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1st and 2nd Quaterly Technical Progress Reports

TITLE: Superacid Catalyzed Coal Conversion Chemistry

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PROGRESS REPORT

Project was initiated September 1, 1983 and first weeks were devoted to start up.

In our laboratories we have previously developed a mild coal conversion process. This involves the use of a superacid system consisting of HF and BF_3 in presence of hydrogen and/or a hydrogen donor solvent.

In order to understand the chemistry involved in the process of depolymerization of coal by the $HF:BF_3:H_2$ system we are carrying out a systematic study of a number of coal model compounds. The model compounds selected for present study have two benzene rings connected with various bridging units such as alkylidene, ether, sulfide etc. From the results of these studies model compounds could be classified into two catagories. The first catagory consist of model compounds where two benzene rings are connected with bridging unit such as $-CH_2$, $-CH_2-CH_2-$, CH_2-O-, $-CH_2-O-CH_2-$, $-CH_2-S-CH_2-$, and $-CH_2-S-CH_2-$. These model compounds

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gave near quantitative conversion with $HF:BF_3$ system in the absence of hydrogen under extremely mild condition (mostly room temperature expect in cases of sulfur containing compound where a temperature of 90° C was used. Condensation products mainly anthracene and methylanthracene were identified in the products form the conversion of these model compounds. The formation of these undesirable side product could be completely eliminated when a good hydrogen donor such as isopentane was used. Morever anthracene and methylanthracenes themselves gave appreciable conversion to light hydrocarbons (C_1 to C4) when treated with $HF:BF_3:H_2$ system at higher temperature (~150° C). The second catagory of coal models includes compound where two benzene rings are connected either directly (biphenyl) or through heteroatoms (diphenyl ether, diphenyl sulfide and diphenyl disulfide) as well as heterocyclic compounds such as quinoline. These compounds required relatively higher hydrogen pressure (800-1000psi) and temperature (150-180° C) for good conversion. Lower hydrocarbons (C_1 to C_4) were produced form the conversion of these model compounds. Clearly conversion of these compounds requires hydrogenation of one of the benzene rings followed by cleavage to the observed products.

From studies so far carried out it appears that high pyridine extractibilities achieved by treating coal at temperature below 100° C results from the cleavage of bridges such as present in bibenzyl, diphenyl methane, dibenzyl ether, dibenzyl sulfide etc. On the other hand the increased cyclohexane extractibility and distillability observed at relatively higher temperatures

and hydrogen pressures reflects the hydrogenation and cleavage of the aromatic backbone in coal structure similar to what is seen in the conversion of model compounds such as biphenyl, diphenyl ether, diphenyl sulfide, anthracene, etc.

We are continuing our studies of coal conversion and reaction of model compounds up to 250° C and hydrogen pressure of 1500 psi. We also plan to continue model compounds studies to include more relevant coal models such as polycyclic aromatics and their derivatives. In addition we also plan to study the structure modification of coal by alkylation, nitration, halogenation, carboxylation etc. and its effect on coal susceptibility to conversion process. As part of these studies solid state magic angle spinning-cross polarization ^{13}C NMR studies will also be carried out . Work is in progress on model systems and their carbocationic analogs.

ARTICLES AND PRESENTATIONS

(1) Superacid Coal Chemistry. 2. Model Compound Studies under Conditions of $HF:BF_3$ Catalyzed Mild Coal Liquefaction, G.A.Olah and A. Husain, Fuel, submitted

(2) A paper presented at the 1983 Internation Conference on Coal Science, Pittsburgh, Pennsylvania. A. Husain and G.A.Olah, Proceedings of 1983 International Conference on Coal Science, 1983, page 191.