		C ₃ H ₈	0.95 (0.98)	C ₆ H ₁₂	-- (0.99)
		C ₃ H ₆	1.01 (--)	C ₇ H ₁₆	-- (1.00)
				C ₇ H ₁₄	-- (1.00) ^b
		C ₄ H ₁₀	0.93 (1.03)	CH ₃ OH	0.18(0.23)
		i-C ₄ H ₁₀	0.95 (--)	C ₂ H ₅ OH	0.41(0.46)
		1-butene	1.00(--)	C ₃ H ₇ OH	-- (0.60)
		2-butene	0.95(--)		

^aThe underlined compounds are the references from which other response factors are calculated.

^bWhen the response factors were not available for the olefins, it was assumed their values are the same as those of paraffins.

^cNumbers in parentheses are from Dietz.²

Table 2. Fixed bed run with Raney iron catalyst (90°C).^a

Reduction = 350°C, 24 hours; Pressure = 500 psig; SV = 2.0 cc/g sec.

Temp (°K)	CO Conv % input-output (output)	carbon mass balance %	O/P	Hydrocarbon Selectivity %		
				C ₁	C ₂ -C ₄	C ₅ ⁺
453	21.4 (4.7)	17.5	1.67	27.1	49.7	23.3
463	26.7 (8.7)	19.8	1.50	25.8	50.7	23.6
473	33.1 (14.9)	21.4	1.34	22.5	49.6	27.6
483	45.6 (32.5)	19.5	0.76	42.5	45.3	12.1
493	62.3 (48.5)	26.8	0.42	45.6	43.4	10.9
503	39.6 (30.2)	13.5	0.37	43.5	44.8	11.8

^aThe catalyst was activated at 90°C in a sodium hydroxide solution.

Table 3. Fixed bed run with a Raney iron catalyst (90°C).

Temp = 423^oK; Pressure = 500 psig; SV = 2.0 cc/g sec; Reduction at 350^oC, 20 hours.

Time on Stream (Hr)	CO Conv % In-Out (Input)	Carbon Mass Balance %	O/P	Product Carbon %			
				C ₁	C _{2-C₄}	C _{5⁺}	CO ₂
0.4	18.3 (1.7)	16.9	1.29	23.6	49.8	15.9	10.7
2.0	16.1 (2.1)	14.2	1.14	27.4	49.9	16.3	6.4
8.75	17.1 (2.7)	14.8	1.33	26.1	51.9	15.4	6.6
15.0	8.4 (2.6)	6.0	1.25	27.2	50.9	15.4	6.5
24	9.5 (2.7)	6.9	1.23	27.8	50.8	14.9	6.5

Table 4. CO conversion with carbided Raney iron catalyst (90°C).

Reduction at 350^oC, 16 hours; Carburization at 240^oC, H₂/CO = 3, 1 atm. for 18 hours.

Temp (^o K)	CO Conversion %, Input-Output (Output Basis)	
	SV = 2.1 cc/g sec	SV = 4.1 cc/g sec
413	3.6 (1.1)	--
423	^a 10.9 (2.8)/5.5 (2.7)	5.0 (1.3)
433	3.7 (3.0)	11.2 (3.1)
443	--	13.4 (6.2)

^aFirst conversion values obtained at 6.5 hr on stream and the second at 15 hr on stream.

BASIC Computer Program

```
00010 @@ PRODUCT ANALYSIS OF FISCHER-TROPSCH PROCESS @@
00020 DIM P$(25),R(25),M(25),N(25),Y(25),V(25)
00030 DIM Z(25),A(25),B(25),W(25),X(25),C(25)
00040 PRINT
00050 FOR I=1 TO 22 READ P$(I)
00060 DATA 'N2','CO','CO2'
00070 DATA 'C1','C2=','C2','C3=','C3'
00080 DATA 'IC4','IC4=','NCA','2C4='
00090 DATA 'IC5=','C5','2C5=','C6=','C6'
00100 DATA 'C7=','C7','MEOH','ETOH','PROH'
00110 PRINT
00120 @@ RESPONSE FACTORS AND RELATIVE SENSITIVITIES
00130 @      DF FID  @@
00140 FOR I=1 TO 22 READ R(I)
00150 DATA 42.1,42.0,61.9
00160 DATA 0.76, 1.02, 1.02, 1.01, 0.95
00170 DATA 0.95,1.00,0.93,0.95,1.04
00180 DATA 1.04,1.04,1.03,1.03,1.00,1.00
00190 DATA 0.19,0.41,0.60
00200 PRINT
00210 @@ MOLECULAR WEIGHT OF HYDROCARBONS @@
00220 FOR I=4 TO 22 READ M(I)
00230 DATA 16.04,28.05,30.01,42.28,44.09
00240 DATA 58.12,56.10,58.12,56.10,70.14
00250 DATA 72.15,70.14,84.16,86.17,98.19
00260 DATA 100.20, 32.04, 46.07, 60.10
00270 PRINT
00280 @@ NUMBER OF CARBON ATOMS IN EACH COMPOUND @@
00290 FOR I=2 TO 22 READ N(I)
00300 DATA 1, 1, 1, 2, 2
00302 DATA 3, 3, 4, 4, 4, 4
00304 DATA 5, 5, 5, 6, 6
00306 DATA 7, 7, 1, 2, 3
00310 @@
00312 @@
00313 PRINT
00314 PRINT
00315 PRINT
00320 PRINT TAB(10); 'INPUT PARAMETERS'
00325 PRINT
00330 PRINT
00340 PRINT 'AMBIENT TEMP.(DEG. C)';
00345 INPUT T1
00350 PRINT 'AMBIENT PRESS.(MMHG)';
00355 INPUT P1
00360 PRINT 'CO AREA(1 CC INJECTION)';
00365 INPUT A1
00370 PRINT 'CH4 AREA(1 CC INJECTION)';
00375 INPUT A2
00380 @@ CALCULATION OF AREA FOR 1 CC GASES @@
00390 FOR I=1 TO 3 A(I)=A1*R(I)/R(2)
00400 FOR I=4 TO 22 A(I)=A2*R(I)*M(I)/(R(4)*M(4))
00405 PRINT
00410 PRINT 'CO CONCENTRATION';
00412 INPUT C1
00415 PRINT 'H2 CONCENTRATION';
00420 INPUT H2
```

```

00425 @@ H2/CO RATIO @@
00430 H1=H2/C1
00440 PRINT 'CATALYST WEIGHT(GRAMS)';
00450 INPUT W
00460 PRINT
00461 PRINT
00462 PRINT
00463 PRINT
00464 PRINT
00465 PRINT 'BOOK AND PAGE NO. ';
00470 INPUT A5,A6
00475 PRINT 'CO CONVERSION TEMP.(DEG. C)';
00480 INPUT T
00485 PRINT 'REACTION PRESS.(PSIG)';
00490 INPUT P
00500 PRINT 'INPUT FLOWRATE(CC/SEC)';
00510 INPUT F1
00520 PRINT 'OUTPUT FLOWRATE(CC/SEC)';
00530 INPUT F2
00532 @@ SPACE VELOCITY @@
00534 S=F1/W
00540 @@ CONTACT TIME @@
00550 K3=W/F1*23.1587*(P+12.5724)/(T+273.16)
00560 PRINT
00570 PRINT TAB(20);'INPUT AREAS'
00580 PRINT
00590 PRINT
00600 FOR I=1 TO 22
00610 PRINT P$(I);TAB(10);
00620 INPUT B(I)
00630 NEXT I
00640 PRINT
00680 @@ MOLE FRACTION OF GASES IN 1 CC @@
00690 FOR I=1 TO 22 V(I)=B(I)/A(I)
00693 FOR I=2 TO 22 W(I)=V(I)*100
00695 PRINT
00700 @@ CARBON MOLE% OF EACH GAS @@
00705 FOR I=2 TO 22 X(I)=N(I)*V(I)
00710 K=0
00715 FOR I=2 TO 22 K=K+X(I)
00720 FOR I=2 TO 22 C(I)=X(I)/K*100.
00725 PRINT
00730 @@ INPUT CARBON NUMBER OF MOLES PER SECOND @@
00731 @ F1(INPUT FLOWRATE)ADJUSTED AT 650 MMHG,18 DEG.C @
00732 G1=C1*F1*650/760/(82.05*291.16)
00733 PRINT
00735 @@ CO CONVERSION% BY INPUT-OUTPUT OF CO @@
00740 D1=G1-V(2)*F2*P1/760/(82.05*(T1+273.16))
00745 D1=D1/G1*100
00746 PRINT
00748 @@ CO CONVERSION% BY OUTPUT BASIS @@
00750 D2=100-C(2)
00755 PRINT
00760 @@ CARBON MASS BALANCE BY INPUT-OUTPUT BASIS @@
00772 @ OUTPUT CARBON NUMBER OF MOLES PER SECOND @
00775 G2=K*F2*P1/760/(82.05*(273.16+T1))
00780 G=(G1-G2)/G1*100
00790 PRINT

```

```

00800 @@ PRODUCT SELECTIVITY PERCENT @@
00805 K1=K-X(2)
00810 FOR I=3 TO 22 Y(I)=X(I)/K1*100
00815 @@ HYDROCARBON SELECTIVITY PERCENT @@
00820 K2=K-X(2)-X(3)
00825 FOR I=4 TO 22 Z(I)=X(I)/K2*100
00830 PRINT
00835 @@ OLEFIN/PARAFFIN RATIO IN C2-C4 @@
00840 Q1=Z(5)+Z(7)+Z(10)+Z(12)
00845 Q2=Z(6)+Z(8)+Z(9)+Z(11)
00850 Q=Q1/Q2
00853 Z1=Z(5)+Z(6)+Z(7)+Z(8)+Z(9)+Z(10)+Z(11)+Z(12)
00856 Z2=Z(13)+Z(14)+Z(15)+Z(16)+Z(17)+Z(18)+Z(19)
00860 PRINT
00870 PRINT 'CONTACT TIME=';K3
00875 PRINT 'SPACE VELOCITY(CC/GR-SEC)=';S
00876 PRINT 'H2/CO RATIO=';H1
00879 PRINT
00880 PRINT
00881 PRINT 'CONVERSION AND MASS BALANCE DIFFERENCE ARE EXPRESSED IN %'
00885 PRINT 'CO CONVERSION(INPUT-OUTPUT)=';D1
00890 PRINT 'CO CONVERSION (OUTPUT)=';D2
00900 PRINT 'CARBON MASS BALANCE(INPUT-OUTPUT)=';G
00905 PRINT 'OLEFIN/PARAFFIN RATIO IN C2-C4=';Q
00906 PRINT 'C2-C4 H.C SELECT. %=' ;Z1
00908 PRINT 'C5+ H.C SELECT. %=' ;Z2
00910 PRINT
00915 PRINT
00920 PRINT '      AREA      INPUT      VOLUME  PRODUCT  HYDROCARBON
00925 PRINT '      1 CC      AREA      PERCENT  CARBON %  SELECT %'
00930 PRINT
00940 PRINT
00945 FOR I=1 TO 22
00950 PRINT P$(I);TAB(4);
00955 X$='#.##### #.#####   ZZ.XXX  ZZ.XXX   ZZ.XXX'
00960 PRINT IN IMAGE X$:A(I),B(I),W(I),Y(I),Z(I)
00970 NEXT I
00971 PRINT
00972 PRINT
00975 PRINT ' SAME CAT.WT.,H2/CO RATIO,CO,CH4 AREA,I1,P1 (YES OR NO)';
00980 INPUT N$
00985 IF N$='YES' THEN 461
00988 PRINT
00990 PRINT 'DO ANOTHER ONE AT OTHER CONDITIONS(YES OR NO)';
00995 INPUT N$
01000 IF N$='YES' THEN 320
01010 @@ END OF PROGRAM @@
02000 END

```

Example of a Computer Printout

INPUT PARAMETERS

AMBIENT TEMP.(DEG. C)? 22.5
AMBIENT PRESS.(MMHG)? 642
CO AREA(1 CC INJECTION)? 1330300
CH4 AREA(1 CC INJECTION)? 300000000

CO CONCENTRATION? 0.3332
H2 CONCENTRATION? 0.6668
CATALYST WEIGHT(GRAMS)? 2.639

BOOK AND PAGE NO. ? 34,14
CO CONVERSION TEMP.(DEG. C)? 160
REACTION PRESS.(PSIG)? 500
INPUT FLOWRATE(CC/SEC)? 5.8501433
OUTPUT FLOWRATE(CC/SEC)? 5.198181

INPUT AREAS

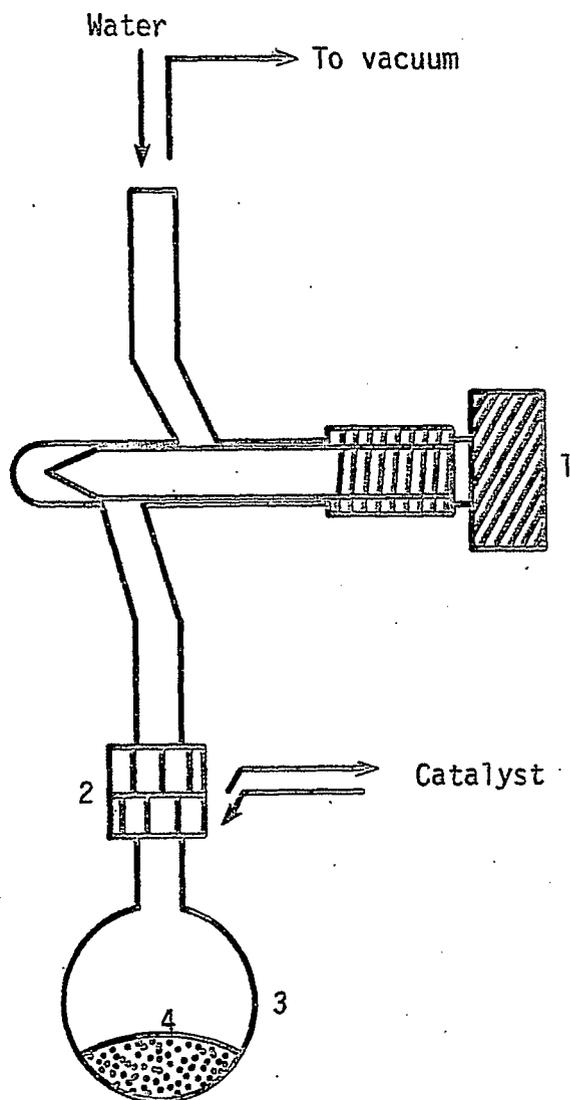
N2	? 9830
CO	? 482600
CO2	? 1266
C1	? 955000
C2=	? 212500
C2	? 366800
C3=	? 620000
C3	? 346500
IC4	? 19600
1C4=	? 413400
NC4	? 285600
2C4=	? 19360
1C5=	? 292600
C5	? 188500
2C5=	? 0
C6=	? 171600
C6	? 137700
C7=	? 103800
C7	? 100500
MEDH	? 0
ETOH	? 0
PRDH	? 0

CONTACT TIME= 12.362148
 SPACE VELOCITY(CC/GR-SEC)= 2.2168031
 H2/CO RATIO= 2.0012005

CONVERSION AND MASS BALANCE DIFFERENCE ARE EXPRESSED IN %
 CO CONVERSION(INPUT-OUTPUT)= 5.9024266
 CO CONVERSION (OUTPUT)= 3.4930067
 CARBON MASS BALANCE(INPUT-OUTPUT)= 2.4966277
 OLEFIN/PARAFFIN RATIO IN C2-C4= 1.2523374
 C2-C4 H.C SELECT. %= 52.29718
 C5+ H.C SELECT. %= 22.205224

	AREA 1 CC	INPUT AREA	VOLUME PERCENT	PRODUCT CARBON %	HYDROCARBON SELECT %
N2	1.333E+06	9.830E+03	0.000	0.000	0.000
CO	1.330E+06	4.826E+05	36.278	0.000	0.000
CO2	1.961E+06	1.266E+03	.065	4.918	0.000
C1	3.000E+08	9.550E+05	.318	24.244	25.476
C2=	7.041E+08	2.125E+05	.030	4.597	4.835
C2	7.533E+08	3.668E+05	.049	7.417	7.800
C3=	1.051E+09	6.200E+05	.059	13.480	14.177
C3	1.031E+09	3.465E+05	.034	7.680	8.078
IC4	1.359E+09	1.960E+04	.001	.439	.462
IC4=	1.381E+09	4.134E+05	.030	9.122	9.594
NC4	1.330E+09	2.856E+05	.021	6.541	6.879
2C4=	1.312E+09	1.936E+04	.001	.450	.473
1C5=	1.795E+09	2.926E+05	.016	6.207	6.528
C5	1.847E+09	1.885E+05	.010	3.887	4.088
2C5=	1.795E+09	0.000E+00	0.000	0.000	0.000
C6=	2.133E+09	1.716E+05	.008	3.676	3.866
C6	2.184E+09	1.377E+05	.006	2.881	3.030
C7=	2.416E+09	1.038E+05	.004	2.290	2.409
C7	2.466E+09	1.005E+05	.004	2.173	2.285
MEOH	1.498E+08	0.000E+00	0.000	0.000	0.000
ETOH	4.648E+08	0.000E+00	0.000	0.000	0.000
PRUH	8.874E+08	0.000E+00	0.000	0.000	0.000

Figure 1. A glass unit to transfer catalyst into reactor bed.



1. Vacuum stopcock
2. Vacuum tight O-ring joint
3. Sample holding flask
4. Catalyst

Figure 2. Product carbon mole %

Raney iron (363^oK) reduced at 350^oC 18 hr
Temp = 423^oK P = 500 psig SV = 2.0 cc/g sec

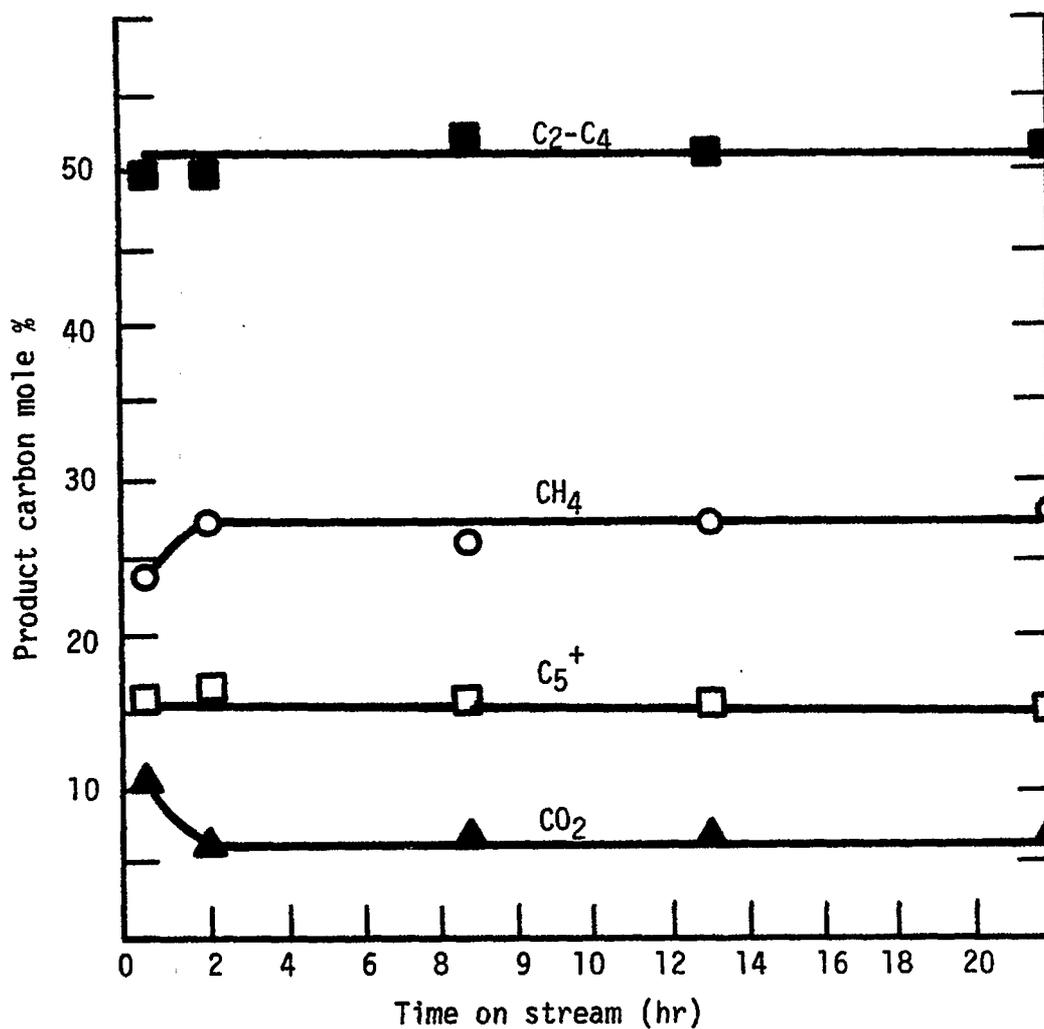


Figure 3. CO conversion %.

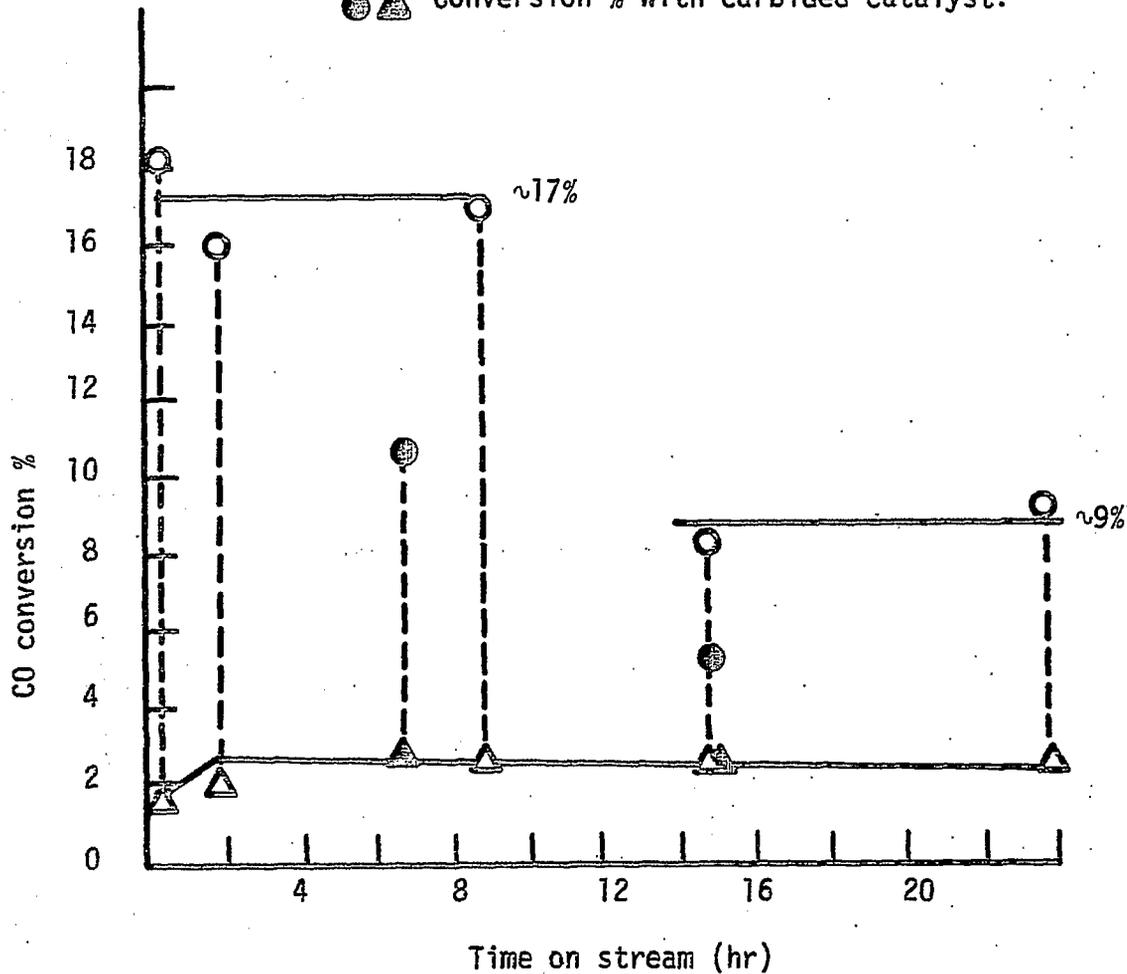
Raney iron (363°K)
Reduced at 623°K for

T = 423°K P = 500 psig SV = 2.0 cc/g sec

○ Conversion % (input-output)

△ Conversion % (output basis)

● Conversion % with carbided catalyst.



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 synthesis of light hydrocarbons from the hydrogenation of carbon monoxide has been studied over a variety of metallic catalysts. The unsupported iron-manganese catalyst was very selective in the production of C₂-C₄ olefins. The screening tests for iron-manganese catalysts were performed in a bench-scale fixed-bed reactor system. The preliminary results have shown that a catalyst, composed of 2 parts Mn per 100 parts Fe (atomic ratio), exhibited a good selectivity for the synthesis of C₂-C₄ olefins. The data for the investigation of the process variable effects agreed mostly with those found in the literature.

A new fixed-bed reactor system described in the previous work has been built to obtain an accurate analysis of the products.¹ Additional procedures are being developed to provide more comprehensive information on the iron-manganese catalyst. These procedures include an accurate mass balance analysis, the characterization of the catalyst, the catalyst preparation technique, the catalyst pretreatment and the calculations for the heat and mass transfer effects. These experiments should provide a clearer understanding of the activity and selectivity.

Project Status

The fabrication of the new fixed-bed reactor system has been completed. The performance tests of the equipment, including the leakage proof of the tubing connection and the functionality of the instruments, were done by use of helium at 1000 psig. An inert packing material (Denstone 57) was tested in the reactor to check the performance of the system and to develop the sampling technique for the product analysis. The results indicated that Denstone 57 has such little activity (e.g., CO conversion < 0.7% at 300°C, H₂/CO = 2/1, 520 psig and 1.18 cm³g⁻¹ sec⁻¹ space velocity) that it will not interact with the Fe-Mn catalyst when it is used for the packing of the catalyst bed.

Four precipitated catalysts were prepared using the coprecipitation method described in the literature.^{2,3} The compositions of the catalysts are pure iron (one catalyst) and 3 Mn/100 Fe ratio (three catalysts). The preparation procedures for these three catalysts with the same ratio are slightly different from one another. The first one was prepared by adding the mixture solutions of iron nitrate and manganous nitrate to ammonium hydroxide. The second one was made by adding iron nitrate solution first to ammonium hydroxide and then manganous nitrate. The third Fe/Mn catalyst was produced using the reverse method of the second catalyst. The gross weight for each of the catalysts was approximately 160 g after oven drying.

Future Work

The catalyst activity and selectivity tests will be performed. The mass balance calculation will be perfected to achieve 97+ weight percent material balances. The optimum catalyst preparation and pretreatment for the maximum production of C₂-C₄ olefins will be investigated. Catalyst characterization studies will be initiated. The literature survey concerning the hydrogenation of carbon monoxide as well as the heat and mass transfer for the fixed-bed reactor will be continued to update the information.

References

1. W.H. Wiser, F.V. Hanson and Y.S. Tsai, DOE Contract No. DE-AC22-79ET14700, Quarterly Progress Report, Salt Lake City, Utah, April - June 1981.
2. C.H. Yang, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1979.
3. Y.S. Tsai, M.S. Thesis, University of Utah, Salt Lake City, Utah, 1980.

V. Conclusions

Detailed Conclusions are included in the reports for each task. Task 4 is no longer funded and has been discontinued. Tasks 12 and 14 are inactive. No work was done under Task 15.