

We were interested in applying superacid catalyzed cleavage-depolymerization and ionic hydrogenation for significantly improved low temperature conversion of coal to liquid hydrocarbon, as well as obtaining information about involved reactions and the structure of intermediates of the coal-liquefaction process. In order to show the feasibility of our proposed research we have carried out preliminary investigation in these areas and obtained the following results.

Hydrogenation of coals producing liquefied products generally follows two main courses: solvent assisted hydrogenation at 300 to 400°C and at 1000-4000 psi or higher-temperature flash pyrolysis (600 to 1000°C), either at ambient hydrogen pressure or hydrogen pressure up to 1500 psi. The solvent-assisted liquefaction has the virtue of being able to obtain a high-yield coal conversion to liquid products of relatively low molecular weight.

The use of catalysts in coal-liquefaction processes causes, in general, significant difficulties. Coal is a solid material with very limited solubility in most common solvents (organic or inorganic). Thus, a major difficulty in transforming coal catalytically is finding means to bring hydrogen gas in proper contact with the coal. This fact obviously causes significant and as-yet unresolved problems, if a solid catalyst is used. Even when employing a very-fine-mesh coal (mesh size 100 μ), there is little surface contact. Also, the organic moiety of coals is a cross-linked polymeric material, which can only be partially dissolved or swelled by organic solvents. Thus, a homogeneous catalyst should also be preferentially soluble and compatible with solvents used or the reaction conditions should be such as to allow the catalyst to make molecular contact with the large organic cross-linked molecules of coals. Further, the large polyaromatic polynuclear coal backbone must be depolymerized during the process to allow the formation of hydrogenated lower molecular weight hydrocarbons.

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Friedel-Crafts catalyst systems, such as zinc chloride or aluminum chloride-hydrochloric acid with hydrogen, were utilized previously in coal liquefaction, but their use is of limited value because these acid catalyst systems cannot be readily regenerated, and in the latter case, results primarily in the formation of gaseous products, such as methane and ethane. Further, elevated reaction temperatures are needed in these energy consuming processes.

The application of Lewis acid catalyzed coal conversion has gained interest in recent years for producing liquid and gaseous products at temperatures between 200 and 500° C, generally 350 to 450° C. Zinc chloride in particular is utilized in the CONOCO process. Further it is known that active Lewis acid catalysts can be effective gasification catalysts under hydrocracking conditions by themselves¹ or with Lewis acid-protic acid conjugate superacid systems, such as aluminium chloride and hydrochloric acid studied by Ross.²

S. Amendola³ described the rapid conversion of coal to a high percentage of liquid hydrocarbons by first reacting it with a protic acid such as hydrogen fluoride to form claimed carbon addition products, which are then reacted with a Group V halide ion acceptor system (i.e., superacid system), such as antimony pentahalides, and thereafter with a hydrogen donor source. All phases are claimed to be carried out at atmospheric pressure and at temperatures of 150 to 500° C.

The group V halides claimed³ are, however, generally unsuitable and impractical catalysts for coal conversion because their hydrolytic ability and generally high chemical reactivity result in irreversible reactions with coals. Also, their redox potential is low, and they are thus easily reduced under the reaction conditions. Antimony pentahalides, for example, generally are not compatible, with hydrogen or hydrogen donors. Further, antimony pentahalides are extremely reactive with water and any other nucleophiles abundant in coals or other carbonaceous materials. When reacted with coals, antimony pentafluoride or its conjugate superacids give insoluble, rock-like materials, which are neither converted to hydrocarbon oils or gases and do not allow recovery of the halide.

The phenol complex of boron trifluoride, a well defined moderately acidic system⁴ was applied by Heredy in studies of depolymerization of coals and model compounds.⁵ This system is, however, a relatively weak acid system, which when heated slowly releases boron trifluoride starting at about 50°C. Practically no boron trifluoride remains at the boiling point of phenol. No liquefaction of coal was reported in the phenol-boron trifluoride system, nor is it expected to be achieved due to the low acidity of the system and its inability to promote ionic hydrogenation. This system is thus entirely different from the hydrogen fluoride-boron trifluoride superacid system,⁶ a system used in the petrochemical industry, for example, for the isomerization of xylenes, but not applied previously in coal chemistry.

Preceding our work there was thus no practical application of a superacid system to coal liquefaction.

Although a wide variety of superacids whose Hammett acidity values (H_0)⁷ range from -11.0 to -28 are available, we have, after extensive screening, found only HF:BF₃,^{8,9} $H_0 = -16$, effective both as acid catalyst and reaction medium for our low temperature coal liquefaction process. This superacid system has several advantages over other superacids such as HF:SbF₅, HF:TaF₅, and FSO₃H:SbF₅. First, HF:BF₃ is non-reducible and therefore is unable to oxidize liquefaction products to useless chars. Secondly, the system provides also a suitable reaction medium to contact coal with hydrogen. Further, both HF and BF₃ are gases at atmospheric pressure and room temperature and thus can easily be recovered from the liquefaction reactor by distillation. Finally, both HF and BF₃ are inexpensive and readily available in bulk. Disadvantages of the system are its corrosive nature, the fluoride donating ability of hydrogen fluoride at lower temperatures to carbocations formed from coal and coal liquefaction products (vide infra), and an upper limiting reaction temperature of 188°C, the critical temperature of HF. These disadvantages, however, can be overcome by suitable selection of the reaction conditions. Since the advantages of the system greatly outweigh its disadvantages, we feel that it is an attractive alternative to current coal liquefaction

processes and we carried out an extensive study of the potential of the HF:BF₃/H₂ system for coal hydroliquefaction.¹⁰

Since the coal structure must first be cleaved (depolymerized) with subsequent hydrogenation of the fragments in order to attain liquefaction, suitable methods of analyzing the effectiveness of the system on raw coal had to be applied in order to ascertain the degree of structural degradation and hydrogenation. Solubility of treated coals is the most common method of determining whether the coal structure is cleaved in a given process. We accordingly solubilized treated coal in solvents of increasing polarity, i.e., cyclohexane, benzene, chloroform, tetrahydrofuran, and pyridine, yielding extracts of varied molecular weight and functionality which are easily studied by conventional spectroscopic methods. Also, an increased solubility in non-polar hydrocarbons such as cyclohexane generally indicates that the hydrogen to carbon (H/C) ratio and thus the hydrocarbon nature is increasing.¹¹

Another technique utilized for studying the effectiveness of the HF:BF₃/H₂ system in coal liquefaction was distillation of treated coals at moderate to higher temperatures (200°-400° C) in vacuum. The distillate consists of chloroform soluble oils and tars which can also be characterized spectroscopically. Distillation data also indicate the degree of degradation of the coal structure, i.e., increasing yields of distillate implies increasing depolymerization, and increasing yields of low boiling materials, those with high H/C ratios, suggests increased addition of hydrogen to the coal structure.

Treated coal which showed high extractability or distillability was usually analyzed for carbon and hydrogen content in order to determine under a set of reaction conditions the increase in its H/C ratio. Some coals, extracts, and distillates were also analyzed for nitrogen and sulfur content so as to learn if the system was able to remove these contaminants from coal. Fluoride contents were determined since this information reveals hydrogen fluoride quenching of carbocations or addition to unsaturations formed under milder conditions in the coal structure. Since at more

elevated temperatures hydrogen fluoride can again be eliminated from fluorinated coal, this side reaction at lower temperatures is not considered detrimental to the process, but as a matter of fact can provide useful mechanistic and structural information.

The coal used in our studies was Illinois No. 6, and uniform samples were donated by the Exxon Corporation. An infrared spectrum of this coal shows the following major stretching absorptions: 3600-3300 cm^{-1} (phenolic O-H), 2960-2860 cm^{-1} (aliphatic C-H), 1650-1550 cm^{-1} (olefinic and aromatic C-C), 1250-1000 cm^{-1} (C-O stretch), and 900-700 cm^{-1} (olefinic and aromatic C-H bend).

In our study on the treatment of coal under varying conditions of reactant ratio, reaction time and temperature we were able to obtain over 95% pyridine extractible product by treating coal in $\text{HF}:\text{BF}_3:\text{H}_2$ system at $\sim 100^\circ\text{C}$ for 4 hours. The coal to acid ratio was 1 : 5 and 900 psi of BF_3 and 500 psi of H_2 were used. These are extremely encouraging results in that the conditions used are drastically milder as compared to any known process such as used in Exxon donor solvent and related processes. At the same time the cyclohexane extractibility of the treated coal was as high as 27% and the yield of liquid distillate at $400^\circ\text{C}/5 \times 10^{-3}$ torr was $\sim 30\%$. Without claiming to have been able to yet fully optimize conditions these results regardless suggest that the coal structure is being substantially depolymerized and hydrogenated by the superacidic system to smaller molecular weight fragments which are soluble in pyridine and cyclohexane and have moderate boiling ranges. The infrared spectrum of product coal, extracts and distillates were distinctly different from starting coal and show a significant increase in the amount of saturates.

The ^1H NMR spectrum of cyclohexane extract of the treated coal shows essentially all aliphatic protons. The spectra of other treated coal extracts show increased amounts and types of aliphatic protons as well as significant amounts of protons bound to unsaturated sites (17% unsaturated H, 83% saturated H). This again indicates that the $\text{HF}-\text{BF}_3$ system is depolymerizing the coal to small fragments which are soluble in non-polar solvents.

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2. George A. Olah and Altaf Husain, Superacid Coal Chemistry. 2. Model Compound Studies under Conditions of HF-BF₃ Catalyzed Extremely Mild Coal Liquefaction, Fuel, submitted.
3. G. A. Olah, M. R. Bruce, E. H. Edelson, and A. Husain, Superacid Coal Chemistry. 3. Electrophilic Substitution of Coals under "Stable Ion" conditions and the Conversion of Functionalized Coals with HF:BF₃:H₂ Liquefaction System, Fuel, submitted