3. Argument and Rationale

I. Introduction

The limitations of using coal as a fuel are related to its physical and chemical properties. Since coal is a solid which contains considerable ash content, it is inconvenient and expensive to transport and utilize on a BTU basis. Also, sulfur and nitrogen compounds are present in coal and these (as well as the fly-ash) lead to air pollution problems when the coal is burned. Efforts are now under way at altering these physical and chemical properties of coal to produce both gaseous and liquid hydrocarbons for use as fuels. The basic problems involved in effecting these conversions are removing the coal ash and increasing the hydrogen/carbon ratio of the product. In addition, it is necessary to reduce the amount of sulfur, nitrogen, and oxygen compounds present for environmental reasons as well as to increase the quality of the product. Implementing such conversions of coal encompasses a variety of processing procedures, many of which depend on the use of catalysts to effect rates and selectivities that would otherwise be unobtainable. In this report, we examine what role catalysts can be expected to play in future coal conversion technology leading to fuels for electric power generation.

II. Catalysts for Liquefaction and Hydrodesulfurization of Coal

Large-scale coal liquefaction processes were investigated in England and Germany during the 1930's. Hydroliquefaction to produce motor and aircraft fuels was carried out in Germany during World War II, but the process was too expensive to be used during less drastic conditions. Part of the high cost was related to the high operating pressures (~10,000 psi) needed with the poor catalysts then available. After the war, the U.S. Bureau of Mines constructed and operated a demonstration plant based on modified German technology. This process was also costly as pressures over 7000 psi were needed. Before economic improvements could be made, the Middle East oil deposits were discovered and the support for this research was terminated. Now, because of the energy shortage, pollution controls, and undesirable dependence on foreign petroleum sources, there is a renewed interest in hydroliquefaction to produce a clean fuel oil from domestic resources. Clean fuel oil from coal for power generation would release the petroleum oils and gas now consumed in this way for use as home heating, industrial and motor fuels, chemicals, fertilizers, etc.

Converting coal into a nonpolluting liquid fuel generally requires the addition of hydrogen. If the hydroliquefaction is mild and the hydrogen content of the fuel is increased by only two or three per cent, then the product is a heavy oil suitable for firing electric power boiler generators. The yield of such heavy oil (specific gravity ~1.1) is about three bbl per ton of bituminous coal completely converted. If the hydroliquefaction is more extensive and the hydrogen content is increased by six per cent or more, distillable light oils and gasoline are produced with specific gravities as low as 0.8 so that the volumetric yield may be over four bbl per ton. The heavy oil is preferred for power generator fuel because it is less costly due to less consumption of expensive hydrogen and it has a higher energy density for transportation and storage.

In discussing processes for coal liquefaction, we shall neglect pyrolysis which is based on thermal rupture of bonds in the coal molecule and does not appear amenable to improvement by catalysts at this time. Pyrolysis does not produce maximum quantities of liquid or gas since the free radicals formed by the bond ruptures usually repolymerize to form char. The COED process of the FMC Corporation maximizes oil (or tar) yield by multibed sequential pyrolysis in fluid beds and yields ~1.5 bbls/ton. A flash pyrolysis process also designed to maximize tar or oil yield is being developed by Garrett Research Company and they predict ~2 bbl oil/ton coal. Sulfur would have to be removed from the tar or oil by second-stage hydrogenation of the pyrolytic products. As mentioned above, these processes also produce large quantities of char and this must also be hydrodesulfurized (which is difficult) in order to produce an acceptable power-plant fuel. Developers of the COED process are considering gasification of the char to convert it into sulfur-free, low BTU gas.

Two liquefaction processes now being developed are the H-Coal process by Hydrocarbon Research, Inc., and the Synthoil process by the U.S. Bureau of Mines. In these processes, a hydrogen-transfer solvent hydrogenates and liquifies the coal molecules which then migrate through the liquid phase to catalyst pellets where hydrocracking and hydrodesulfurization takes place. The catalysts used are commercial hydrodesulfurization catalysts such as cobalt molybdate or tungsten sulfide. Cracking takes place at various stages during hydrogenation depending on the temperature and degree of hydrogenation. The proposed mechanisms will be discussed in Section VII. In the H-Coal process, an oil slurry of finely ground coal flows together with hydrogen through an ebullating or suspended fluidized bed of particulate hydrodesulfurization catalyst. The Synthoil process employs a fixed bed of Co/Mo catalyst pellets and rapid turbulent flow of coal, oil, and hydrogen through the fixed bed. The Synthoil conversion minimizes hydrogenation of the products from the primary liquefaction, which is important for minimizing the consumption of expensive hydrogen. Both processes include very good removal of sulfur (as H_2S) via catalyzed hydrodesulfurization.

Recommendations

The Bureau of Mines had made an extensive study of hydroliquefaction and hydrodesulfurization catalysts to provide a basis for selecting the best catalyst for use in their Synthoil process. Experiments with Mo, Sn, Ni, Co, and Fe impregnated as single components on high- and low-surface area supports showed that Mo catalysts were best for sulfur removal and Sn catalysts were best for conversion of coal to oil. Single-component catalysts did not appear to be promising for combined liquefaction and desulfurization. Based on activities for both liquefaction and desulfurization of coal, the best catalyst tested was a commercial, high-surface area, silica-promoted catalyst containing 2.4% Co and 10% Mo on an alumina support. This catalyst is being used in the

Synthoil pilot plant.

Research is needed in the following areas:

1. Continue searching for improved catalysts for the Synthoil process. As the process is further developed on a larger scale, some unforeseen problems with the durability of the Co/Mo catalyst may arise. It is known that vanadium in crude oil (~1000 ppm) poisons the Co/Mo catalyst. It remains to be seen if the V present to ~10 ppm in coal has a similar effect.

2. The mechanism of bond-breaking in coal liquefaction must be further investigated. This will be discussed in Section VII.

3. Hydrocracking requires a catalyst that is insensitive to high concentrations of sulfur and nitrogen and which can be readily regenerated from the sulfur and nitrogen compounds that it might form. In this regard, the catalytic hydrogenation of the hetero sulfur, nitrogen, and oxygen atoms should be investigated. These atoms can be removed from the liquid product as gaseous H_2S, NH_3, and H_2O. Various recovery mechanisms are then available for collecting these compounds for sale or disposal.

   Work at the Bureau of Mines has shown that sulfur removal reactions are diffusion-hindered and that increased desulfurization resulted when their Co/Mo catalyst was pulverized. Maximum desulfurization activity apparently requires a high surface-area catalyst and results from a combination of the catalytic activity of supported metal components and the promotional effect of the support surface. High desulfurization activities were achieved only when less than a monolayer of metal component was deposited on the support. Even with a low surface-area support, the application of less than a monolayer increased the desulfurization activity.

The Bureau of Mines has also characterized the organic sulfur components of various classes of coals. Thiophenes, especially dibenzothiophene and its methyl derivatives were found to be the most difficult compounds to crack and hydrogenate. We recommend continuing catalytic hydrodesulfurization research using various thiophenes as model compounds.

Far less is known about the removal of heteronitrogen atoms than sulfur atoms. Experimental programs should be started to study catalytic nitrogen removal during coal liquefaction using polynuclear pyrroles, carbazoles, pyridines, quinolines, and amines as model compounds.

4. The effect of various coal minerals on liquefaction should be studied. This will be discussed in Section IV.

5. Experimental studies of catalysis of the rehydrogenation of the hydrogen-transfer solvent should begin. Research should focus on the catalytic effect of intrinsic coal minerals as well as externally added catalysts. Such catalysts for solvent rehydrogenation might be added to the hydrodesulfurization

catalysts in the H-Coal and Synthoil processes. Methods of hydrogen transport and activation should be studied.

6. An experimental program is needed to evaluate the effects of the coal particle size. An understanding of the contacting of the coal with the catalyst is important. This will be further discussed in Section III on gasification reactions.

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III. Catalysts for the Production of Low-Sulfur, Low-BTU Gas from Coal

The gaslight era was illuminated by coal gas. Since then, research into ways to increase the heating value and lower the cost of coal gas has been occasionally energetic, more often fitful. Most of the research has been conducted in Western Europe which has ample coal but had no oil or natural gas until the recent North Sea discoveries. When pipeline technology made it possible to bring natural gas from the American Southwest to the East Coast, U.S. research on coal gasification withered. Now that we are facing a shortage of natural gas, interest in coal gasification is on the rise again.

Gas made from coal could substitute directly for natural gas, although the old gasification technology must be improved in order to produce a gas with the heating value of natural gas (~1030 BTU/cubic ft.). In addition, unenriched low-sulfur coal gas (with heating values of from ~125 to ~600 BTU/cu.ft.) could serve for a number of industrial applications and for electric power generation. This would free a large amount of natural gas for other applications. It is, therefore, not surprising that coal gasification is being re-examined as a major source of clean energy from domestic resources.

The cheapest gas to make from coal would be "producer gas." It has a heating value of 110-160 BTU/cu.ft. which means that it cannot be transported great distances since the cost of compression and pumping would be prohibitive. Producer gas would serve well, however, as a clean fuel for power generation if the gas were made locally so that distribution costs were small.

Producer gas can be made in a continuous process in which a bed of hot coal or coke is blasted with a mixture of steam and air:

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

Since reaction (1) is endothermic, air is added to burn some of the coal which provides the heat necessary to drive the reaction:

$$2C + O_2 \rightarrow 2CO \qquad (2)$$

$$C + O_2 \rightarrow CO_2 \qquad (3)$$

The final product necessarily contains nitrogen from the air and carbon dioxide resulting from the combustion. The CO_2 can be removed, but the nitrogen serves to dilute and lower the heating value of the product gas which contains H_2, CO, and some CH_4 distilled from the coal. The sulfur present in the coal is hydrogenated to H_2S which can be removed from the product gas along with the CO_2 with a hot-carbonate scrubber. Some thiophenes will probably remain in the gas, but the level will be low enough to meet EPA standards. The producer gas is then ready for combustion as a clean fuel.

Reaction (1) is endothermic and is not thermodynamically favorable below 800°C. Although no catalyst is needed for this reaction, additives have been found that increase the total amount of carbon gasified and vary the ratios of the products. Some Bureau of Mines data are shown in Table 1. This work, plus some additional research, lead to the following conclusions:

a. A significant increase in gasification rate and production of desirable products can be effected through the addition of a large number of inorganic compounds.

b. A significant increase in CH_4 production occurs with Li_2CO_3, Pb_3O_4, Fe_3O_4, MgO, and Raney Ni.

c. Ash containing potassium compounds from initial additions is an effective catalytic agent.

d. Catalytic effectiveness decreases above 750°C.

e. Various classes of coals gasify at markedly different rates. This may be due to catalytic activity of inherent coal minerals and ash. Lignite ash is a particularly good gasification catalyst.

The Kellogg coal gasification process employs molten sodium carbonate for the dual purpose of catalyzing the coal-steam reaction and as a heat-transfer agent. Experiments show that the presence of the coal ash in the molten sodium carbonate enhances the gasification rate (lbs. of carbon gasified per hour per cubic foot of molten Na_2CO_3 used). Dolomite ($CaCo_3 \cdot MgCo_3$) is used as an additive in the CO_2-Acceptor process. Additions of 5% dolomite to the coal results in a 20% increase in carbon gasified, 15%

Table 1

Catalytic Influence of Various Additives On Coal Gasification

(Gasification carried out between steam and bituminous coal at 850°C and 300 psig. Coal was dry mixed with 5 wt. % catalyst).

Catalyst	Per Cent Increase			
	CH_4	H_2	CO	Carbon Gasified
Li_2CO_3	21	55	72	40
Pb_3O_4	20	39	52	30
Fe_3O_4	18	33	60	23
MgO	17	35	28	26
Cr_2O_3	16	25	55	26
CuO	15	37	49	22
Al_2O_3	14	33	45	22
K_2CO_3	6	83	91	62

increase in H_2 yield, 25% increase in CH_4, and 26% increase in CO at about 945°C.

Additives are helpful in another respect for the coal-steam reaction. The throughput of the operation can be increased by raising the operating temperature. However, at temperatures of ~950°C, slagging begins to occur which causes physical problems. Use of various additives allows an increase in temperature to 1000-1050°C before slagging begins. Limestone is particularly effective for this problem.

Most, if not all, present processes for the manufacture of methane from coal start with coal that has been exposed to air. There is evidence, however, that this exposure to air may have a significant adverse effect. The U. S., Russian, and Japanese literature indicate that coal and its reactions are changed significantly by exposure to air or oxygen. These changes are rapid, at least partially irreversible, and are particularly noticeable with coals of low rank. On gasification, most of the methane produced is released directly from the coal in a rapid initial stage of the reaction. The oxygen present reacts just as rapidly and at the same time.

The question of whether the effects of oxygen added by exposure to air are chemical, chemisorptive, or catalytic is partly a matter of semantics, and partly a question of data needed which might be answered by techniques now available. The evidence suggests that a definite increase in yields of methane from lignite or subbituminous coals might be realized by carrying out all steps of mining, transport, grinding, drying, and initial gasification in the complete absence of air. The importance of this approach has been derived from indications in the literature for various stages of the process, but the combination has not been fully explored:

a. Any exposure to air inhibits hydrogenation of coal.

The increase in activity of freshly ground coals is well known, particularly for lignite. A typical set of data by Appell and Wender are shown in Table 2:

Table 2

Hydrogenation of Lignites at 380°, 1500 psig
Using CO and H_2O

Lignite Sample Ball-Milled	Conversion wt% benzene soluble
Fresh (19% water)	89
Four weeks in air (13% water)	77
105°C, 24 hours in air (<1% water)	54
100°C, 0.5 hr in vacuum (<1% water)	86

An irreversible change occurs in the coal on aging in air, and aged lignites produce less desirable products. The large loss in reactivity indicated on drying in air and the minor decrease on drying under vacuum is taken as evidence that the deactivation is largely a result of oxidation. These data are amply supported by literature on the harmful effects of weathering on coals of all ranks.

b. Deactivation due to oxidation penetrates coal beds to a considerable depth.

Data on this by Terpogosova (USSR) were obtained on samples of coal taken from a mine face which had been exposed for several months, and also from a fresh cut. The further away from the wall surface, the less deactivation. The effect was attributed to the protective action of methane in the unmined coal to exclude oxygen, and the differences observed were still detectable at a depth of 1.0-1.2 meters. This observation is supported qualitatively by other references which indicate that larger yields have been obtained in low-temperature gasification by increasing the grain size of coal. There are other indications, however, that in high-temperature reactions such as the oxidation of anthracite by CO_2 or pyrolysis to acetylene, particle size does not have the same effect.

c. Unexposed coal develops new structures on exposure to air.

ESR studies by Ohuchi show the development of new active spin centers during exposure of coals to air which are not reversible on subsequent evacuation. The increment is greater for coals of lower rank, and linear in intensity with the sum of volatile matter and moisture in the original coal. Ohuchi concludes that air oxidation forms free radicals in the aliphatic/alicyclic content of the unreacted molecule. Other evidence suggests that this might include the addition of oxygen at a point of rupture. The exact nature of the neutral oxygen compounds removed during initial degradation of coal has been the subject of intensive study. The present consensus is that they consist largely of ether bridges and an unreactive carbonyl grouping which may be chelated to a neighboring hydroxyl.

Since this attack by molecular oxygen takes place most aggressively with lignites, it is entirely possible that the most reactive methane-forming sites are the first to be lost to any O_2 present. Pertinent data may be available from current research at the U. S. Geological Survey (Project 00448). Earlier studies both by chemical methods and by infrared have suggested that CO_2 formed in the oxidation of lignites is derived from methylene structures, either in bridged rings or in longer alkyls. These are considered a significant source of methane on hydrogenolysis, and thus of the larger amounts of methane which might be derived from lignite.

On this basis, any oxidation of lignite alkyl groups by molecular oxygen could lead to an increase in CO_2 with a corresponding decrease in preformed CH_4. Evidence in this direction has been found by the exposure of coal to ^{18}O followed by high-temperature pyrolysis, where 60% of the combined ^{18}O appeared in the volatile fraction. No report was made in these experiments of the particular type of oxygen bonds enriched in the remaining part of the coal macromolecule. Oxygen bridges established at this point would represent a type of condensation polymerization between adjacent rings, with a corresponding loss in volatility.

d. Critical changes occur during drying, particularly in lignites.

The necessity of grinding certain lignites either in an inert atmosphere or before complete drying is commonly recognized. The loss of water from lignites includes both free and combined HOH even at 105°C, and at 110° carbon dioxide begins to be evolved by the decomposition of carboxyl groups. This decarboxylation can be promoted by cations present, particularly Ca, and is apparently related to their tendency to form hydrates in aqueous solution. The loss of this combined CO_2 and HOH both create active sites in the molecule and at the time when this occurs the coal is particularly susceptible to re-attack by atmospheric oxygen. Drying in the complete absence of air is possible. One method which might be suitable is a thermal dewatering process for brown coal recommended by Murray, using liquid phase separation under pressure at 150-300°C.

e. The same portions of the macromolecule give rise to CH_4, CO_2, or C_2-C_4 hydrocarbons on initial degradation.

While pictures of the molecular structure of coal continue to change with additional data and more refined methods of analysis, there is general agreement that the changes between ranks during coalification correspond to gradual shifts in ring saturation and substituent groups in macromolecules which are similar for all ranks. The basic unit in configuration apparently has about 3-4 rings plus substituents, and a molecular weight of about 300-500. In coals of the lowest ranks, only one of these rings may be aromatic and others either hydroaromatic or carbocyclic, derived from humic acid or carbohydrate structures which are still rich in combined oxygen. Humic acid structures include a high proportion of C_6 rings which have not been reduced to hydrocarbons.

The alkyl groups present are predominantly methyl in coals of all ranks, but the lignites include a significant amount of longer methylene chains. Gasification of lignites under very mild conditions can give a small amount of C_2 and C_3 olefins and paraffins, but their amount is inversely related to the yield of CH_4 from a given coal. No significant amounts of hydrocarbons above C_3/C_4 are reported from such treatment in the absence of hydrogenation sufficient to rupture a hydroaromatic ring. This suggests that the alkyl chains as well as carbocyclic rings may be derived in part by the reduction of cellulose residues which have been bonded into the initial macromolecule during coalification. Residues of this type would explain centers of high chemical activity formed by mild heating and degradation.

These lines of evidence reinforce the suggestion that completely "anaerobic" mining of lignite or subbituminous coal may be worth careful evaluation, from a closed pit mine all the way to the initial rapid stage of gasification and methane formation, which may be as short as one second or less, depending on the temperature, and requires only a mild pressure of hydrogen of 600 psig or less for maximum CH_4 yield. Low initial temperatures in the range of 300-400°C are recommended in processes now under development, such as BiGas and Hydrane. This helps minimize unnecessary hydrocracking of $C_2=$ and $C_3=$ to CH_4, which consumes more hydrogen for a given product BTU. Additional data on the effects of the exclusion of air would be useful at a number of points, and the use of isotope tracing coupled with magnetic resonance measurements are promising tools for this investigation.

Recommendations

The use of catalysts to enhance the gasification of carbonaceous solids has received a good amount of experimental attention during the last 50 years. However, little work has been done relating catalysis to the gasification of actual coals. Due to the potential improvements that the use of catalysts may bring about in coal-conversion processes now being developed, and due to the urgent need to develop these processes, an intensified broad program to study coal gasification catalysis is justified. The study of additives at the Bureau of Mines seems to be a good line of investigation and should be continued. This and other programs should include research in the following areas:

1. Transport and contact problems in bringing together the coal and the catalysts. In order to study the transport problem, research must be done on the physical form and particle sizes of both potential catalysts and the coal itself. Studies to date have indicated that impregnating the coal with catalyst solutions is an effective method of obtaining contact, but additional experiments are needed. These would include studies in which the porous structures, particle sizes, and surface areas of the coal and of the catalyst are

varied and comparisons made between situations in which the catalyst is outside the coal particles as compared to within the pores. Such work should be carried out systematically using various catalysts and coals of well-defined properties. Results of such work might lead not only to practical improvements in methods of contacting coal, but also to the development of contacting standards to be employed in experiments for comparing the activities of various catalysts.

2. Kinetics of the gasification reactions. For any gasification system, improved knowledge of the kinetics can result in a decreased reactor size and lower operating temperatures and pressures. The objective of this program should therefore be to determine the effects of different catalysts and conditions on gasification kinetics. The selectivity of a catalyst in maximizing the desired products should also be studied.

3. Catalytic properties of coal ashes and minerals. Lignite ash has been found to be an effective gasification catalyst. We will discuss coal mineral catalysis further in Section 4.

4. Maximize the amount of methane produced. It is generally favorable to operate any gasification process under conditions which favor the exothermic formation of methane, rather than the endothermic formation of carbon monoxide. This minimizes the fuel requirements of the process leading to increased efficiency. It is known that methane is also

produced during the devolatilization of coal which precedes significant gasification. It appears that the coal should first be "demethylated" at a low temperature to recover as much methane, ethylene, and propylene as possible. The remaining char can then be gasified. This process will maximize the amount of hydrocarbon gases recovered.

5. Chemical state of the catalyst. This area has many important implications in catalysis of coal gasification. The chemical state of the catalyst is of major importance in affecting its catalytic activity. In the reaction $C + CO_2 \rightarrow 2CO$, for example, it is necessary to keep the catalysts in a reduced state. This can be controlled by the gaseous environment. To what extent the mineral matter in coal affects the chemical state of the catalyst is unknown and must be studied. This information could be utilized in gasification schemes.

6. Underground gasification. Perhaps techniques learned from current gasification processes will enable us to gasify coal right in the underground seams. This would be most desirable for economic, environmental, and humanitarian reasons.

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