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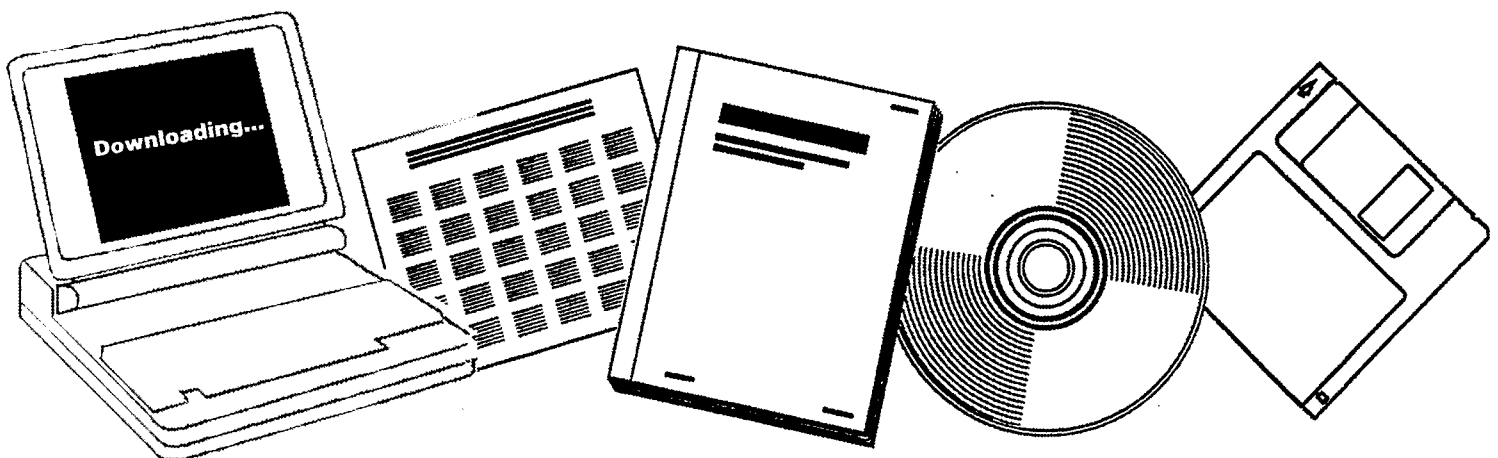
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**APPLIED RESEARCH AND EVALUATION OF PROCESS
CONCEPTS FOR LIQUEFACTION AND GASIFICATION
OF WESTERN COALS. QUARTERLY PROGRESS
REPORT, APRIL--JUNE 1978**

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

JUL 1978



U.S. Department of Commerce
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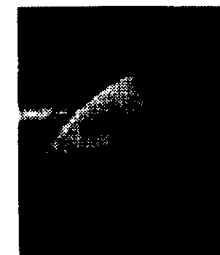
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FE200612



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

Quarterly Progress Report
for the Period Apr - Jun 1978

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II. OBJECTIVE AND SCOPE OF WORK

The research reported herein is all of fundamental importance in support of either a process for development of liquefaction of coal, catalysis or some related research. The information which will be gained by research on this contract should materially assist the application of coal in the solution of the energy problems now facing the United States and the world. In particular, the projects reported herein are intended to apply the expertise developed by the coal research team at the University of Utah to problems in four general areas:

- a) Evaluation of process concepts in relation to liquefaction and gasification of coal,
- b) Catalysis studies of fundamental importance in liquefaction and gasification of coal,
- c) Studies of fundamental principles involved in processes for liquefaction and gasification of coal,
- d) Properties of coal and coal conversion products of significance in liquefaction and gasification of coal.

A-1 Coal will be gasified by direct catalytic hydrogenation to produce a high-BTU gas. A liquid will be produced in a first stage reaction at 400-450°C. This product will be further hydrogenated to produce a high-BTU gas. Catalysts and reaction conditions for each stage will be studied.

A-2 Kinetics, yields and optimum reaction conditions for extraction of coal will be determined. Hydrogen donor solvents, ultrasonic energy, hydrogen pressures and catalysts will be employed. Extraction products will be analyzed and characterized.

A-4 Aromatic liquids derived from coal hydrogenation or extraction will be considered as feedstocks for steam reforming to make a high-BTU gas. Optimum conditions for the production of hydrogen or high-BTU gas, optimum catalysts, the effects of poisons and the degree of coke formation will be determined.

A-6 The gasification of coal char will be studied at 2000-3000 psi to produce hydrogen for coal hydrogenation. Steam and oxygen will be used for gasification. The thermal efficiency of producing hydrogen at the pressure at which it will be used will be studied.

A-7 Thermal hydrogenolysis of coal slurried with recycle solvent will be studied as such or in the presence of a vapor-phase catalyst to determine the extent of upgrading.

- A-8 Fischer-Tropsch synthesis of C₂-C₄ hydrocarbons will be studied. New catalysts will be developed and a continuous test unit for long-term catalyst testing will be constructed.
- A-9 The capacity and durability of a previously developed high-pressure gas recycle pump will be increased. A goal of 3000 psi operating pressure at 500°C is desirable.
- B-1 Adsorption properties and penetration of aromatic molecules on typical cracking catalysts will be determined. These properties will be used to evaluate the ability of such catalysts to crack the large molecules present in coal-derived liquids.
- B-2 (alternate) The mechanism of deactivation of molybdena hydrodesulfurization catalysts by coal-derived liquids will be studied. Kinetic studies involving the model compound benzothiophene will be employed.
- B-3 Hydrogen transfer by metal halide catalysts during coal hydrogenation will be studied. Deuterium labeled hydrocarbons will be used to elucidate reaction mechanisms.
- B-4 The mechanism of catalytic hydrogenation of coal by metal halide catalysts will be investigated. The nature of active catalyst sites will be studied. Changes in properties of the reacting coal will be determined and the nature of reaction products will be determined. Catalyst regeneration will also be studied.
- C-1 The mechanism of pyrolysis of coal will be studied by the use of isotopically labeled model compounds. Products of pyrolysis will be examined to determine their precursors in coal.
- C-2 Fluid mechanics and heat transfer studies involving gas-solid suspensions in vertical downward cocurrent flow systems will be conducted to obtain information on the effect of these variables in the University of Utah coal hydrogenation reactor.
- D-1 The effect of coal and catalyst properties and pretreatment on the hydrogenation of western coals will be studied in the University of Utah short-residence-time, entrained-flow reactor.
- D-2 The effect of coal structure on reactivity to hydrogenation, pyrolysis and dissolution will be studied. Pretreatment of the coal by specific reactions will be used to obtain samples with special structural features.
- D-4 Liquid products from coal hydrogenation in the University of Utah reactor will be separated and characterized. Coal pyrolysis and hydrogenation mechanisms and model compound reactions will be studied.

III Summary of Progress to Date

Research Highlights

This report is a summary of the first three years of progress on Contract No. FE-2006. It also includes a statement of anticipated results for each project. This report was prepared at the request of the Department of Energy.

Publications, Presentations & Activities

H. Itoh, D.M. Bodily and W.H. Wiser, "Structural Analysis of Acid and Base Fractions Produced by Coal Hydrogenation," Japan Chem. Soc., Tokyo, April 4, 1978.

S. Yokoyama, D.M. Bodily and W.H. Wiser, "¹³C Nuclear Magnetic Resonance Spectra of Heavy Oil From High Pressure Coal Hydrogenation," Japan Chem. Soc., Tokyo, April 4, 1978.

R. Pugmire, "Inferences on Coal Structure Based on C-13 NMR Spectra of Coal and Extraction Products," Gordon Research Conference on Fuel Science, New Hampton, New Hampshire, June 27, 1978.

W.H. Wiser, Session Chairman, Gordon Research Conference of Fuel Science, New Hampton, New Hampshire, June 1978.

F. Hanson, Co-Chairman, Catalysis Club of Philadelphia Spring Symposium, Widner College, Chester, Pennsylvania, May 25, 1978.

PROJECT A-1
Catalytic Gasification of Coal to High-BTU Gas

Wendell H. Wiser, Investigator

2 Graduate Students

Objective

Traditional processes for production of high Btu gas from coal involve the introduction of oxygen and steam for the production of synthesis gas, CO and H₂. The oxygen is necessary to react with coal to achieve temperatures of 900°C or higher to accommodate the steam-carbon reaction. The steam-carbon reaction, coupled with a water-gas shift, in turn produces most of the CO and the H₂ for the methanation reaction. In all advanced processes, except the hydrane process, a majority of the carbon finally resulting in methane passes from the reduced state in the coal to the oxidized state in CO, then again to the reduced state in methane or other hydrocarbon. The heat produced in the exothermic methanation reaction cannot be effectively utilized for the strongly endothermic steam-carbon reaction because it is produced at a temperature much lower than that required for the steam-carbon reaction. These phenomena lead to reduced thermal efficiencies. It is of interest to examine the possibility of conducting all of the reactions in the same stage without the introduction of molecular oxygen, in order to avoid the transitions from reduced state to oxidized state then reduced state and to maximize the use of energy produced in the methanation reaction. In such a system the overall reactions are almost thermally neutral. The objective of this work is to evaluate these various factors and to develop and/or test catalysts which may accomplish these objectives. It is desired that temperatures shall not exceed 550°C during any part of the reaction.

Research Results Obtained to Date

Dr. Ying-Hsiao Li completed his Ph.D. thesis while pursuing the direct catalytic hydrogenation in two stages. At the completion of his work, he was using the same catalyst, namely a Ni-Mo catalyst, in both stages. The coal was dissolved in a solvent in the presence of a Ni-Mo catalyst at 480°C and 2,000 psi hydrogen pressure. Conversions in this stage yielded 22% gas, 63% liquid and 15% char. These materials then passed to stage two, again involving a Ni-Mo catalyst, with temperatures at 600°C and hydrogen pressure of 1750 psi. Much of the liquid material was converted to gases with a small amount of additional char produced. The final product distribution based upon the initial coal feed to stage one was 62.5% gases, 9.5% light liquid (gasoline range), 7% middle oil (200°C to 300°C boiling range), 2% heavy oil boiling above 300°C and 19% char. The gas was mostly methane, the methane yield representing 49% of the weight of the coal initially fed. The heating value of the gas, which included some gases in the C₂ to C₄ range, was 1202 Btu per standard cubic foot.

Considering the value of the light liquids and the need for energy input into a liquefaction system which could thereby utilize the char and the heavy liquids, these results appear encouraging. It was, therefore, decided that the possibility of achieving comparable or better results in a single stage at temperatures below 550°C should be investigated. The first task performed with this objective in mind was to prepare a computerized thermodynamic analysis for such a system which would introduce only coal, molecular hydrogen and steam as reactants. Figure 1 is a representation of this equilibrium thermodynamic analysis.

Anticipated Results

At the present time, two graduate students are working on this project. One, a Ph.D. candidate, is working on the engineering aspects of the process development. The second student, a Master's degree candidate, is working on the improvement of the catalyst to enhance the methane yield in the single stage.

Very significant progress is now being made in the direction of high methane yield in a single stage. We do not yet have reportable results because experimental difficulties are still being encountered which require attention to overcome them. We are very optimistic about the technological potential of this approach to pipeline gas from coal. It remains to be seen whether the economics of this approach will be attractive.

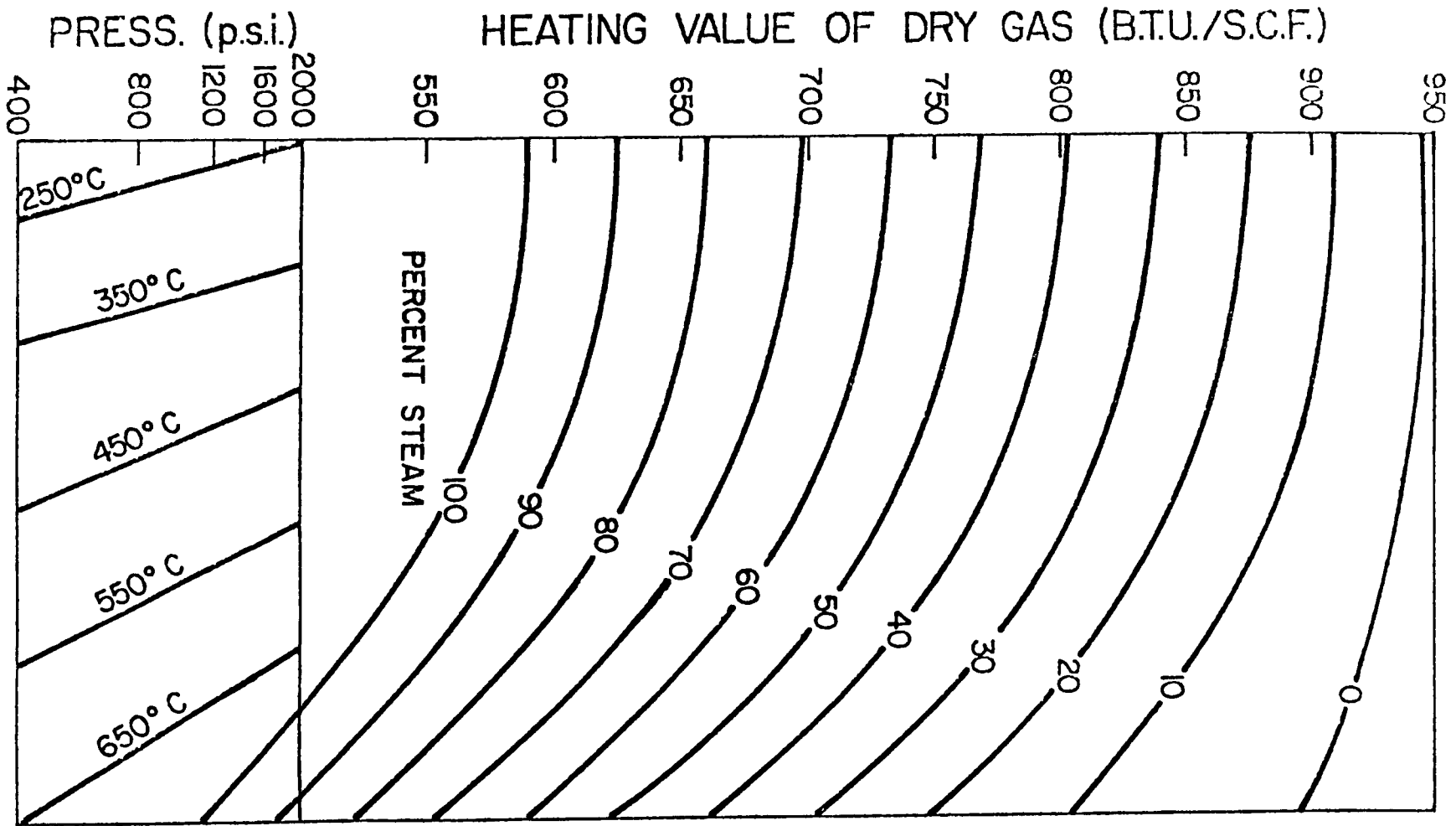


Figure 1

PROJECT A-2

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

Larry L. Anderson, Investigator

4 Graduate Students

Objective

Due to extensive research and some process development on several methods of liquefying coal by solution, there is a need for understanding the chemistry and specific products of such reactions. This project has as its objective to ascertain as completely as possible the reactions between coals (especially bituminous coals) and hydrogen donor solvents. As part of this objective, the reactions which the solvent experiences at reaction conditions are being studied. The reactions of coal by hydrogenation in tetralin or other H-donor solvents is being studied both as to extent of reaction at subcritical temperatures and the nature of products produced. Special conditions of reaction are being studied such as the use of ultrasonic energy, specific catalysts, etc. to determine their effects on the kinetics of the reaction, the yield of product and the chemical nature of coal-derived materials produced by the reactions.

Research Results Obtained to Date

The kinetics of solvent extraction of two high volatile bituminous coals, Utah (Hiawatha) and Kentucky (#14), have been studied. Data have been published on the yields, rate of extraction (at temperatures up to 400°C), and the consumption of hydrogen at various conversion levels. Using Hiawatha, Utah coal and tetralin (1:9), over 80% of the maf coal is converted to pyridine soluble material at 400°C with less than 3.0% hydrogen added. Kentucky #14 reacts slower and produces products different from those obtained from Western high volatile coal of similar rank. These data were not available in the literature for such reactions at very short residence times (down to six seconds) in a differential reaction system. The system used was designed and operated as part of this project.

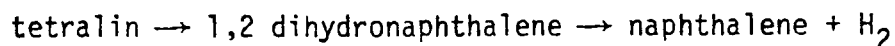
Results from hydrogen donor extraction using tetralin as a solvent have been obtained which show the solvent does not participate in initial reactions. The initial reactions were found to be thermal rupture of bonds resulting in high molecular weight (700 to over 900 depending on the feed coal) products. These primary products subsequently reacted with the donor solvent or gaseous

hydrogen to produce smaller molecules. At least two reaction regimes were observed and studied as to the chemical types of compounds produced, the size of the molecules and the hydrogen required for the reactions.

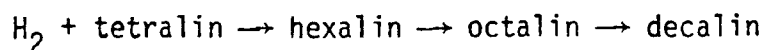
Extensive analytical work has been done on the extraction products to determine the elemental composition of the various fractions (benzene soluble-hexane insoluble, hexane soluble, pyridine soluble-benzene insoluble), the important functional groups in the products and the stability of these products. Ultimate analyses (carbon, hydrogen, oxygen, sulfur, and nitrogen) have been obtained as well as molecular weight, functional group by infrared and ultra-violet spectroscopy, proton nuclear magnetic resonance, carbon-13 magnetic resonance and routine gas chromatographic analyses have been obtained. The results of these studies are useful in the determination of the nature of the reactions taking place as well as the fundamental properties of the feed materials, particularly coal. For example, the significance of oxygen bonding in coal and primary coal-derived products appears now to be vital in understanding not only the process of solvent extraction (or solvent refining) but all conversion reactions involving coal. At least some of the types of oxygen bridges present in coal derived liquids (CDL) that are primary products are present in the feed coal. Identification of such bonding groups may be used to select more effective solvents or permit the use of specific catalysts which may make liquefaction or gasification of coal easier, more efficient, or capable of producing entirely new kinds of products.

Kinetic studies using tetralin as a solvent have shown that the solvent is changed by the extraction process. The reactions which tetralin undergoes include:

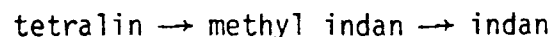
1. Dehydrogenation



2. Hydrogenation



3. Isomerization



All of these reactions have been observed in the experiments conducted on this project. The information on the rate of the reactions involved, as well as the conditions of such reactions when extracting coal, have been made available. These results will be useful for those involved in the solvent extraction or refining of coal and maintaining solvent reactivity for the process.

The change in properties of CDL's under conditions of temperatures up to 400°C and under hydrogen and nitrogen atmospheres has been studied. Results indicate that aromaticity increases with time for these liquid products while molecular weight, oxygen content and the quantity of certain heterocyclic and function groups decreases with time. The value of the molecular weights of CDL's from different coals was found to be significantly different. The reactivity of CDL's from different coals was also observed.

PROJECT A-4

Steam Reforming of Aromatics

Alex G. Oblad, Investigator

1 Graduate Student

Objectives

The processes which are presently used to produce synthesis gas or hydrogen are steam reforming of methane and heavier paraffinic hydrocarbons contained in light naphtha. Conditions for methane are pressures to 500 psi, steam to methane mole ratio of 2-4, temperatures to 850°C and nickel supported on high alumina cements as a catalyst. In light naphtha reforming, M.W. Kellogg and ICI developed an alkali promoted nickel on calcium aluminate-alumina catalyst that works very well without carbonization. In the case of light naphtha, reforming is not possible without the alkali promotion. Variations of the naphtha steam reforming process have been used extensively to make a high Btu gas known as town gas. This gas contains as much as 65% methane as well as CO, H₂ and CO₂.

Naphtha steam reforming is successful and depends on the composition of the catalyst and selection of the feed stock which is low in naphthenes and very low in aromatics. As a matter of fact, catalyst activity in naphtha reforming can be detected by aromatics in the products. Thus, aromatics are known to be difficult to reform with steam.

Again, alternative ways of producing synthesis gas from coal are commercially available and substantial effort is underway to improve coal gasification. Presently most effort is going into coal gasification using partial oxidation, the reactants being steam and oxygen. This requires the production of oxygen which is a large item of investment and operating cost in coal gasification.

Considering this background information, we are carrying out an extensive program on steam reforming of aromatic compounds such as benzene, substituted

benzenes, naphthalene, tetralin and phenanthrene. Our objective is to determine the effects of the main variables on the reaction; temperature, pressure, contact time and steam/aromatic ratio,

1. to develop a catalyst of suitable activity and sufficient life for these reactions (sulfur resistant),
2. to determine reaction mechanisms, and
3. to determine kinetics of the reactions.

These data will be important for understanding coal gasification and showing directions for improvement of this process and more importantly could lead to simpler coal gasification schemes. As an example of the latter, it is very probable that much improved coal liquefaction processes will be developed in the near future. Liquids from such a process would then be available for steam reforming by the techniques and catalysts developed in our present program. Potentially, coal liquids could be reformed directly in a single step to high Btu gas just as is presently done in the town's gas process with naphtha.

Research Results Obtained to Date

Where do we stand in this development? We have assembled a flexible, relatively simple apparatus in which to carry out our studies. Runs have been made with methane, methanol and ethanol to check out the reaction system, our product recovery and analytic procedures. Our results with methane check well with literature data showing that our systems are satisfactory. The data with methanol and ethanol are new and will be published. If and when methanol and ethanol or other alcohols become available as important fuels, simple steam reforming will readily convert these to synthesis gas or hydrogen.

We are presently engaged in developing a catalyst for aromatic reforming. We have determined that benzene and toluene can be reformed without deposition of coke with an alkali promoted nickel on cement catalyst but the catalyst composition and properties must be optimized in future work. We have found that we can reform aromatics to a gas having heat contents as high as 450 - 500 Btu/ft³. We are very encouraged by these findings.

Anticipated Results

Future work will be concerned with developing a catalyst having activity equal to naphtha reforming catalysts and equivalent stability. Promising

catalysts will be used in determining the effects of the important variables such as temperature, pressure, contact time, steam/hydrocarbon ratio on the steam reforming reactions. The effects of sulfur poisoning on the steam reforming catalysts selected for study will be determined.

Finally, the kinetics of steam reforming as a function of aromatic structure will be determined for selected catalysts. The data in total will then be used to outline optimum processes for the reforming of aromatics to high Btu gas and hydrogen and to suggest new process concepts for converting coal to gas.

Conversion of Coal Oils to Gasoline In a Fluidized Bed

Alex G. Oblad, Investigator
1 Graduate Student

Objective

The objective of this work was to determine the feasibility of vapor-phase fluidized-bed hydrocracking of potential commercial feedstocks obtained from coal, petroleum, tar sands, bitumens or oil shale. Vapor-phase fluidized bed operation has several advantages over the conventional fixed-bed operation. Some of these are:

1. Minimization of diffusional effects in mass transfer of reactants and products to and from the catalyst surface through use of smaller catalyst particle sizes.
2. Control of catalyst activity level by continuous withdrawal-injection of catalyst to and from the reactor.
3. Better control of reactor temperature.
4. Operation at lower pressures.

Research Results Obtained to Date

A bench-scale continuous 1" I.D. fluidized bed reactor system was built for this feasibility study. A coal and oil fraction (250 - 412°C) from Synthoil and a petroleum catalytic cycle oil (250 - 342°C) were processed as feed. The catalyst was a commercial nickel-tungsten oxide supported on silica-alumina ground to 49.8 micron size.

Many parameters of the fluidized regime under anticipated operating pressures were studied prior to operation with feed and these data were correlated

with known fluidization data obtained at atmospheric pressure. The minimum-fluidization velocity studies at high pressure conditions indicate a smooth transition from the fixed-bed to the fluidized state and an absence of channeling and slugging in the operating range studied.

The effect of pressure, temperature and contact time on conversion were determined. In the operating range of this study, the feedstocks allowed a smooth and stable operation of the fluid-bed without agglomeration of the catalyst particles.

For the ranges of parameters studied regarding fluid-bed hydrocracking of the cycle oil feedstock, the mode of gas/solid contacting appears to be plug-flow as the overall hydrocracking reaction at constant pressure fits pseudo-first-order kinetics, assuming a plug-flow regime. The coke formation reaction for the hydrocracking of the cycle oil in the fixed-bed reactor (at 1250 and 1500 psig) and in the fluid-bed reactor (at 1000, 1250 and 1500 psig) fits the concentration-independent first-order decay rate law.

The apparent activation energy of the hydrocracking of the cycle oil in the fluidized bed, using fine catalyst particles, ranges from 14.6 to 17.0 kcal/mole. This suggests that the chemical reaction is the rate limiting step.

Pore-diffusional effects due to coke formation on bigger catalyst pellets were observed by comparing the conversion data obtained by hydrocracking the cycle oil in the fixed-bed (using 1/12 inch catalyst pellets) with those obtained, under identical conditions, in the fluidized-bed (using 49.8 microns catalyst particles). After a certain catalyst on-stream time, higher product yields are obtained for hydrocracking in the fluid-bed using fine catalyst particles as compared with fixed bed operation using 1/12 inch pellets.

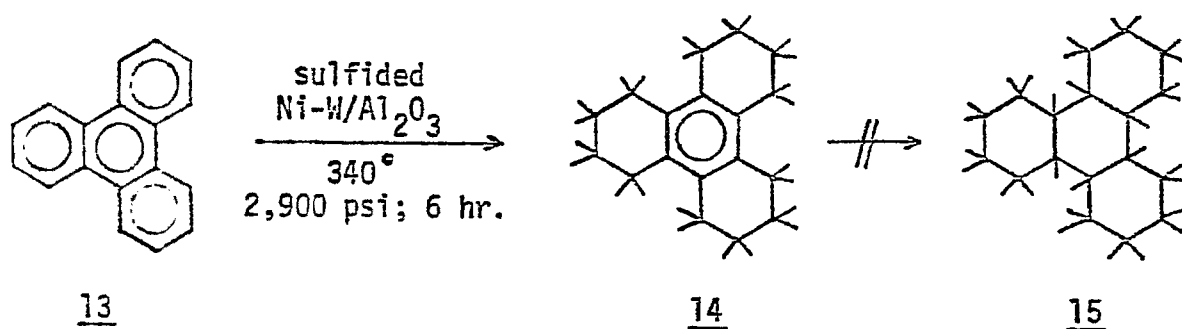
The rate data for the fluidized bed hydrocracking of the coal-oil fraction does not follow pseudo-first-order kinetics assuming a complete mixing flow mode.

Vapor-phase fluidized bed hydrocracking and hydrotreating appear to be very attractive alternatives to both fixed-bed and ebullating bed for upgrading CDL and other hydrocarbon liquids.

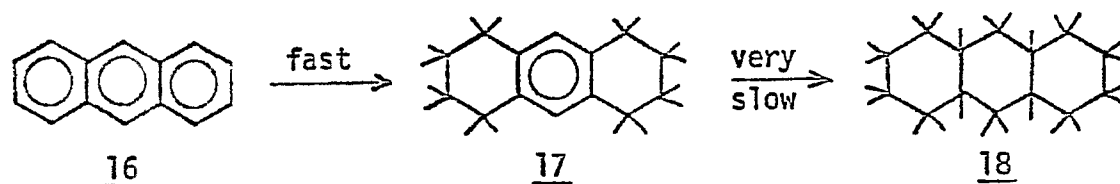
Anticipated Results

The results of this study were sufficiently promising that additional studies are warranted. These will be concerned with: (a) application of the process to hydrotreating for removal of S and N from CDL and (b) hydrogenation

was also investigated. It is found that hydrogenation of the peripheral rings in 13, to give dodecahydrotriphenylene (14) is fast, but subsequent hydrogenation of the residual central aromatic ring in 14 to give perhydrotriphenylene (15) does not occur to any important extent, even under drastic experimental conditions:



Anthracene (16), which is a suitable representative compound of the class of condensed linear arenes, was also systematically investigated. It is found that stepwise hydrogenation of 16, leading to formation of 1,2,3,4,5,6,7,8-octahydroanthracene (17) is a fast reaction, but subsequent hydrogenation of the middle ring in 17, to give perhydroanthracene (18) is a very slow step (catalyst, sulfided Ni-W/Al₂O₃; temperature, 300 - 340°C; hydrogen pressure, 2000 - 2900 psi):



The rate of hydrogenation of 17 to 18 is found to be much lower than that of the corresponding hydrogenation of octahydrophenanthrene (4) to perhydrophenanthrene (1) (*vide supra*). This may be due to steric hindrance for adsorption of 17, involving either a flatwise or edgewise orientation of the residual aromatic ring.

Results obtained in the above studies show the following important limitations for hydrogenation of polycyclic arenes in the presence of conventional sulfided catalysts: (a) For non-linear condensed arenes, hydrogenation of tetrasubstituted aromatic rings is a sterically hindered, slow process. Further, fully substituted (hexasubstituted) aromatic rings show strong resistance to hydrogenation; (b) For linear condensed arenes, hydrogenation of residual tetrasubstituted aromatic rings (flanked by two hydroaromatic rings) is a very slow process.

The results obtained provide a plausible explanation for the observed resistance of coal-derived liquids to complete hydrogenation in the presence of conventional sulfided catalysts (vide infra, paragraph C), even in case the aromatic saturation equilibria are fully displaced in the direction of saturation. The results also indicate the necessity of a systematic structural-activity study of sulfided catalysts at the molecular level, with the specific ultimate objective of designing and optimizing catalysts of this and related types for coal-liquid upgrading, including hydrogenation of polycyclic arenes. (A research proposal on this subject is being prepared in collaboration with Dr. F. Massoth.)

B. Study of metal sulfide-catalyzed hydrogenation-hydrodenitrogenation of condensed N-heterocyclics as a function of molecular structure and experimental conditions. The study provides basic information on the relative rate, mechanism, and stereochemistry of hydrodenitrogenation of structurally distinct multiring (ring number ≥ 3) N-heterocyclics, found as typical components of coal-derived liquids. Following is a short summary of results reported² so far:

Marked differences are observed in comparative high pressure (500 - 2,900 psig) hydrogenation of 5,6-benzoquinoline (1) and 7,8-benzoquinoline (2) in the presence of sulfided Ni-W/Al₂O₃. The first reaction step, involving hydrogenation of the pyridine ring, is faster by at least one order of magnitude with 1 as compared with 2. This can be attributed to the steric effect of the 7,8-benzo group, which prevents edgewise adsorption of 2 through the pyridine nitrogen. In contrast, such adsorption, which could polarize the pyridine ring and facilitate hydrogenation, is easily attained with 1. In the subsequent reaction step, the intermediate from 2, viz. 1,2,3,4-tetrahydro-7,8-benzoquinoline (3), undergoes direct hydrodenitrogenation to yield 6-n-propylnaphthalene (4). In contrast, the intermediate from 1, viz. 1,2,3,4-tetrahydro-5,6-benzoquinoline (5) undergoes essentially complete hydrogenation of the end benzene

ring to form 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline (6). prior to the hydrogenolysis step. The latter ultimately yields 5-n-propyl-1,2,3,4-tetrahydronaphthalene (7). The direct hydrogenolysis of 3 is apparently due to the destabilizing steric effect exercised by the peri H-atom at C-14 upon the C-N bonds in the hydrogenated pyridine ring.

The strong influence of steric effects, mode of adsorption, and catalyst surface structure, upon the rate and direction of hydrodenitrogenation is clearly evident also with other model compounds, e.g. 1,10-phenanthroline and phenanthridine, which are presently under investigation. Results obtained strongly indicate the necessity of continued studies of catalytic hydrodenitrogenation at the molecular level, in order to acquire sufficient basic knowledge for designing specific hydrodenitrogenation catalysts for coal-liquid upgrading (vide infra, paragraph C).

C. Study of metal-sulfide catalyzed hydrogenation of coal-derived liquids.

The hydrogenation of Synthoil and fractions derived from Synthoil was systematically investigated (in a specially designed fixed bed flow reactor) as a function of experimental variables, e.g. process time, temperature, pressure, hydrogen/substrate ratio, and space velocity. The indicated optimal conditions for hydrogenation of Synthoil, as reflected in the depth and selectivity of the process, are as follows: 340°C, 2900 psig, and LHSV = 0.5 hr⁻¹ (catalyst, sulfided Ni-Mo/Al₂O₃). At temperatures > 350°C, the hydrogenation selectivity is lower due to side reactions, in particular cracking. It is found that even under the above indicated optimal conditions the hydrotreated product contains 15-20% of residual aromatic rings, while the nitrogen content is reduced to ~30% of its original value in the feedstock. Since under such conditions the aromatic saturation equilibria of polycyclic arenes are displaced in the direction of saturation,³ it is concluded, in line with results obtained with model compounds, that the resistance to complete hydrogenation of coal liquids is probably due to the presence of sterically hindered aromatic rings in certain multiring components. Likewise, sterically hindered N-containing rings could account for the observed resistance to complete hydrodenitrogenation. Results obtained indicate that conventional sulfided catalysts are not sufficiently active and/or structurally adapted for effecting complete saturation and/or exhaustive hydrodenitrogenation of coal liquids.

The hydrogenation of maltene (cyclohexane-soluble) and asphaltene-preasphaltene (cyclohexane-insoluble) fractions from Synthoil were also systematically studied in the presence of sulfided Ni-Mo/Al₂O₃. It is found that

the maltene fraction undergoes hydrogenation to a considerable depth (residual H-aromaticity, 8 - 8.5%) at 340°C and 2900 psig, whereas the asphaltene-preasphaltene (A-P) fraction shows markedly higher resistance to hydrogenation (residual H-aromaticity, ~28%) under the same set of conditions. This difference can be ascribed in part to the higher complexity and proportionally higher concentration of sterically hindered inner rings in polycyclic systems found in the A-P fraction. For instance, in a hexacyclic system such as dibenzo[d,h]chrysene the two completely substituted inner rings represent 33.3% of the total condensed system. The extent of hydrogenation of the A-P fraction could be somewhat increased (residual H-aromaticity, ~25%) by increase in reaction temperature to 380°C, but this seems to be close to a limiting value with conventional sulfided catalysts. The important observation is also made that the solubility of the hydrotreated A-P fractions in cyclohexane increases sharply with decrease in H-aromaticity and heteroatom content [solubility, wt. %: 34(34), 74(28), 85(25), numbers in parentheses giving the percentage of residual H-aromaticity].

The main achievements of project (1), at this stage, could be summarized as follows:

A. The catalytic hydrogenation of a typical coal liquid, using a flow pressure system, was systematically investigated and optimal operating conditions determined.

B. The relative rate, direction and stereochemistry of hydrogenation and hydrodenitrogenation reactions of model multiring compounds were systematically investigated. The results obtained serve as a basis for a thorough understanding of the chemistry and kinetics involved in hydrotreating of coal liquids, and provides a well founded explanation for the observed resistance of such liquids to complete hydrogenation and hydronitrogenation.

C. The inability of conventional sulfided Ni-Mo/Al₂O₃, Ni-W/Al₂O₃, and Co-Mo/Al₂O₃ catalysts to effect exhaustive hydrodenitrogenation and saturation of coal liquids has been clearly demonstrated. It is deduced, that future progress in solving this problem would require (a) continued systematic hydrogenation and hydrodenitrogenation studies at the molecular level; (b) systematic structural - activity studies of sulfided catalysts, in conjunction with (a); and (c) design and optimization of sulfided catalyst systems for specific applications in coal liquid upgrading, on the basis of information obtained in (a) and (b).

Project 2. Catalytic Cracking of Hydrogenated Coal Liquids and Related Polycyclic Naphthenes.⁴

In spite of the great industrial importance of catalytic cracking processes, there are relatively insufficient molecular-level data on the variation of product composition as a function of catalyst type, type of feedstock, and operating conditions. This is particularly true in regard to catalytic cracking of polycyclic naphthenes, as essentially no data are available on the exact structure of product components even from simple bicyclic naphthenes, e.g. decalin. Since hydrogenated coal liquid feedstocks consist mostly of polycyclic naphthenic components, detailed information on the behavior of the latter type of compounds under cracking conditions is a prerequisite in developing and optimizing a catalytic cracking process for such coal-derived feedstocks. Accordingly, research project (2) is concerned with the following interrelated subjects:

A. Systematic catalytic cracking studies of model polycyclic naphthenes found in hydrogenated coal liquids, i.e. decalin, perhydrophenanthrene, perhydroanthracene, and perhydropyrene;

B. Systematic catalytic cracking studies of hydrogenated coal-liquid feedstocks.

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

Results obtained with conventional cracking catalysts (e.g. Mobil Durabead) show that polycyclic naphthenes or hydrogenated coal liquids are excellent feedstocks for catalytic cracking, yielding primarily light liquid products. For example, in the mild temperature range of 350 - 450°C, and conversion levels of up to 80%, decalin yields 75 - 90 wt. % of light liquids and only 10 - 25 wt% of gaseous products (mainly C₃ - C₄ components). The liquid

*A research proposal specifically concerned with the future development of large-pore CLS catalysts for upgrading of coal liquids was submitted to the Department of Energy in November 1977 by A. G. Oblad, J. Shabtai, and W. H. Wiser.

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

The main achievements of project (2), at this stage, are as follows:

A. The studies are providing basic information on the catalytic cracking behavior and potential of hydrogenated coal-derived liquids (hydro-CDL);

B. It has been demonstrated that polycyclic naphthenes and hydro-CDL are excellent feedstocks for catalytic cracking under mild operating conditions, yielding mainly light liquid products, with relatively little concurrent gasification. It is indicated that, due to their unusually high content of hydroaromatic ring structures, hydro-CDL feedstocks are superior to conventional cracking feedstocks, which usually contain lower proportions of hydroaromatic components.

C. Considerable experimental support has been obtained concerning the feasibility of applying a hydrogenation-catalytic cracking process sequence for upgrading of coal liquids.

Project (3). Hydropyrolysis of Coal-Derived Liquids and Related Model Compounds.

This project is at an advanced stage of investigation and has already led to the development of a new process concept for upgrading of coal liquids and other heavy crudes or fractions. As indicated in section I, this new approach involves application of hydropyrolysis, which can be described as hydrogen-modified thermal cracking, for conversion of heavy coal liquids or semi-solids into light liquid products, and/or $C_2 - C_4$ gases. The study has included so far the following subjects:

A. Construction of a flow reactor system specifically designed for controllable, quantitative hydrolysis of heavy liquids under pressures of up to 3,500 psi.

B. Hydrolysis of model compounds, e.g. n-paraffins, polycyclic naphthenes, and polycyclic naphthenic-aromatic systems.

C. Hydrolysis of coal liquids and other heavy crudes or fractions.

Following is a short description of developments and typical results:

A. The hydrolysis reactor is basically different from previously described flow systems for study of thermal reactions. Its novel features, which provide an efficient answer to the essential requisite of temperature uniformity, have been described in detail elsewhere.⁵

B. In this section of the project the product composition obtained from hydrolysis of structurally distinct model compounds is systematically investigated as a function of experimental conditions. All studies are performed in comparison with thermal cracking under nitrogen pressure.

Following are some typical results obtained with n-hexadecane (1) and decalin (2):

In the entire temperature range (500 - 600°C) and pressure range (500 - 2,250 psi) studied, the rate of hydrolysis of 1 is markedly higher as compared to the thermal cracking rate of the same compound under nitrogen. Further, unlike thermal cracking, hydrolysis is an easily controllable process, which by proper selection of temperature, hydrogen pressure and contact time, can be operated for preferential production of any desired molecular weight range lower than that of the starting material. For example, at 525°C and a hydrogen pressure of 1,000 psig, hydrolysis of 1 yields mainly (~55% b.wt.) of C₅ - C₁₂ liquid products, whereas at 575°C and a pressure of 2,250 psig 1 is converted almost entirely, viz. 92% by wt., into C₁ - C₄ gaseous products (methane formation is low, and C₂ - C₃ hydrocarbons comprise 76% of the total gas product). Variation in experimental conditions affects also the structural type distribution of the products. For a given pressure, 1-olefins decrease, while paraffins and internal olefins increase in concentration (and ultimately tend toward a stable level) with increase in temperature. Further, for a given temperature, the concentration of paraffins increases, while that of 1-olefins quickly decreases with increase in pressure; internal olefins increase slightly and then remain at a stable level with increase in pressure. Results obtained in the systematic study of 1 provided a basic understanding of the hydrolysis

processes and allowed for the outlining of a chain mechanism which involves formation and participation of hydrogen atoms in the propagation step of the reaction.

While the study of 1 and other n-paraffins led to the necessary mechanistic elucidation of hydrolysis, the systematic investigation of 2 provided basic information on the reaction patterns of the more important class of polycyclic naphthenes. It is found that the product composition from hydrolysis of 2, and its change as a function of reaction variables, is markedly different compared to that from 1, as illustrated by the following data: (a) liquid ($C_5 - C_{10}$) products are strongly predominant (yields 60 - 95% by wt.) between 500 - 600°C; correspondingly, the relative yield of $C_1 - C_4$ products is much lower compared to that from 1 under identical conditions; (b) at 500 - 525°C, practically the only products from 2 are C_{10} alkylcyclohexenes and 1,2,3,4,5,6,7,8-octahydronaphthalene; between 525 - 600°C, these primary products gradually evolve into lower ($C_6 - C_8$) cyclohexenes and $C_5 - C_8$ open-chain (mainly branched) hydrocarbons, and to a small extent into $C_6 - C_8$ arenes; the conversion temperature of the initial products into lower ($C_5 - C_8$) liquid products can be reduced by an increase in the operating hydrogen pressure; (c) under any set of identical operating conditions thermal cracking of 2 under nitrogen proceeds with much lower overall conversion and with formation of large amounts (10 - 40% by wt.) of high boiling condensation and aromatization products (in comparison, no products higher than the feedstock are found in hydrolysis of 2).

C. Hydrolysis of Coal Liquids and Some Heavy Crudes

Hydrolysis studies are being carried out, using the following types of feedstocks:

1. Synthoil - characterized as a mostly aromatic coal liquid;
2. Asphalt Ridge (Utah) tar sand bitumen -- a highly naphthenic crude; and
3. Altamon (Utah) crude -- a highly paraffinic solid material.

Results obtained so far show that hydrolysis (in the range of 450 - 515°C and a hydrogen pressure range of 250 - 1500 psig) is a very efficient process for conversion of such heavy feedstocks into light liquid products. This is illustrated by the following examples:

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

2. Asphalt Ridge tar sand bitumen, which is a solid material distilling only to the extent of 40% by wt. up to 530°C, is hydrolyzed at 500°C and a hydrogen pressure of 1,500 psig to yield 17% of gaseous products and 83% of a light oil distilling between 105 - 450°C; at 525°C and 1,500 psig the yield of light oil, distilling between 30 - 400°C is 73% by wt.

3. Altamon crude, which is a solid material distilling to the extent of 90% between 160 - 450°C (as determined by simulated distillation) is hydrolyzed at 550°C and a hydrogen pressure of 1,000 psig to yield 75% of a light liquid product distilling between 30 - 350°C; at 575°C and a pressure of only 250 psig the yield of light liquid, distilling between 50 - 400°C, is 71% by wt.

The main achievements of project (3), at the present stage, are as follows:

(a) The high efficiency and versatility of hydrolysis in conversion of heavy coal liquids into light liquid products and/or C₂ - C₄ gases has been demonstrated. This provides a new process concept for upgrading and utilization of coal liquids;

(b) The mechanism of hydrolysis has been elucidated by systematic studies with model compounds. This allows for multipurpose application of hydrolytic processes with a considerable degree of predictability;

(c) Data on the hydrolysis of coal liquids and related model compounds are being submitted for patenting.

Remarks

1. Intensive studies in the framework of the above described three projects will be continued until the end of the present research contract (May 31, 1979). It is expected that during the remaining period it would be possible to accomplish the following:

(a) Accumulate sufficient basic information on the hydrogenation-catalytic cracking sequence, as devised for upgrading of coal liquids, and possibly submit this process scheme for examination and evaluation by interested factors;

(b) Accumulate additional basic data on the feasibility of hydrolysis as a process for coal liquid upgrading, and submit these data for possible commercial evaluation by interested factors.

2. Additional major equipment -- a research grade gas chromatograph is needed in order to increase the efficiency of the present research effort.

3. It would be very undesirable to try and complete the above described projects at a date earlier than July 1979. In effect, it would be very important to continue part of these studies in the framework of a renewed contract.

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PROJECT A-8

Synthesis of Light Olefins From CO and H₂

Alex G. Oblad, Investigator
Frank E. Massoth, Investigator
Francis V. Hanson, Investigator
Scott W. Cowley, Investigator
5 Graduate Students

Objective

Since 1974 we have been engaged in studying the production of light hydrocarbons C₂-C₄, particularly olefins, from CO and H₂. We reasoned that present starting materials for making these important petrochemical intermediates would become scarcer in the future and that substitute sources would have to be developed. This transition has become apparent in recent years as heavier feedstocks such as gas oils and whole crudes are now being used as source materials for C₂-C₄ olefin production in place of ethane, propane, natural gasoline, and light and heavy naphthas. Fischer-Tropsch synthesis has been looked upon as a substitute source of light olefins but indirectly through synthesis of gasoline-boiling materials followed by conventional cracking of these to light olefins. It seemed worthwhile to begin studies on the direct synthesis of light olefins from CO and H₂ which has not been the main interest in previous Fischer-Tropsch work.

A second objective is to supplement the high pressure reactor studies by detailed examination of the catalyst properties which enhance catalyst activity and selectivity. This is accomplished by characterization studies performed on the same catalysts which have been run in the reactor. Work thus far has concentrated on the $\text{CoCu/Al}_2\text{O}_3$ catalyst which has shown some potential for producing low molecular weight hydrocarbons.

A third objective of this study is to supply detailed information about the surface mechanism for the selective formation of $\text{C}_2 - \text{C}_4$ hydrocarbons. An understanding of the surface reaction and kinetics involved can provide valuable information in the development of effective catalysts, rather than relying on the time consuming trial and error technique.

Research Results Obtained to Date

Very adequate testing apparatus, catalyst preparation techniques, and analytical methods have been developed and large numbers of potential catalysts have been synthesized and tested for direct synthesis of light olefins from CO and H_2 . These have included cobalt, nickel, iron, thoria, copper, manganese, molybdenum, zinc, chromium and others as metals or oxides where stable, and as combinations. Our catalysts mostly have been prepared by coprecipitation methods. We have tried impregnation on alumina and silica-alumina. The impregnated catalysts do not appear as active as the coprecipitated catalysts. In this work we have found catalysts which give better than 50% yields of $\text{C}_2 - \text{C}_4$ hydrocarbons (basis: CO converted) with olefinic contents better than 75%. The best catalysts are promoted cobalt and iron. The effects of various promoters such as K_2O , Al_2O_3 , CaO , MgO on metallic catalysts, particularly iron, have been investigated. Some of these materials have important effects on iron. We have indications of means to control CO_2 formation as a product rather than water.

Techniques were developed for measuring the extent of reduction and metal area present. It was found that H_2 pretreatment of the oven-dried catalyst was necessary to achieve reasonable metal areas. Furthermore, a low temperature hold in H_2 during pretreatment gave even better metal dispersions. A synergistic relationship was discovered in that metal dispersions for the composite catalyst were significantly higher than for the simple component catalysts; cobalt helped to better disperse the copper while copper aided in reduction of the cobalt to the active state. Catalyst activities correlated well with total metal area as measured by oxygen chemisorption. Product

selectivity to $C_2 - C_4$ was shown to be related to the reduced Cu/Co ratio, being a maximum at about Cu/Co = 3.

Any conclusions about a surface reaction mechanism depend upon the amount of information available. Since there are no direct methods of observing a surface reaction, this information must come from: (1) a complete knowledge of the reactants and products; (2) knowledge of the reaction kinetics and (3) knowledge of the effects of changes in the reaction environment upon the reaction products and kinetics. The use of isotopically labeled and non-labeled intermediates provide detailed information about important reaction pathways. The use of a gradientless flow reactor ("Berty" reactor) will allow rate data to be obtained directly and at conversions high enough to observe intermediates with ease.

Anticipated Results

With a wealth of attractive catalysts available, future work will be concerned with determining the best reactor systems for light olefin synthesis. The effects of the main variables on the reactions will be determined and catalyst life and regeneration will be studied on our most promising catalysts. We plan to investigate a fluid bed reactor, a catalyst slurry reactor system, as well as fixed bed with inter-stage cooling as reactors.

While this work is underway, work on catalyst preparation and optimization will be continued so that in another year or so we will have available a process and catalyst ready for further development on a pilot plant scale. We are very much encouraged by our work, and we expect this progress to continue.

Current work on the $CoCu/Al_2O_3$ catalyst is concentrating on the nature of the synergistic effect in an attempt to identify whether an alloy or metallic bicluster is present. A special infrared cell has been devised for this purpose. In addition, the nature of the active surface will be investigated by temperature-programmed desorption measurements. These, together with some selective chemisorption measurements, should provide valuable insight into the nature of the active species.

Catalyst characterization studies have just started on iron-based catalysts. These catalysts have been found to be even better than the $CoCu/Al_2O_3$ catalyst for selective reaction to $C_2 - C_4$ products, giving better olefin yields. Similar techniques as have been developed in the $CoCu/Al_2O_3$ catalyst study will be applied here. Additional techniques will also be developed for characterizing the iron-based catalysts, including ESCA, electron microscopy

and reflective spectroscopy. These studies will be compared to catalyst activity in an effort to identify active phases and measurement of active sites.

The work on the $\text{CoCu/Al}_2\text{O}_3$ catalyst will be essentially completed by the end of the current contract period. The work on the iron-based catalysts will only reach a preliminary stage by the end of this period.

The construction of equipment for the surface mechanism studies is nearing completion. The initial testing of the equipment and preliminary experiments will be made in the very near future. It is important to understand what catalyst functions are responsible for the selective formation of $\text{C}_2 - \text{C}_4$ hydrocarbons. It is desirable to have large olefin to paraffin product ratios. The goal of this study is to obtain information about the intermediates responsible for initial olefin formation and to establish the fate of $\text{C}_2 - \text{C}_4$ olefins over selected catalyst by the conclusion of this contract.

PROJECT B-1

Development of Optimum Catalysts and Supports

Frank E. Massoth, Investigator

2 Graduate Students

Objectives

This project involves assessing diffusional resistances of large multiring aromatics (as might be found in coal-liquids) with amorphous-type catalyst pores.

Research Results Obtained to Date

When molecular dimensions approach pore size diameters, the effectiveness of the catalyst is significantly reduced owing to mass transport resistance. The first phase of this project involved development of experimental and analytical techniques to measure the diffusion of chrysene in two commercial aluminas. This was accomplished by continuous monitoring of the adsorption of chrysene from a solution heptane. The continuity equations describing the combined processes of adsorption and diffusion were solved for two limiting cases. The experimental data correlated well with a model based upon rapid, irreversible adsorption. Effective diffusivities were found to be higher than predicted based on simple diffusion theory. A surface diffusion contribution was postulated to account for the higher diffusivities.

The second phase of this project extends the study to larger molecules and smaller pore catalysts. It was found that the surface diffusion contribution decreased with increased molecular size. Preliminary data indicate a

possible restricted diffusion rate for the largest molecule tested in the catalyst having the smallest pore diameter.

Anticipated Results

By the end of the current contract period, we hope to confirm the restricted diffusional effect of large molecules. Also, we expect to develop a better understanding of the apparent surface diffusion effect encountered in these systems.

The ultimate objective of developing quantitative relationships between diffusional flow and molecular and catalyst pore size cannot be completed in this contract. Several years more effort is anticipated to reach this goal.

PROJECT B-2

Effect of Poisoning on the Desulfurization Activity of Cobalt Molybdate Catalysts

Frank E. Massoth, Investigator
1 Graduate Student

Objectives

Cobalt molybdate catalysts are currently being studied for hydrodesulfurization and liquefaction of coal slurries and coal-derived liquids. These complex feeds result in rapid catalyst deactivation. This project aims to gain an insight into the deactivation mechanism by detailed kinetic studies of benzothiophene hydrodesulfurization before and after addition of various poisons and coke precursors.

Research Results Obtained to Date

Two new reactor designs, incorporating continuous weight measurements simultaneously with catalytic activity, were developed and tested. Initial results with the fresh catalyst showed the rate of benzothiophene reaction to be first order in benzothiophene and hydrogen, and to be inhibited by benzothiophene, hydrogen sulfide and pyridine, but not water. Benzothiophene, ethylbenzene and pyridine were found to form coke in the absence of hydrogen. A pyridine-poisoning series showed a linear decrease in reaction rate of benzothiophene with pyridine weight gain, which allowed an estimate to be made of the maximum number of active sites on the catalyst.

Anticipated Results

A partial metal version of the reactor is being fabricated to avoid the

frequent breakage of the earlier glass models. This will be tested for gas transport and mixing effectiveness. After obtaining reaction kinetics on fresh catalysts with the new reactor, some limited poisoning runs can be made.

Only a cursory examination of deactivation effects will be possible during the balance of the contract period. Additional detailed studies needed to develop poisoning correlations will not be possible within this period of time.

PROJECT B-3

Fundamental Studies on Hydrogen Transfer

Scott W. Cowley

1 Graduate Student

Objectives

The hydrogen transfer properties of $ZnCl_2$, an important "coal hydrogenation" catalyst, are not well understood. It is well known that $ZnCl_2$ is not a good hydrogenation catalyst. The objective of this study is to determine the role of $ZnCl_2$ in hydrogen transfer reactions. The Lewis acid properties of $ZnCl_2$ may play an important role in its ability to transfer hydrogen. Deuterium exchange reactions provide the basis for observing this process.

Research Results Obtained to Date

Hydride transfer between deuterium-labeled hydrocarbons and non-labeled hydrocarbons were studied. The catalysts used were $ZnCl_2/SiO_2$, $ZnCl_2/\alpha-Al_2O_3$, $ZnCl_2/coal$ and coal. The results were compared to exchange reactions occurring over well-known solid acid catalysts, such as $\gamma-Al_2O_3$ (a Lewis acid), $SiO_2-Al_2O_3$ (combined Lewis and Bronsted acidity), and a polyphosphoric acid/kieselguhr (a Bronsted acid).

The results indicate that $ZnCl_2$ readily complexes with water via a Lewis acid-Lewis base interaction. The resultant complex demonstrates Bronsted acid properties in transferring hydrogen. $ZnCl_2$ apparently forms a very strong interaction with coal and also demonstrates Bronsted acid properties in hydrogen transfer. However, hydrogen transfer occurs more slowly over $ZnCl_2/coal$ than $ZnCl_2/SiO_2$ or $ZnCl_2/\alpha-Al_2O_3$. The reduced rate of hydrogen transfer is likely due to the strong interaction of $ZnCl_2$ with oxygen-containing structures in coal. $ZnCl_2$ complexing with phenolic compounds or H_2O would demonstrate Bronsted acidity, but $ZnCl_2$ complexing with ether or carbonyl compounds would show no acid properties. The latter interactions may play an important role in the breaking of ether linkages.

Anticipated Results

Coal consists of a complex mixture of structures and their accompanying linkages. It is an impossible task to look at coal hydrogenation products and determine the exact role of $ZnCl_2$. It is important that a systematic study be made of the catalytic involvement of $ZnCl_2$ with well defined model systems (model compounds) of varying types and linkages. The fact that $ZnCl_2 \cdot H_2O$ demonstrates the ability to transfer hydrogen (protons) indicates an enormous potential for cleavage of methylene or ether linkages adjacent to aromatic systems. Recent studies have shown that Lewis acid complexes can play an important part in the transfer of hydrogen from saturated to non-saturated systems.

There may be other Lewis acid complexes possessing hydrogen transfer capability. An understanding of these interactions may produce a catalyst with a high degree of selectivity in its attack of linkages or a catalyst capable of higher conversions than $ZnCl_2$ or a catalyst more easily recovered from the char.

PROJECT B-4

Mechanism of Catalytic Hydrogenation By Metal Halide Catalysts

David M. Bodily, Investigator

Ralph E. Wood, Investigator

1 Post-doctoral Fellow

1 Graduate Student

Objectives

Metal halide catalysts are known to be very active in the hydrogenation of coal. They are used as molten salts and as impregnated catalysts. High yields of liquid products are obtained. This research is directed at understanding the mechanism by which impregnated metal halide catalysts act to hydrogenate coal at short residence times. The products of the reaction will be characterized structurally as the catalyst and other reaction variables are altered. Information on the changes in the products will be related to coal structure and to possible catalytic mechanisms to elucidate the reaction mechanism. The problems of corrosion and high costs associated with metal halide catalysts may be circumvented by the proper choice of catalyst, reactor design and reaction conditions, once the mechanism is understood.

The related techniques of ESCA (Electron Spectroscopy for Chemical Analysis)

and Auger Electron Spectroscopy are being used to investigate the bonding of coal structures with metal salt catalysts. This information will be useful in understanding the mechanism of catalytic coal hydrogenation.

The appearance of two "new" peaks in the auger spectra of Kaiparowitz Utah Coal impregnated with zinc chloride has been taken as evidence for an interaction between coal and catalyst. Recent efforts have been directed to finding the physical basis for the appearance of this spectral change.

Research Results Obtained to Date

Techniques of separation involving extraction and liquid chromatography have been applied to the heavy oil produced by coal hydrogenation. The oil has been separated into asphaltene, acidic, basic, saturate, one-ring aromatic, two-ring aromatic, three- to four-ring aromatic and polar-hexane-soluble oil fractions. Each of these fractions has been separated into subfractions on the basis of size by gel permeation chromatography. Analysis of these subfractions by ^1H and ^{13}C nuclear magnetic resonance spectroscopy, mass spectrometry, gas chromatography, molecular weight infrared and ultraviolet spectroscopy and elemental analysis provided detailed information not attainable from unseparated samples.

The effect of the amount of ZnCl_2 applied during hydrogenation was shown to be a progressive breakdown of the heavy oil to lighter products as the ZnCl_2 was increased. The products of the reactions did not show significant changes in structure as far as the carbon skeleton is concerned as the reaction progressed. With more catalyst, the reaction progressed more rapidly, but the products were of the same structural type. The results can be explained in terms of depolymerization and/or dissociation of structural units with the progress of the reaction. Although the unit structures vary in size and other structural features, they are all of the same basic type.

The unit structures in the heavy oils were shown to be composed of condensed aromatic ring systems with alkyl and alicyclic groups attached. The oxygen functionality has not been determined. The average number of aromatic rings, length of alkyl groups, number of saturated rings and other parameters were determined for each subfraction, thus providing a detailed characterization of the total sample. Long alkyl chains (up to 25 carbons) were identified in the saturate fraction. Long alkyl groups were found to be attached to the aromatic rings.

Carbon-13 nuclear magnetic resonance spectroscopy was applied to the sub-

fractions. Previous workers had applied this technique only to more complex mixtures of coal liquids. Various carbon types were identified in the various subfractions and the results compared with other techniques of characterization. Carbon-13 NMR was demonstrated to be a useful technique for characterizing coal liquids, although there are problems of slow relaxation times and overlap of signals from certain types of carbons. The acidic and basic fractions of the heavy oil were separated by both elution chromatography and gel permeation chromatography. Resulting subfractions were characterized by various instrumental techniques.

The heavy oil from coal hydrogenation with $ZnCl_2$ has been compared with similar liquids produced by catalytic hydrogenation with $Co-Mo-Al_2O_3$ and with solvent refined coals. The yield of hexane-soluble oils was greater with the hydrogenation using $ZnCl_2$ and the yield of asphaltene less. Structural analysis of the samples shows similar structures from each process, but significant differences in yields and important variations in some properties. The type of process has an important effect on the liquid products of the reaction.

ESCA and Auger measurements on coals and product chars from hydrogenation tests indicated a change in the auger spectra of the $ZnL_{3M_{2,3}M_{4,5}}$ emission band after reaction. This spectral change was reproducible as measured with a DuPont 650 B electron spectrometer. The change consisted of two "new" peaks between the expected pair of zinc peaks. The "new" peaks represented a smaller energy difference than before and was interpreted as a change in bonding of Zn 3D electrons with some part of the coal structure. A change in spectrometer to a Hewlett-Packard 5950 unit created a problem because the "new" peaks were no longer found.

Further work has indicated that the new peaks were produced by calcium contamination from the coal that was concentrated at the char surface as a function of increased coal reaction temperature. Coincidentally, as the calcium at the surface was increased in concentration, the zinc was decreased at the surface by diffusion into the char particles and by evaporation from the surface. Hence, the illusion of a zinc peak shift in energy was created. The "new" peaks were not measured with the Hewlett-Packard instrument because the energy source is an aluminum target x-ray tube rather than magnesium as in the DuPont. This energy shift causes the auger system to be shifted with respect to the ESCA spectra. The Ca ESCA lines were shifted with respect to the Zn auger lines and no longer were superimposed upon the Zn lines.

Anticipated Results

The mechanism of coal hydrogenation in the early stages of the reaction is now being studied. Several catalysts are being studied. Conversions are varied from low values up to those previously studied. In the early stages of coal conversion by a number of processes there is a rapid reaction apparently involving occluded and highly reactive materials in the coal. This stage of the reaction can be related to volatile matter content and other properties of the coals. Later stages of the reactions are slower and are more independent of coal type. These studies of the early stages of the reaction should further elucidate the mechanism of the hydrogenation reaction. In addition, they will provide information on the behavior and suitability of different catalysts for short-residence-time reactions.

We expect to use ESCA and Auger electron spectroscopy to measure changes in surface oxygen, nitrogen and sulfur bonding types as a function of mild and severe hydrogenation of coal samples. Further, we expect to use the infrared absorption technique of ATR (Attenuated Total Reflectance) to measure bonding changes as a function of temperature, pressure and catalyst concentration as coal is reacted.

PROJECT C-1

The Mechanism of Pyrolysis of Bituminous Coal

Wendell H. Wiser, Investigator

1 Graduate Student

This project only recently became active because no student had selected it for a thesis research project.

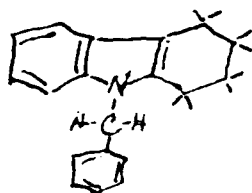
Objectives

In our present state of knowledge concerning the fundamental chemistry of coal liquefaction, it is believed the liquefaction reactions are initiated by thermal rupture of bonds in the "bridges" joining configurations in the coal, yielding free radicals. The different approaches to liquefaction, except for Fischer-Tropsch variations, represent ways of stabilizing the free radicals to produce molecules. Hence, the stabilization involving abstraction of hydrogen from the hydroaromatic structures by the free radicals, believed to be the predominant means of yielding liquid-size molecules in coal pyrolysis, is of major importance in all coal liquefaction, except Fischer-Tropsch variations. It is the objective of this research project to understand the chemistry of this pyrolytic operation.

Research Results Obtained to Date

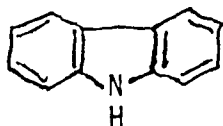
It has been consistently observed in kinetic studies of coal pyrolysis at the University of Utah that the overall kinetics are second order. Second-order kinetics suggest a two-body collision in the slow or rate-determining step. This observation could also possibly be explained on the basis of a series of consecutive (but overlapping) first-order reactions.

If the kinetics are really second order, the thermal bond rupture may be rapid followed by a slower abstraction of hydrogen from a hydroaromatic structure by the free radical in a two-body collision. A model compound has been synthesized to be representative of this type of structure in coal, namely:

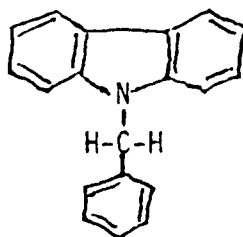


Equipment has been assembled to permit pyrolysing this compound in the temperature range 350° to 450°C. The products are analyzed at various times at each temperature by MS - GC. Preliminary results to date show toluene to be a major pyrolysis product, resulting from scission of the bond between N and CH₂, followed by abstraction of hydrogen from the hydroaromatic portion, as revealed by yields of other compounds,


e.g.



;



; etc.

The data are not yet complete enough to judge whether hydrogen abstraction is from the same molecule which yielded the  or from a neighboring molecule. Also, the order of reaction has not yet been determined.

Anticipated Results

The kinetic order of the pyrolysis of this model compound will be determined.

is less than in the upflow as is expected because in downflow the gravity enhances the particle flow motion, whereas in upflow it opposes the particle flow motion. The effect is that the actual particle velocity is greater in downflow. However, as the solids-loading ratio increases above the transition value, the holdup in both types of flow systems approaches seemingly the same value, while the frictional pressure drop in downflow becomes less than in upflow. This result means that while volumetric heat capacities of the two configurations remain the same, the power loss in the downflow system is less than in the upflow. This is a significant practical advantage for the downflow system.

The system performance for the heat transfer experiment has been confirmed by running with gas alone; the suspension heat transfer data will be obtained in the near future.

Thus far, the air-glass bead studies have shown that compared to the upflow system, the downflow system results in less energy consumption and more operational versatility. Future studies on the heat transfer will yield a correlation for the design of such a downflow system.

An analytical study was completed on the effect of gravity on the vertical motion of single, spherical particles suspended in an infinite gas flow field by solving the particle motion equation and obtaining velocity and position histories for a particle starting at rest. Both cocurrent-cogravity and cocurrent-countergravity configurations were considered, and the effect of particle size was investigated. The results clearly indicated that in the cocurrent-cogravity configuration, the effect of particle size on the position histories of the particles is much less than in the cocurrent-countergravity configuration. Thus, in a downflow coal reactor, coal particles of different size would have more nearly the same residence time. This is considered highly desirable for practical reactor operation. Preliminary comparison of upflow and downflow has also led to the confirmation of the other advantages of the downflow. These advantages include a lower pressure drop due to the static head of the flowing mixture and a wider range of operable conditions due to the absence of a minimum transport velocity for the gas such as exists in upflow.

Studies concurrently with those on the air-glass bead system have been carried out with an air-coal particle system. First, a literature survey was conducted to investigate the various methods of making two-phase flow measurements. A particle-tagging and injection technique of determining particle velocity was selected as being the most applicable to the coal particle-air system. The tagged particles are injected into the flowing mixture and the velocity calculated

from the time interval between the outputs of two detectors placed a known distance apart on the tube. Although radioactive tagging is the only method reported in the literature, a phosphorescent pigment used in the production of paint was selected as the tagging substance. Radioactive tagging would have subjected the experiments to very strict control and regulation by the University. The outstanding advantage of the particle-tagging technique for velocity measurement is that it gives the investigator the freedom to study the effect of particle size or other property by allowing him to inject whatever particles he wishes.

A study was conducted to ascertain the dangers of coal dust explosion in a pneumatic transport system, and an apparatus that minimizes this danger was designed and constructed. It consists of a 22-foot-long vertical flow section constructed of 5/8 inch seamless stainless steel tubing with 1/2 inch I.D., with 11 pressure taps spaced two feet apart for the measurement of pressure drop profile. Two photomultiplier tubes detect passage of the phosphor-tagged coal samples, which are introduced through an air-pressure injection apparatus. The flow section allows for a length-to-diameter ratio of nearly 500. A Syntron vibratory feeder with a feedback loop for constant stroke control allows for excellent control of a wide range of coal particle feed rates. The gas supply and regulating system is capable of delivering air at flow rates high enough to achieve a gas Reynolds number of 30,000.

Pulverized samples of a typical Western grade coal were obtained from the Castle Gate Mine in Helper, Utah. The samples were screened with a Sweco Vibro-Energy Separator and separated into three size ranges: -28/+48 mesh, -48/+100 mesh, and -100/+200 mesh.

Pressure drop data for air alone flowing at several different Reynolds numbers from 10,000 to 30,000 compared favorably with accepted correlations, thus lending credence to the reliability of the pressure taps and manometer system. Operation of the equipment with the -28/+48 mesh coal has also been successful. Coal particle velocities were successfully measured by injecting particles where the phosphor was applied with a sodium silicate solution used as the "glue". Pressure drop profiles for the two-phase flow showed that, as in the case of studies with glass beads, the solids flow rate greatly affects the hydraulic entry length while the gas flow rate has little effect. For the air-coal particle system, experimental methods have been established; and the equipment has been constructed for the fluid mechanic measurements. The techniques and equipment for heat transfer will be identical to those for the air-glass bead system.

Anticipated Results

By the completion of the project, correlations of experimental friction factors and wall-to-bulk heat transfer coefficients covering both the air-glass bead and air-coal systems will be developed. The results will be of substantial significance by providing design correlations for a flow configuration that has been largely ignored in the literature and which offers several inherent advantages in the design of a short-residence-time, continuous reactor for the hydrogenation of coal.

PROJECT D-1

Coal Characteristics and Hydrogenation Reactivity

Ralph E. Wood

1 Graduate Student

Objectives

This research effort is directed toward the measurement of the effect of coal characteristics with respect to hydrogenation reactivity. The approach has taken the form of measuring coal conversion to liquid and gaseous products as a function of particle size, temperature, pressure, and catalyst concentration. Existing continuous coal hydrogenation equipment developed under ERDA project FE (49-18) - 1200 is used for treating dry coal which has been impregnated or mixed with metal salt catalysts (primarily $ZnCl_2$). The reaction zone consists of a series of coiled tubes 3/16" or 1/4" inner diameter, adjustable from 20 to 120 feet in length in 20 foot increments.

Research Results Obtained to Date

The residence time of the coal in the reactor zone is of critical importance and measurement of this variable is essential. To accomplish this measurement, a detector device was constructed on the principle that a ferromagnetic material (powdered iron) will perturb the magnetic field of an oscillating high frequency circuit. Appropriate oscillators and coils were constructed and placed at the beginning and end of the reactor tube. With a flow of dry coal and hydrogen, a small amount (10-20 mg) of powdered iron is added to the stream. An electrical pulse at the recorder signals entry of the iron, and a later more protracted signal perturbation indicates exit of the iron. The intervening time period is a measure of the time required for the solid-liquid product to pass through the reactor zone.

The measurement of residence time has been used to assess the effect of coal particle size on the ultimate conversion of coal to liquid and gaseous products.

The dependence of the coal hydrogenation reaction rate in the "coiled tube" reactor on hydrogen pressure and catalyst concentration have been measured. The turbulent gas, used to propel the coal through the reactor zone, can be as little as 50% hydrogen without seriously reducing the conversion. The catalyst application must be above 3% ($ZnCl_2$) on a moisture-free-coal basis to achieve results for most coals. Less reactive coals require more catalyst to achieve the same result.

The particle size effect as a function of residence time in the reactor is shown in the accompanying figure (Figure 2).

An extrapolation of the coal data in Figure 2 at constant conversion levels to zero particle size shows the improvement to be expected if it were possible to feed very small particle size material. This figure (3) indicates that a minimum reaction time is required to achieve a specific level of conversion regardless of the reduction in particle size.

Anticipated Results

There is a need to learn how to feed extremely small size (1-5 micron diameter) dry coal particles in order to verify the extrapolations made from larger particles. It is apparent that micron size coal particles will react (hydrogenate) in reactor contact times of the order of seconds. Grinding the coal to this size is within reason from the economic viewpoint. However, feeding these small particles is difficult with conventional coal hoppers because of packing, bridging and failure of the mass to flow properly. Plans are to build a stirring device into the hopper which will permit mixing of the coal mass to prevent agglomeration of the fines and to facilitate feeding.

Likewise, plans call for verification of the size effect, pressure, and catalyst effects, with coals of other ranks, such as lignite, low volatile and medium volatile coals.

PROJECT D-2

The Effect of Structure on Coal Reactivity

David M. Bodily

2 Graduate Students

Objective

The structure of coal is very complex and varies in detail from sample to

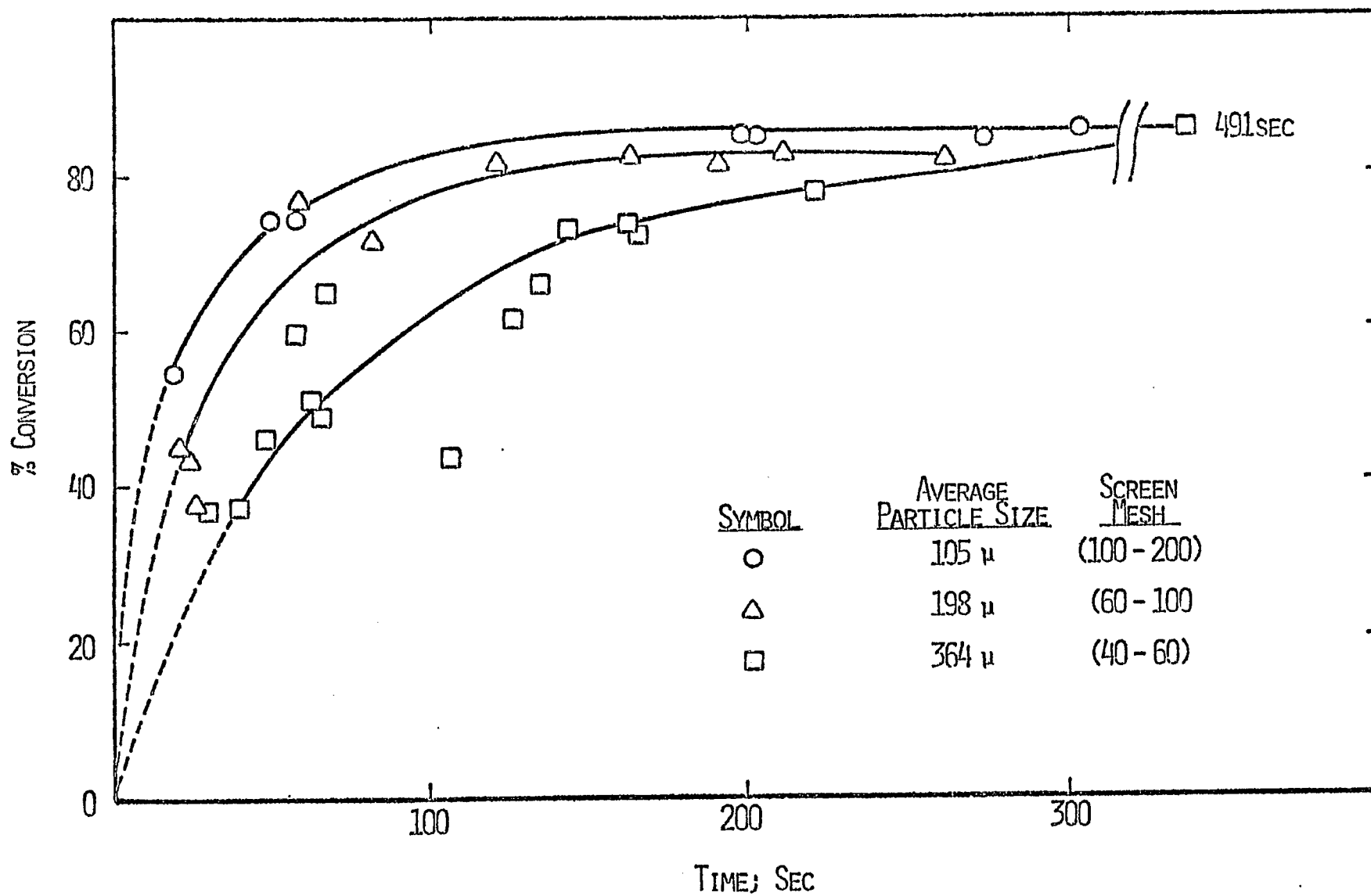


FIGURE 2. AVERAGE RESIDENCE TIME OF COAL OF VARIOUS PARTICLE SIZES, IN THE COILED TUBE REACTOR
 TEMPERATURE - 920°F; PRESSURE - 1800 PSIG; CATALYST - 6.25 % $ZnCl_2$.

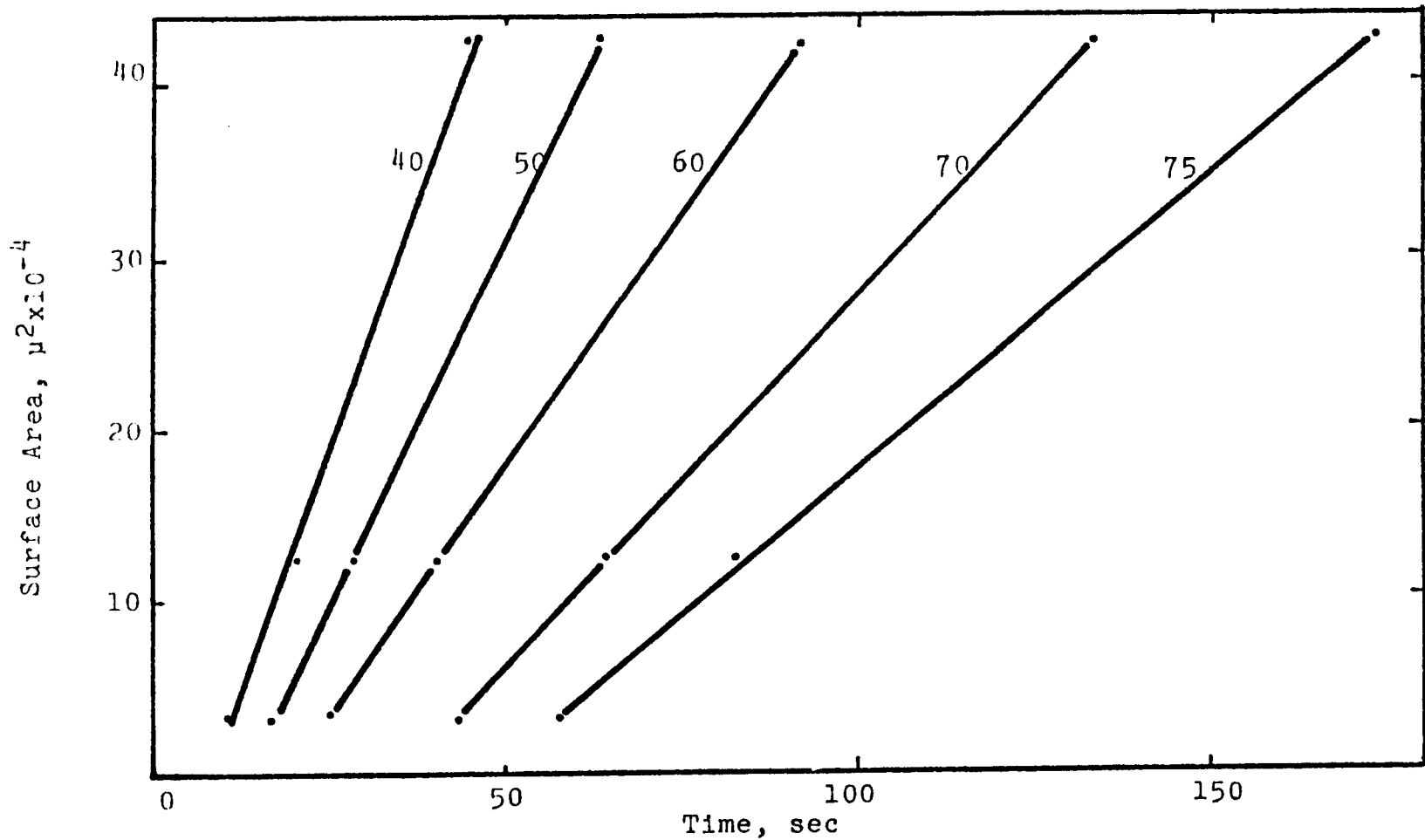


Figure 3. Correlation of Surface Area vs. Residence Time of Coal Particles at Various % Conversion Levels; Temp=920°F, Press (H₂)=1800 psig, Clear Creek, Utah Coal, Catalyst= 6.25% ZnCl₂. (Details in Table 1.)

sample. However, there are certain structural features that are common to all coals and are important in the conversion of coal to liquid products by a number of reaction processes. The chemical structure also plays a role in determining physical properties, such as the pore size distribution, and hence accessibility to gaseous and liquid reactants. The objective of this project is to ascertain some of these structural features and how they are affected by potential reactants and catalysts.

Research Results Obtained to Date

The interaction of $ZnCl_2$ with coal has been investigated. Previous studies with a bituminous coal demonstrated that pyrolysis of coal in the presence of $ZnCl_2$ resulted in suppression of the evolution of volatile matter and increased evolution of hydrogen gas at low temperatures. The micropores were greatly enlarged during this reaction. This study has been extended to coals of various rank, from lignite to medium volatile bituminous coal. All show the same effect of dehydrogenation and decreased tar and gas evolution although the degree of change depends on the rank. Zinc chloride is thought to react with the hydro-aromatic structures to make them more reactive. It is not certain whether this is a chemical or a physical effect.

Anticipated Results

The study of the interaction of $ZnCl_2$ with coal is expected to yield information on the nature of the interaction and on the structure of coal. The $ZnCl_2$ was shown to lose its Lewis acidity on heating with coal. A complex between zinc and coal (perhaps an intercalation complex) is proposed. It is expected that further information on the possible complex will be obtained.

The chemical structure of coal-derived asphaltenes are being studied. Experiments indicate that they are obtained by the progressive depolymerization/disassociation of coal. They appear to be composed to a large degree of polymers of average structural units. Information on the bonding of these units in asphaltenes should provide information on bonding in coal.

PROJECT D-4-I

The Separation and Characterization of Coal-Derived Liquids

Robert R. Beishline, Investigator
Weber State College

Objectives

1. To determine the extent to which coal hydrogenation liquids can be separated by fractionation through a spinning band (SB) distillation column.
2. To evaluate the effectiveness of SB distillation in combination with preparative gas chromatography (PGC) as a method for separating and isolating pure compounds from coal hydrogenation liquids.
3. To identify the isolated compounds.
4. To develop an analytical scheme for the characterization of light coal hydrogenation liquids.

Research Results Obtained to Date

It has been shown that SB fractionation of crude coal-derived liquids does not give distillates consisting of pure compounds, but does effectively cut the pot charges into less complex fractions which often consist of only a few compounds.

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

An analytical scheme using SB distillation and GC for the characterization of light coal-derived liquids is in the later stages of development.

Anticipated Results

With some additional work, the development of the analytical scheme can be completed.

The analytical method has the advantages of being rapid, and easy to perform. It also fills a special need, since it is specifically designed to identify the light compounds which are lost in the solvent separation procedures employed in many analytical schemes.

PROJECT D-4-II

A Pyrolysis-Gas Chromatography Study of Coals and Related Model Compounds

Robert R. Beishline, Investigator

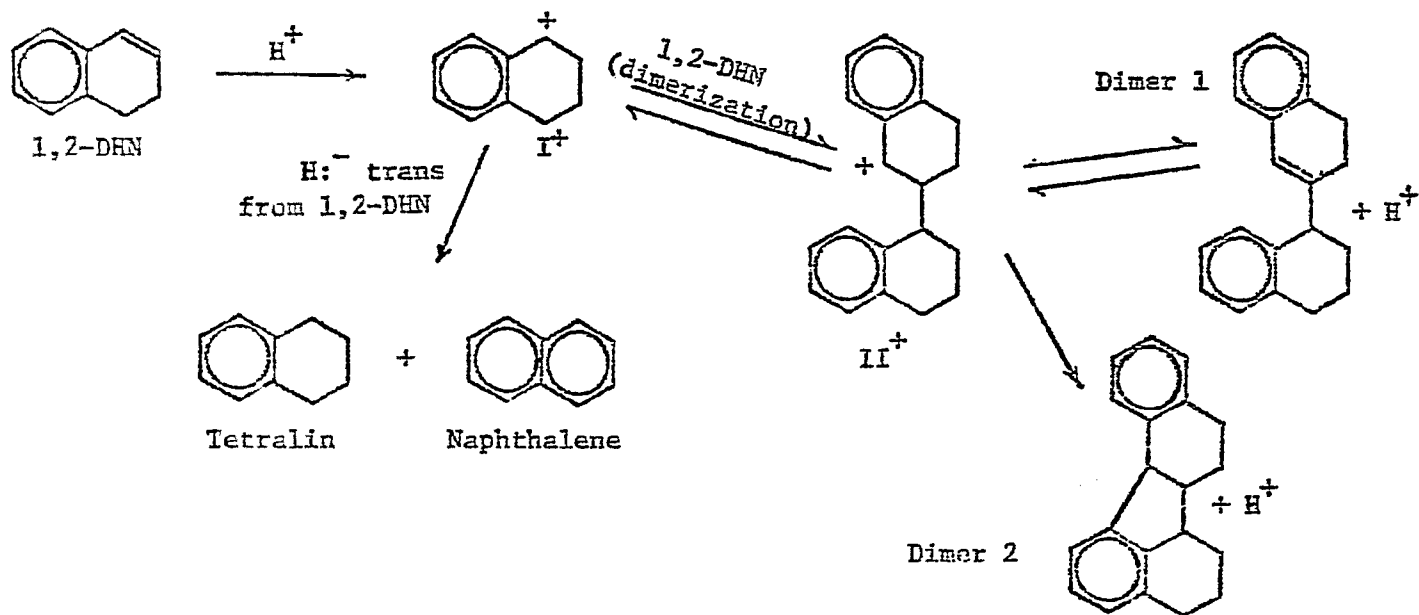
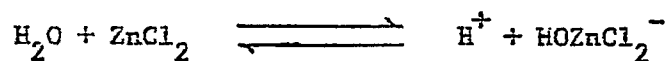
Weber State College

Objectives

To study the pyrolysis of coal-related model compounds in the presence and absence of catalysts with the goal of elucidating the catalyzed and uncatalyzed mechanisms.

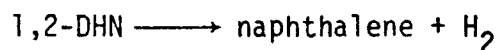
Research Results Obtained to Date

The zinc chloride catalyzed decomposition of 1,2-dihydronaphthalene (1,2-DHN) has been studied. Product identification, experiments in which the mole ratio of zinc chloride: water was varied, and deuterium tracer experiments clearly support the mechanism shown below, with regard to the role of water, the carbonium ion nature of the reaction, and the fact that zinc chloride functions as an agent to transfer protons from water to the double bond of 1,2-DHN.



Zinc chloride is a commonly used catalyst for the hydrogenation of coal and polycyclic aromatic hydrocarbons. The results of this study should therefore make a substantive contribution toward the understanding of the zinc chloride-catalyzed processes that occur in coal hydrogenation.

The uncatalyzed pyrolysis of 1,2-DHN (>350°C) has been shown to yield tetralin and naphthalene, but no dimers. Preliminary results from a kinetic study now underway indicate the mechanism to be simultaneous first and second order reactions, i.e.,



When tetralin is used as a hydrogen donor solvent for coal hydrogenation, 1,2-DHN has been shown to be an intermediate in the final formation of naphthalene. The study of these 1,2-DHN reactions is therefore of considerable importance, since these reactions constitute part of the hydrogen transfer system that operates during the coal hydrogenation.

Anticipated Results

The 1,2-DHN hydrogen transfer studies will be continued. We hope to obtain activation energies, demonstrate the generality of these reactions for other hydroaromatic compounds, and initiate studies on the hydrogen transfer reactions of tetralin itself. It should be emphasized that these results will be directly applicable to the hydroliquefaction of coal in hydrogen donor solvents.

V Conclusions

Progress over the past three years is covered in this report. Conclusions are listed for each project.

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