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THIRD QUARTERLY SUMMARY REPORT
April 1 - June 30, 1980
Chemistry and Morphology of Coal Liquefaction
Contract ET-78-G-01-3425

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Introduction:

All six tasks have been active during the quarter. The long time required in an academic surrounding to compare and set up equipment, test it and man the effort by finding graduate students or post docs is coming to a close. Experimental work is underway for four of the tasks and will be initiated in the other two during the next quarter. The equipment which has been built for Tasks 3 and 4 is unique and will probably not be found elsewhere. New insights are expected from its use. In this report, each task summary is preceded by a brief statement of what successful conclusion of the work would mean for the technological outlook.

During the report period, meetings of all task managers have been held at regular intervals to discuss progress of work and ideas. These meetings have established an interaction of different disciplines which will materially contribute to future progress and probably result in utilizing methodology and equipment interchangeably. They also serve to bring pertinent outside information, acquired at professional society meetings and literature study to the attention of all concerned. They are particularly valuable in establishing needs for background research on the basis of technological needs.
Task 1: Selective Synthesis of Gasoline Range Compounds for Synthesis Gas; Task Manager: A. T. Bell

This task is concerned with better understanding and control of a Fischer-Tropsch reactor. If successful, it may lead to preferred product distributions by changes in catalyst composition and by recycling of certain products. It will also prevent hydrogen savings by rejection of oxygen as CO₂ rather than water.

Construction of the experimental apparatus required to carry out this task is now well along and should be completed within the coming quarter.

Since it is expected that the fixed bed reactor system will be completed first, experimental work will be initiated using this unit. It is proposed to investigate first the performance of alumina-supported iron and ruthenium catalysts with different levels of potassium promotion. Three objectives have been set for these studies. The first will be to establish empirically the influence of conversion on the distribution of organic products formed. Preliminary studies suggest that low molecular weight olefins formed via primary reactions are reincorporated during the latter stages of reaction, thereby suppressing the formation of methane and very high molecular weight products. The implications of these initial results will be examined to determine whether secondary reactions can be used to control significantly the ultimate distribution of hydrocarbons formed. The second objective will be to determine the extent to which the oxygen released during Fischer-Tropsch synthesis can be rejected as CO₂ rather than water. The influence of gas space velocity on the
extent of conversion will be examined as well as the effect of potassium loading. Here again, initial studies have shown that the extent of CO$_2$ formations relative to H$_2$O increases as an iron catalyst is promoted with potassium. The extent to which a ruthenium catalyst might be similarly affected is little known and worthy of investigation.

Once the rotating basket reactor and its associated gas handling system are completed, the catalysts screened in the fixed bed unit will be examined for the effects of mass transport on the apparent kinetics and selectivity. Of particular significance in this context will be to establish whether the H$_2$/CO ratio at the catalyst surface can be enhanced relative to that in the feed as a result of rapid H$_2$ transport through an oil phase surrounding the catalyst but a less rapid transport of CO. These investigations will hopefully help clarify why H$_2$/CO ratios of 0.6 to 1.0 can be used in slurry reactors for extended periods of time but lead to catalyst deactivation or plugging in fixed bed reactors.

**Task 3:** Electron Microscope Studies of Coal During Hydrogenation.  
**Task Manager:** J. W. Evans

This task is beginning to reveal important structural differences in coal and coal constituents. It should eventually permit us to investigate the catalytic influences of ash and/or added catalysts during pyrolysis and to identify primary products of coal-steam or coal-hydrogen reactions. This in turn would provide information on control of product selectivity during pyrolysis and liquefaction.
The present work on coal microstructures is concentrating on very careful specimen preparation so as to correlate the maceral content with the microstructure and mineral content as seen in the transmission electron microscope. This involves careful thinning by hand grinding until the coal is optically transparent when both transmission optical and reflected light optical micrographs reveal the macerals and the viewing area for the electron microscope can then be selected to examine a given maceral. At the present stage of this work, this procedure has revealed many microstructural differences between different macerals and mineral bands within the coal. The work has focused on a high volatile Class A bituminous coal and is beginning to investigate sub-bituminous coals due to their abundance and their probable use in many gasification and liquefaction processes. Some preliminary experiments have also been made by heating coal specimens in the Hitachi 650kV microscope under the influence of the microscope vacuum environment. However, little detail has been seen in these experiments and it may be that volatile gases are driven off during the ion-thinning procedure and thus the new procedure for careful thinning will also improve the coal specimens. One final phase of the research is that high rank metaanthracite coals are found to show a pronounced argon peak in the X-ray spectrum, whereas the low rank coals do not. Experiments are under way to ascertain whether this is due to the more crystalline nature of the high rank coals and/or the graphitic nature of the carbon skeleton.
Task 4: Catalysed Low Temperature of Coal  
Task Manager: G. A. Somorjai

This task is designed to provide information on the surface phenomena occurring during catalytic hydrogenation of coal. It is expected to supply information on catalyst behavior poisoning and interaction with the coal. Such information can be extrapolated to larger scale operations.

During the past quarter, the new equipment described in the previous two reports was completed and has now been installed in the laboratory. The postdoctoral fellow assigned to the project arrived in May and is now testing and calibrating the complex equipment. Experimentation will commence in the next quarter.

Task 5: Selective Hydrogenation, Hydrogenolysis, and Alkylation of Coal and Coal Liquids by Organo Metallic Systems - Task Manager: K. P. C. Vollhardt

Two major objectives of the task are: (1) cleavage of carbon-carbon bonds in aromatic hydrocarbons by transition metal complex catalysis. (2) Alkylation of aromatics by CO or ethylene. The former can lead to novel methods of coal depolymerization to simple molecules easy to hydrogenate. The second may provide a new synthesis route by side chain formation on aromatics with subsequent dealkylation to low molecular weight hydrocarbons.

We have for the first time demonstrated the reversibility of an organometallic activation step which is of significance in its potential as a novel method to coal liquefaction by aromatic ring
cleavage. This step is an insertion of a transition metal into an \( \text{sp}^2-\text{sp}^2 \) carbon-carbon bond. This very basic organometallic step has been demonstrated by the observation of the unimolecular diastereoisomerization of racemic and enantiomerically enriched cyclobutadiene cobalt complexes. If applicable to benzene derivatives, this could become an important activation step for the ring opening depolymerization of coal. In addition, this reaction could potentially be applied to the further functionalization of aromatic molecules with coal-related structures (for example, addition of ethylene, alkynes, carbon monoxide, etc.)

In a second project concerned with the utilization of benzene dication complexes as model systems for the potential transition metal mediated alkylation of coal molecules we have discovered that nucleophilic addition reactions, although unsuccessful with a large variety of nucleophiles, may evidently be achieved with nucleophiles of moderate basicity (e.g., methoxide anion, malonate anion, cyclopentadienyl anion) to afford doubly alkylated cycloyexadiene complexes. This appears to be a significant breakthrough in a project that was ready to be abandoned.

**Task 6: Chemistry of Coal Solubilization and Liquefaction Pyrolysis Studies**

**Task Manager:** R. G. Bergman

The task is concerned with the mechanisms of hydrogen transfer from a donor solvent to an acceptor molecule. Model compounds are used to study this. Information gained is applicable to all currently practiced direct hydrogenation processes of coal.
a) Chemical Activation of Tetralin

We have recently elucidated the thermal reactivity of tetralin in the gas phase, and are presently directing our efforts toward an understanding of the reactivity of chemically activated tetralin (1).

Three sources for activated tetralin have been investigated. Thermal rearrangement of bicyclopropenyl (2) has been studied in the gas phase over a span of five decades in pressure, and the yields of benzocyclobutene (5) and tetralin have been found to be pressure dependent. Di-ethynyl olefin (3) has been found to rearrange to tetralin and has given preliminary evidence that the yield of tetralin varies with pressure. The bicyclopropyl diene 4 has also been investigated and only gives rise to chemically activated products at the lowest pressures studied. The energy of 1 formed from activation by 2 is calculated to be 150 Kcal/mol, by 3, 123 Kcal/mol, and by 4, 100 Kcal/mol.
(b) **The Spin State of 1, 4-dehydrobenzenes at Elevated Temperatures**

We have employed two methods to determine the spin state of 2,3-dialkyl-1,4-dehydrobenzenes (e.g., compound 1 in Scheme I) populated in the thermal reaction of diethynyl olefins (2,3). The first is based on our ability to determine the ratio of cage to escape reactions of the radical pair generated upon abstraction of hydrogen from 1,4-cyclohexadiene (3), Scheme I) when a $d_0/d_4$ mixture of the trapping agent is used. The analysis relies on the "spin correlation effect" which postulates that singlet radical pairs will undergo both cage (combination and disproportionation) and escape reactions while triplet radical pairs can only undergo escape from the cage. The spin state of the radical pair is assumed to be the same as the 1,4-dehydrobenzene from which it is generated. We have found that the ratio of cage/escape observed in the reaction of 2,3-di-n-propyl-1,4-dehydrobenzene (1) is 0.6, indicating that only the singlet is present.

The same conclusion was reached by application of a second method: chemically induced dynamic nuclear polarization (CIDNP). CIDNP was observed when a solution of 2,3-dimethyl-hexa-1,5-diyne-3-ene (4) in hexachloroacetone was heated to $160{^\circ}$C in the probe of a 90 MHz NMR spectrometer. The major product, 1,4-dichloro-2,3-dimethylbenzene, showed emission in the signal due to the aromatic protons; this is interpreted as evidence for the formation of a singlet radical pair in the abstraction reaction (Scheme II).
Both experiments indicate the presence of only the singlet state of 2,3-dialkyl-1,4-dehydrobenzenes under the reaction conditions. This stands in contrast to theoretical studies which have predicted in all cases that singlet and triplet 1,4-dehydrobenzene are very similar in energy; in some studies the triplet was predicted to be the ground state. The lifetime of the 1,4-dehydrobenzenes generated at these temperatures is estimated to be < 10^{-6} sec. Thus, it is possible that the ground state of these molecules is indeed a triplet, but that intersystem crossing from the singlet is slow relative to unimolecular and bimolecular reactions at elevated temperatures.
Scheme I

\[ \text{Scheme II} \]
Task 7: Coal Conversion Catalysts-Deactivation Studies

Task Managers: A. V. Levy and E. E. Petersen

Studies of spent cobalt-molybdena-alumina catalysts from coal hydrogenation service have shown existence of metal sulfide skins on the external surfaces of the pellets. The task is designed to form such films under closely controlled conditions to learn how they are formed and how their formation may be inhibited. It will also be determined what are the porosity and diffusion characteristics of the films.

A laboratory apparatus for studying the controlled deactivation of hydrotreating catalysts has been designed. The pilot plant and industrial hydrotreating processes of the petroleum industry usually use trickle bed reactors. The fluid dynamics and mixing characteristics of trickle-bed reactors are complex and have not been adequately understood. Uncertainties exist as to the extent of component transfer between the phases, and the degree of catalyst wetting due to channeling effects. It is desirable to carry out the initial deactivation experiments using a batch reactor which permits an easier interpretation of activity data. The results and conclusions of the batch study would form a basis for the experimental investigation using a laboratory trickle bed reactor.

It is planned to carry out preliminary catalyst testing runs in a stirred batch autoclave reactor with catalyst contained in a basket to avoid attrition of catalyst pellets. The major components of the apparatus, viz. two-liter autoclave, valves, backpressure regulator, filters temperature controller, etc. have been ordered. Meanwhile, the design of a continuous fixed catalyst bed reactor system for
deactivation studies is underway.

The catalysts used in this investigation will be the commercial catalysts HDS-16A \((\text{CoO-Mo})_3/\text{Al}_2\text{O}_3\) and HDS-9A \((\text{NiO-MoO}_3/\text{Al}_2\text{O}_3)\) manufactured by American Cyanamid Company, Bound Brook, New Jersey. Sufficient deactivation data on commercial catalysts should lead to further studies using laboratory made catalysts with varying surface area and pore size distribution with a view to maximize the catalyst life. It is noted that the existing hydrodesulfurization catalysts which were developed for petroleum feed stocks are not the best for treating coal-derived liquids.

The feedstock used to study the catalyst aging will be gas oil enriched with metallic naphthenates of iron, vanadium, nickel, titanium, calcium, manganese, and sodium. Generally speaking, the metallic naphthenates form a convenient method of obtaining a metal radical in an oil-soluble form. This feedstock will have the advantage of being less viscous as compared to residual oil, and at the same time it will permit an easier variation of the concentration of metals in the feed. It is noted that the residual oils and coal-derived liquids contain many metal compounds of unspecified nature. The dominant metals in synthetic liquids may be different than in petroleum liquids. A typical metal analysis by previous workers has revealed that synthetic liquids have high iron and titanium contents while the petroleum liquids contain significant amounts of vanadium and nickel. It is believed that the metallo-etioporphyrin series are found in petroleum, while
the nature of metals in coal-derived liquids is not well understood. Therefore it is also planned to enrich gas oil with some of the naturally occurring model organometallic compounds of vanadium, nickel and titanium. The model metal compounds that we have in mind are metal derivatives of etioporphyrin-I and octaethylporphyrin.

The assembly and operation of the batch reactor system will commence as the various components are procured. Meanwhile, techniques for analyzing the catalysts and liquid products will be perfected. It is planned to study the structural and chemical properties of the fresh and deactivated catalysts using following techniques: X-ray diffraction, BET method, mercury porosimetry, electron microscopy (scanning and energy dispersive X-ray), electron microprobe, and atomic absorption. The analysis of the liquid products will be carried out using following techniques: sulfur analysis by X-ray fluorescence, metals by atomic absorption, and carbon-hydrogen by combustion.

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