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Coal Science: Basic Research Opportunities

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The inevitable depletion of petroleum and gas reserves and the need for replacement synthetic fuels derived from coal are generally recognized. The technology bases for utilizing coal directly by combustion and for the conversion of coal to liquids and gases are available. However, in our opinion, considerable improvements in overall thermal efficiency, hydrogen utilization, and the ability to meet strict environmental requirements are needed.

Summary. More fundamental knowledge of coal (knowledge of its structure and its behavior during conversion processes) is essential before we can generate new technologies necessary for the efficient use of coal in the future. Herein are suggested specific basic research opportunities in the areas of coal characterization, gasification, combustion, and liquefaction, along with an assessment of the impact such research programs could have. Critical characterization needs include qualitative and quantitative determination of the chemical forms of carbon, oxygen, nitrogen, and sulfur and reliable methods for the measurement of surface area, pore volume, and weight-average molecular weights. Mechanistic studies aimed at increasing understanding of the thermal breakdown of the functionalities in coal, the behavior of coal in the presence of molecular and donor hydrogen environments, and carbon gasification and hydrocarbon synthesis reactions starting from carbon monoxide and hydrogen will lay the scientific foundation for the development of new processes for converting coal into clean usable fuels and chemicals.

Coal may be utilized as an energy source in three ways. It can be burned directly to generate heat, or it can be converted to gaseous and liquid products which can be burned. It is obviously desirable to make clean liquid and gaseous fuels from coal. There is technology available today to carry out these conversions, although not without serious energy and economic inefficiencies.

Coal may be converted to gas by the reaction of carbon with steam

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

reports of which can be traced back to at least 1780 (*1*). The synthesis gas that is produced from this reaction (carbon monoxide plus hydrogen) may be burned or further converted to methane (synthetic natural gas) by the reaction discovered in 1902 by Sabatier (*2*):

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

In general, the thermal inefficiency of the reaction that converts coal to methane arises from the fact that Eq. 1 is highly endothermic at a relatively high temperature of about 800° to 900°C, whereas Eq. 2 is highly exothermic but at a relatively low temperature of about 300° to 350°C.

Coal has a ratio of hydrogen to carbon of less than unity. To make desirable liquids, with hydrogen to carbon ratios of 1.5 to 2 or more, one must either remove carbon or add hydrogen. The former method of producing liquids is pyrolysis, the latter hydroliquefaction. Coal pyrolysis is an exceptionally old technology, which probably was started on a commercial scale during the industrial revolution. In 1869 Berthelot reported treating coal with hydrogen to make liquids (*3*). In the period from 1910 to 1920, Bergius developed a commercial coal hydroliquefaction process (*4*).

A third method of making liquids from coal is by hydrocarbon synthesis from carbon monoxide and hydrogen, the Fischer-Tropsch reaction, discovered in 1925 (*5*). Selectivity to products is a major limitation.

Today, sophisticated and elegant engineering work is being directed toward developing better conversion processes, but these developments are based on the use of very old chemistry. Key limitations of this chemistry include poor selectivity and high hydrogen consumption. New and better processes will develop as a result of breakthroughs in our understanding of the chemistry of coal utilization, and these breakthroughs will necessarily come from a better understanding of coal.

Coal Characterization Needs

What follows is our assessment of the research areas critical for improving current coal conversion processes and for providing the fundamental understanding that will ultimately lead to new technologies. Our assessment touches on refining current techniques and on devel-

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oping new techniques to attack the limitations of current knowledge.

We view coal as an organic rock. As such, it has an organic, an inorganic, and a physical structure; sophisticated knowledge of each of these structures is needed. Moreover, methods to characterize coal conversion products, which in many cases represent several hundred to a thousand compounds present in amounts from 0.1 to 1 percent of the whole, are needed.

We do not believe it will be possible now or in the foreseeable future to actually determine the "structure" of coal absolutely in the way that we can with, say, organic compounds. Coal is heterogeneous by nature and varies in structure from millimeter to millimeter in the same seam; there is no less variation between coals of different rank formed from different species of plant matter in swamps hundreds or thousands of miles apart. Nevertheless, we believe it is possible to determine key structural features of coals which affect utility and reactivity. The following determinations are critical.

Heteroatom determinations. The most abundant element in coals after carbon and hydrogen is oxygen. This element is present in various organic and inorganic functional groups. What is needed is a reliable (that is, accurate and precise) method to determine total oxygen. Unfortunately, oxygen is determined by difference after carbon, hydrogen, nitrogen, sulfur (total), and ash are found. Clearly, these oxygen values are affected by a number of errors, including the fact that ash weighs less than the original mineral matter. Moreover, methods that can differentiate and quantify the various oxygen functional groups (hydroxyl, ether, carbonyl, oxides, carbonates, and others) are needed. These methods would ultimately make it possible to determine the role of the oxygen functionality in coal structure and reactivity.

Although adequate methods are available to determine total sulfur and inorganic sulfur, organic sulfur is determined by difference. An independent method for determining organic sulfur directly is essential. The forms in which the organic sulfur exists in coal are virtually unknown. Methods are required to qualitatively and quantitatively characterize the forms of organic sulfur. Ultimately, knowledge of the forms of organic sulfur will allow us to remove this element from the coal or char matrix.

Little is known about the forms of organic nitrogen in coal, although assumptions have been made that they consist of basic pyridines or quinolines or weakly acidic or neutral pyrrole, indole, or carbazole derivatives (*6*). It is necessary to know how nitrogen is incorporated in the organic matrix, since it is becoming apparent that nitrogen compounds play a key role in coal asphaltene behavior (*7*), and it is likely that this functionality plays a role in coal conversion chemistry.

There is evidence to suggest that titanium in coal exists as or is converted during processing to an organotitanium complex (*8*). Because titanium is a catalyst poison, knowledge of how it exists in native coal could lead to ways to alleviate problems due to its presence.

Carbon skeleton. With the coming of ^{13}C nuclear magnetic resonance (NMR), the hope of determining how carbon is arranged in coal becomes real. What is required is an increase by an order of magnitude in the resolution acquired by the use of ^{13}C NMR in solids. This will require very sophisticated instrumentation and the coupling of ultrahigh fields (using superconducting magnets) with pulse sequencing and "magic angle" spinning. It is also necessary to be able to conduct these ^{13}C NMR experiments at high temperatures. This could lead to ways of characterizing high-boiling coal "liquids" which are solids at room temperature, of following the extent of conversion reaction, and ultimately of determining the mechanisms of coal conversion reactions.

Coal mineral matter. Most U.S. coals contain about 10 percent mineral matter; these minerals include inorganics deposited before, during, or after coalification of partially decayed biomass. Methods are available to remove carbon (low-temperature plasma asher) and to study the residue (*9*). Techniques more sensitive than x-ray diffraction and Fourier-transform infrared spectroscopy are required to characterize this mixture.

The mixture of inorganic materials that remains after the coal has burned is called ash. Techniques are needed that will enable us to characterize the chemical compounds in ash, many of which are nonstoichiometric. Sensitive techniques are needed to determine the particular compounds in which trace (toxic) elements are present in native coals and in ash.

This information can be applied to all forms of coal utilization including combustion, gasification, and liquefaction. Identification of the chemical species responsible for catalytic behavior in coal conversions could lead to ways of enhancing the catalytic benefit. Determination of compounds that make up the slag found in furnaces might lead to ways of controlling the slagging phenomenon.

Physical structure. A method for determining meaningful surface areas and pore volumes for coals is badly needed. Depending on the coal, the gas, the equation, and the procedures, surface areas of from 2 to 200 square meters per gram have been reported for the same sample (*10*). This knowledge could lead to the establishment of a predictive correlation between the surface area and pore volume and between the chemical reactivity and physical properties of coal.

Coal-derived products. The characterization of coal products is as important as the characterization of coal itself. We believe that better understanding of these products and their properties will lead to better and more efficient ways to use them. Characterization techniques are needed in several key areas.

The number-average molecular weight ($\bar{M}_n$) is usually obtained by vapor-pressure osmometry. However, no satisfactory method is available for determining the weight-average molecular weight ($\bar{M}_w$), which is useful in predicting rheological properties. The most readily available technique today is gel-permeation chromatography (GPC). However, there are no satisfactory calibration standards which have known molecular-weight ranges and structures (chemical and physical) similar to those of the materials to be analyzed. Consequently, GPC can be used only on a relative basis (one sample to another) and not on an absolute basis. Furthermore, molecular associations in solution are not corrected for. Identification of GPC standards other than polystyrene is needed. Further, techniques such as light scattering and ultracentrifugation, which are considered primary methods, need to be critically assessed to establish their applicability in determining $\bar{M}_w$.

Rather complete molecular-weight characterizations can be obtained from the mass spectrometry of volatile components (*11*). The new techniques of field-ionization and field-desorption mass spectrometry should be applied to heavy coal liquid products (for example, solvent-refined coal and coal asphaltenes) (*12*).

Coal liquids are known to contain significant quantities of associated species such as tar acids and bases, components which hydrogen-bond and affect physical properties such as viscosity (*13*). Techniques that can help to identify monomeric units in these liquids would allow us to understand and perhaps control the chemical and physical properties of coal products.

A conceivable major limitation to the

utilization of coal liquids is problems in toxicology (for example, carcinogenicity). Studies will be required to pinpoint the toxicological and environmental problems associated with the transportation and utilization of coal liquids. Correlations of these problems with coals of various ranks, types, and grades might be possible.

Coal Combustion

In order to decide what research in coal combustion might be valuable, one needs to ask where one can discern connections between poorly understood phenomena and ways in which coal combustion is unsatisfactory and potentially capable of improvement. The most obvious such connection centers around the formation of the air pollutant nitric oxide from fuel-bound nitrogen in the coal. Coal combustion occurs in two stages. During the first stage, the fresh coal particle pyrolyzes, converting to char and volatiles, with the volatiles burning in a diffusion flame which surrounds the particle. When the production of volatile materials ceases, the flame attaches to the particle and the second stage of combustion, char combustion, occurs. Since some of the fuel nitrogen evolves with the volatiles and some remains in the char, nitric oxide formation occurs during both stages. In both stages the factors controlling the fraction of the fuel nitrogen which goes to nitric oxide rather than to molecular nitrogen are understood only in gross empirical terms (*14*). It is reasonable to hope that a deeper understanding of these factors would permit development of new coal combustion technology characterized by low emission of nitric oxide, and indeed a great deal of current research is based on this hope.

Another area in which the chemistry of coal combustion is ill-defined and potentially capable of improvement concerns the reactions of the mineral matter during combustion. During combustion the coal mineral matter is converted largely to a glass by an ill-defined set of reactions (*15*). The importance of these glassmaking reactions is several sided. First, the slagging and fouling characteristics of the product determine a major portion of the cost of the combustion process. Second, the glass-forming process generates submicron-sized particulates. The electrostatic precipitators commonly used on coal-fired power plants are ineffective at removing these small particles from the flue gas, but human lungs are quite effective at collecting them. Third, many of the toxic elements present in the original coal tend to be present in disproportionate amounts in the submicron-sized particulates and on their surfaces; these toxic elements are present not as inert glasses but in such a form that they are readily absorbed into body fluids (*16*).

Another interesting problem is the emission of unburned hydrocarbons, especially polynuclear aromatics. Such emissions represent a failure of the combustion process to go to rigorous completion. In classical combustion engineering lore, it was believed that all such failures were due to imperfect mixing and could be eliminated by improving the mixing. More recently, investigators have become increasingly aware that there are also real chemical limitations on the combustion process (*17*). Thus one is led to wonder whether the combustion of polynuclear aromatics and other hydrocarbons can go to rigorous completion. Combustion is well known to be a free-radical chain process which cannot be initiated unless the reactants are present in certain minimum concentrations, the flammability limits (*18*). It is conceivable that there are other minimum concentrations at which the combustion process inherently must stop.

The factors that control the length of time necessary to burn a coal particle are only partially defined and are of practical importance. With oil in dwindling supply, it would be highly desirable if one could burn coal in previously oil-fired boilers. There is the difficulty that these boilers generally lack ash-handling facilities, but this problem may be avoided if one uses solvent-refined, ash-free coal. The greater difficulty is that these boilers lack the firebox volume needed for the larger coal flames, a problem that is directly related to the length of time needed to burn coal particles.

Finally, there is a need to analyze the pollutants emitted as a result of coal combustion. Despite great effort to date, there may be significant problems which remain unrecognized and unmeasured. Moreover, as new coal combustion technologies are developed both to expand the use of coal and to solve one or another pollution problem, these technologies must be checked for the whole spectrum of possible pollutants.

Gasification to Synthetic Natural Gas

One key objective in coal gasification is the production of high-energy gas (~ 900 British thermal units per standard cubic foot). This is achieved by maximizing the amount of methane produced. The technology currently available to accomplish this can be considered a sequence of four discrete steps, not including coal preparation and gas cleanup.

The first step is the devolatilization of the coal. This thermal treatment produces methane as well as tars, liquids, and oxides of carbon. This process also leads to the formation of a residual char high in carbon, which is subsequently gasified by reaction with steam to produce a mixture of carbon monoxide and molecular hydrogen. Some of the carbon monoxide is allowed to react with steam, according to the water gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (3)$$

to adjust the hydrogen/carbon monoxide ratio to that required for methanation.

With conventional technology, it is thermodynamically more efficient to produce methane by devolatilization of the coal than at a later stage; the cost of producing methane from the coal's volatile matter is only about 25 percent of that required to produce it from the char. It is therefore very important to maximize methane production in the devolatilization step. Pyrolysis of coal to produce methane consists of two major reactions. The first is hydrocracking, whereby internal transfer of hydrogen takes place within the coal structure; the second is hydrogenolysis, the reaction of hydrogen with carbon singly bonded to carbon. It is known that Lewis acids will increase the amount of methane produced and will minimize coke formation; moreover, rapid heating and high temperatures will produce more methane. However, ways of maximizing methane production at high temperatures can only be devised when we have acquired a better understanding of the chemical and physical processes taking place during coal pyrolysis, particularly at high pressures.

Large quantities of carbon are left over after pyrolysis, in the form of a char. In order to produce methane from this char, additional hydrogen is needed. Generally, methane is produced in situ by the strongly endothermic carbon-steam reaction (Eq. 1), which consumes 31.38 kilocalories of heat. This reaction is responsible for the very large thermal inputs that characterize all gasification schemes. In fact, it can account for as much as one-third of the process cost. The amount of heat and the way it is supplied to the gasification reaction are highly critical to the economics of the overall process. The major problem of present-day gasification technology is an inefficient thermal balance. Whereas the total reaction that produces methane is essentially thermoneutral, the exothermic heat of the water gas shift and methanation reactions is unfortunately generated at lower temperatures than the gasification step and cannot therefore be used efficiently (Table 1). One solution to this dilemma is to gasify coal at 600 to 650 K. This is thermodynamically possible, but at these temperatures the reaction is kinetically limited. It therefore requires an efficient catalyst which as yet is unavailable.

Table 1. Heats of reaction of the steps in the coal gasification-methanation process.

Reaction step	Heats of reaction at 298 K (kcal/mole)	Reaction temperature
Gasification		
$2C + 2H_2O \rightarrow 2CO + 2H_2$	+62.76	1250 K
Shift		
$CO + H_2O \rightarrow CO_2 + H_2$	− 9.83	600 K
Methanation		
$3H_2 + CO \rightarrow CH_4 + H_2O$	−49.27	650 K
Net		
$2C + 2H_2O \rightarrow CH_4 + CO_2$	+ 3.66	

Research Opportunities in Coal Gasification

In attempting to describe the kinetics of coal gasification, one is hampered by a lack of fundamental information. To be sure, numerous measurements of the rates of burning of coal and steam gasification have been made, but all too often the data were of limited scope and were obtained in a way that precluded the drawing of unifying principles. More information is available about the behavior of various types of carbon and graphite. Graphite is a semiconductor, and the electronic band structure of the entire crystal could be affected by metal atoms with the attendant raising of the Fermi level and the possibility of cooperative interaction. With less highly ordered structures, the sphere of influence of the catalyst will be reduced. This might well be the reason for the observed high sensitivity of pure graphite to catalysis (*19*). By comparison, larger amounts of catalysts are needed to affect less well-ordered carbon structures. There is a need to apply what is known about the behavior of semiconductors doped with foreign atoms of the problem of carbon gasification.

Coal gasification with steam consists of Eqs. 1 and 3 plus

$$C + CO_2 \rightarrow 2CO \qquad (4)$$

and at sufficiently high pressures

$$C + 2H_2 \rightarrow CH_4 \qquad (5)$$

Detailed information on the basic chemistry of these reactions, particularly at high pressures, is not available. A heterogeneous reaction that results in the gradual disappearance of a solid phase such as in carbon gasification is a unique process. Its study presents experimental and theoretical difficulties and challenges not generally encountered in other types of kinetic studies. The nature of the carbon varies widely. For graphite, carbon atoms on the edges of hexagonal network are considerably more reactive than those in the basal planes. Defects and dislocations which can expose more edge carbons greatly affect reactivity; so do chemical impurities. Furthermore, the structure and composition of coal and coal char, particularly with regard to mineral matter, are sufficiently different from the structure and composition of graphite and pyrolytic carbon that any extrapolations, useful though they may be, must be made with caution.

A unique feature of carbon gasification is that many of the rate-controlling parameters such as the Brunauer, Emmett, and Teller area, pore size, and surface contamination vary with the extent of reaction. Transport limitations can also mask the true chemical kinetics of the reaction. Coals and, therefore, coal chars contain minerals which themselves can act as catalysts or which interact positively or negatively with deliberately added catalysts. Hence, it is also necessary to learn more about the chemical and physical behavior of inorganic matter in coal. This knowledge would also shed light on other technical problems that can arise as a result of the presence of ash in coal, for example, slagging, clinkering, and corrosion.

Studies undertaken to elucidate the mechanism of gasification reactions invariably stress the controlling role exercised by surface oxide complexes that form as soon as a fresh carbon surface comes into contact with oxygen. At least five different oxides of varying stability can thus be formed (*20*). There is a need to know more about the nature of these oxides and their chemistry, particularly under reaction conditions, that is, at high temperatures and pressures. The modern tools of surface physics should be particularly useful and find a fertile field of application here.

One of the practical problems associated with the use of catalysts to promote gasification is the need for proper contact between the catalyst and the coal. Good contact is difficult to achieve on a large scale. The availability of a gaseous catalyst could help; the use of supercritical fluids or molten bath reactors might be other approaches.

Shift conversion has been commercially practiced for many years in connection with the manufacture of hydrogen, ammonia, and methanol. It does not appear to present any special problems for coal gasification. The reaction is exothermic and, although an increase in temperature is beneficial insofar as it increases the reaction rate, it also reduces the equilibrium conversion of carbon monoxide. The shift conversion is therefore usually carried out in two stages, a high-temperature reaction at 650 to 700 K and a low-temperature one at 450 to 500 K to reduce the carbon monoxide content to the required level.

Methanation is not as yet a commercially well-established step in coal gasification. It is usually carried out over a nickel-based catalyst at 525 to 650 K under pressures as high as 70 atmospheres. The reaction is strongly exothermic and requires good temperature control to prevent deterioration of the catalyst. In view of the large heat of reaction, it is desirable to operate the methanator in a state of fluidization or in any other way that is capable of removing heat rapidly. Catalysts are needed that are rugged enough to withstand high temperatures and to sustain attrition in fluidized beds and that are less sensitive to sulfur poisoning.

The conversion of coal into synthesis gas is a somewhat simpler process than the production of pipeline gas (gas with a heat value greater than 900 British thermal units per standard cubic foot) since no methane needs to be made, only carbon monoxide and hydrogen. But here too the critical problem is one of thermal efficiency.

Carbon monoxide may be produced by the reduction of carbon dioxide by carbon, the so-called Boudouard reaction (Eq. 4) (*21*), the carbon dioxide normally being obtained from the combustion of carbon or coal in another part of the fuel bed. Carbon monoxide and hydrogen are produced simultaneously by the oxidation of carbon with steam (Eq. 1).

In order to increase the yield of carbon monoxide with respect to molecular hydrogen, present technology requires that excess steam be used. This is costly since eventually the steam has to be condensed out. The availability of a suitable catalyst for this reaction and for the

Boudouard reaction would substantially reduce the cost of gasification.

Pretreatment of many bituminous coals to prevent agglomeration is required in a number of gasification processes. This is an expensive step. Such pretreatments result in a loss of about 5 to 20 percent (by weight) of the coal. Not only is carbon lost this way, but the hydrogen content of the coal is also reduced. It would thus be highly desirable to be able to gasify raw coal or less pretreated coals directly or alternatively to prevent agglomeration by techniques other than oxidation.

Pyrolysis

We now set forth research recommendations in coal science and utilization related to one of the processes that generate coal liquids: pyrolysis. In the next section we treat the other process for coal liquid generation: liquefaction. For each research area we discuss technical problems, needs, and knowledge gaps.

Pyrolysis of coal is generally taken to mean destructive distillation. The major product of pyrolysis is a solid carbonaceous material called char; volatile liquid and gaseous products are generated in much smaller amounts. To be commercially viable, any pyrolysis scheme must be coupled with a way to use the char. There are a number of critical technical problems and knowledge gaps associated with the liquid products.

In all pyrolysis liquids there are significant amounts of oxygen-containing products. Lesser, but still important, amounts of sulfur- and nitrogen-containing products are also present. The approximate proportions of heteroatoms in coal tars, which will vary depending on the starting coal, are as follows: oxygen, ~ 4 to ~ 7 percent (by weight); sulfur, ~ 0.4 to ~ 2 percent; and nitrogen, ~ 0.4 to ~1 percent. Methods are needed to permit one to identify and quantify the forms of oxygen (aliphatic or aromatic hydroxyl, ether, carbonyl, carboxylate), sulfur (aliphatic or aromatic mercaptan, sulfide, or disulfide) and nitrogen (pyrrole, pyridine, quinoline, carbazole) functionalities in coal pyrolysis liquids. These determinations must be coupled with quantitative determinations of the functional groups in the starting coal. By understanding in what linkages the heteroatoms from the parent coal are present in the pyrolysis products, we will be better able to understand the role of heteroatom functionality in coal structure as it relates to pyrolysis chemistry and reactivity.

There are significant end-use problems associated with pyrolysis liquids. Historically, most pyrolysis liquids which had an end use as fuels were initially treated with hydrogen. The large heteroatom content of these liquids may make treatment with hydrogen economically unattractive in today's market. On the other hand, a variety of potentially valuable products can be obtained from low-temperature pyrolysis liquids by a combination of separation techniques that do not consume hydrogen. Since different coals produce somewhat different pyrolysis liquids upon pyrolysis and since the same coal will produce different pyrolysis liquids depending on the particular process conditions used (for example, temperature, residence time, pressure, reactor design, and gas-phase composition), a determination of potential uses for pyrolysis liquids and by-products is necessary. If, as expected, an initial large-scale need is as a fuel, then a number of questions about product quality must be answered.

How can the pyrolysis process be tailored to make an optimum fuel product, and are the fuel quality parameters for pyrolysis liquids similar to those for petroleum-derived liquids or are they entirely different? The answers to these questions will come with complete characterization data on coal, liquid products, and char, coupled with greater understanding of the mechanism and kinetics of the pyrolysis reaction.

Kinetic and mechanistic studies of model compounds and coal pyrolysis studies can be a most profitable enterprise for organic and physical chemists. In this area the chemist's arsenal of weapons, both spectroscopic (NMR, infrared, ultraviolet, gas chromatography-mass spectrometry, and electron paramagnetic resonance) and classical wet chemical, can be effectively utilized. Understanding fundamental pyrolysis chemistry better should make it possible to better control the process.

Toxicological problems are of enormous significance in the utilization of pyrolysis liquids. Studies are required to define potential toxicological and environmental (specifically those related to carcinogenicity) problems. Included in this area are questions associated with the combustion of pyrolysis liquids and aqueous effluents and the transportation and handling of pyrolysis liquids; all of these processes have the potential of liberating carcinogens into the environment.

Two other areas that are badly in need of investigation are the fate of inorganic elements in pyrolysis and the catalytic effects of mineral matter. For example, is any of the heteroatom content in pyrolysis liquids derived from the mineral matter? If so, what is the mechanism of incorporation? Answers to these and related questions may give direction toward the appropriate choice of pretreatments to remove heteroatoms, especially sulfur and nitrogen, from the coal.

It is known that certain minerals exhibit definite catalytic effects in gasification (*22*), and others exhibit catalytic effects in liquefaction (*23*). The effect of mineral matter on the pyrolysis yield and on the product slate is, however, a fairly open question. Can pyrolysis product quality or quantity, or both, be controlled by the proper selection of mineral matter in the feed coal? How does mineral matter affect the temperature at which the most desirable pyrolysis products are generated? Can mineral matter act as a scavenger for labile organic sulfur or nitrogen?

The relationship between the physical structure of coals and the pyrolysis product slate needs definition. How important are mass transfer effects in pyrolysis yields and yield structures? What is the optimum particle size? Which pyrolysis products are initial reaction products, and which are re-reaction products? What properties determine particle integrity upon pyrolysis?

As complete a characterization profile as possible is needed for the char. Both qualitative and quantitative analyses of functional groups are needed. By complete acquisition of char characterization data, the best possible parameters for a combined pyrolysis-char utilization process can be better selected. Among the specific needs are a reliable determination of total oxygen, a direct method for determining organic sulfur, and a method for determining the nitrogen functional groups. A knowledge of the type of carbon (aromatic versus aliphatic) may be of enormous importance in predicting char behavior in combustion or gasification. Carbon-13 NMR of solids is a new tool which promises to shed light on this question.

Since the mineral matter content of a char is greater than that of the parent coal and since its composition is altered from that of the mineral matter in the coal from which it is derived, the inorganic portion of the char needs to be fully characterized. A comparison of the results of a chemical cleaning of the parent coal versus the same treatment of the char as a means of reducing sulfur content would be one approach.

The combustion characteristics of the char versus those of the parent coal will need to be determined if we are to design appropriate pyrolysis equipment. Included in this investigation is a fundamental study of char combustion kinetics.

Liquefaction

In many respects, liquefaction is closely related to pyrolysis. They share an identical initial step, the thermal generation of radicals from the coal by way of homolytic bond scission. In pyrolysis these radicals are either capped by an internally transferred hydrogen or they combine with carbon to form material with heavier molecular weight (char). These two events also occur in liquefaction, along with transfer of hydrogen to the radicals from a hydrogen source. The net effect is that liquefaction produces greater amounts of liquid and gaseous products than conventional pyrolysis but at the expense of additional hydrogen consumption. Liquids from hydroliquefaction are substantially depleted of heteroatoms as compared with either the parent coal or pyrolysis liquids.

A wide range of different techniques is used to make liquids from coal, even though they all share the thermal conversion step. These methods differ in whether the hydrogen is provided from an organic donor or from molecular hydrogen either catalytically or noncatalytically. They also differ in whether and what kind of solvent is used. Thus, study of the physical properties of solutions of coal macromolecules in various solvents as well as the colloidal nature of the solutions would be helpful. An understanding of the phase behavior at high temperatures and under high hydrogen pressures would help to elucidate the liquefaction process.

The interaction of coal mineral matter with coal liquids is very important to the problem of how to economically remove mineral matter from liquefaction products. Why is it so difficult to get these solids out, and what new approaches could be developed to solve this problem? The techniques of physical chemistry could help answer these questions.

Many of the research areas outlined for pyrolysis are applicable to high-pressure, high-temperature liquefaction as well. In fact, the characterization of coal liquids from liquefaction processes has been the subject of numerous recent research papers (*11*, *12*). In particular, NMR studies of coal liquid samples have proved very valuable (*24*).

Despite the fact that some liquefaction liquids have been treated with hydrogen, they are still unstable and show a tendency toward increased viscosity with time. More detailed information on the nature and mechanism of this viscosity increase (liquid instability) is needed.

Catalysis in liquefaction has received much attention, although thus far the use of such catalysts as cobalt-molybdenum has not altered process temperature or pressure requirements (*25*). Research should be carried out to develop catalysts that will positively affect the initial coal conversion. It is relatively easy to affect the course of reactions after the primary products are out of the coal particle. However, by this time the product distribution may already have been determined. If a catalyst could be found which could influence the product distribution of the primary products as they are formed, entirely different types and quantities of products might result.

It would be of lesser importance, but still valuable, to determine whether use of catalysts in coal liquefaction improves the quality of the liquid product. Comparisons of the heteroatom content, aliphatic/aromatic ratios, viscosity, and compatibility with petroleum liquids of catalyzed and noncatalyzed coal liquids would be valuable in determining the best disposition of various coal liquid fractions. It would also be valuable to determine the effects of mineral matter, to establish the ultimate dispositions of elements, to better understand the kinetics and mechanism of the reaction, and to develop data which link coal characteristics to process conditions and to product type, quality, and ultimately utilization.

Conversion of coal to synthesis gas (carbon monoxide and molecular hydrogen) and its conversion to fuels and chemicals is carried out today on a small commercial scale in South Africa (*26*). Traditional catalysts appear to produce either one carbon product (for example, methane or methanol) selectively or a broad distribution of compounds with poor selectivity to any given compound. The challenge is to discover and develop catalysts that will selectively convert synthesis gas to desired chemical or fuel products. Application of traditional physical-organic research tools, such as labeled compounds and the determination of initial product compositions, will go far toward uncovering the fundamental chemistry of the Fischer-Tropsch reaction.

Other areas in need of additional research include improved technology for removing impurities from synthesis gas, development of more sulfur-resistant catalysts, and the whole area of homogeneous catalysis as applied to synthesis gas conversion. Homogeneous catalysis should be directed at high-value products rather than at fuels because of the catalyst cost.

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