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RESEARCH IN COAL TECHNOLOGY. THE UNIVERSITY'S ROLE

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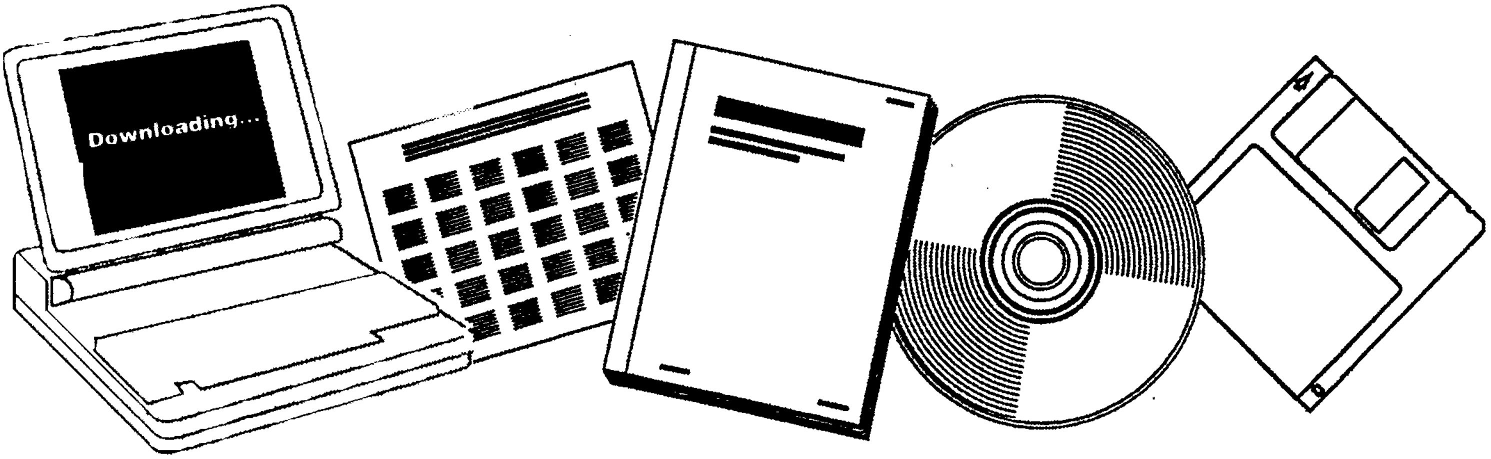

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RESEARCH IN COAL TECHNOLOGY - THE UNIVERSITY'S ROLE

Proceedings of the Workshop held at the
State University of New York at Buffalo
October 21 and 22, 1974

Sol W. Weller, Program Chairman

Joseph A. Bergantz, Associate Program Chairman

David T. Shaw, General Chairman

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The Office of Coal Research

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PREFACE

Exactly one year ago (October 1973) a workshop on Advanced Coal Technology was sponsored by NSF-RANN and held at Carnegie-Mellon University. The problems associated with the manifold utilization of coal have not fundamentally changed during the past year. However, the total world energy situation has changed dramatically in that period, and the level of activity in attempting to make efficient use of our large coal supply has correspondingly increased by a large factor. The present workshop was conducted with the intention of involving our universities in this major national program to a much larger extent, and also of updating a consensus on urgent research needs in coal utilization.

The objectives of the workshop were stated as three-fold: (1) to identify the kind of constructive research projects that can be best carried out in universities, (2) to provide some time and financial perspective on these projects, and (3) to develop some guidelines on methods to effectively bring the universities "on board" and have them contribute both to research and to training efforts. Examination of these Proceedings will indicate that the first objective was achieved; the second could only be partially achieved because of time constraints; and the third was to a substantial extent accomplished by the very existence of the workshop, which brought together many interested persons from universities around the country.

This report is constituted of two major sections. The first is the compilation of invited papers, both general and specific, which were presented during the first day of the workshop. The second section is made up of the conclusions and recommendations of four working panels. These panels, each chaired by one of the principal speakers, were established to consider the individual areas of Coal Liquefaction, Coal Gasification, Chemistry of Coal, and Coal Combustion. The position papers produced by each of these panels were reviewed by the entire group of Workshop participants on the final afternoon, so that the recommendations contained in these Proceedings constitute to some degree a consensus by the technical community represented by the Workshop.

WORKSHOP PANEL CO-CHAIRMAN

Coal Combustion	Professor Robert H. Essenhigh
Coal Gasification	Professor Arthur M. Squires
Chemistry of Coal	Dr. Heinz W. Sternberg
Coal Liquefaction	Professor Wendell H. Wiser

ACKNOWLEDGEMENTS

Gratitude is due to many people for their contribution of time and effort to this Workshop; only a few can be mentioned here. These are: Drs. G. Alexander Mills and Paul Scott of OCP and Donald Senich of NSF-RANN; Dr. Nicholas Miskovsky of The Pennsylvania State University; Professor John Medige of SUNY/Buffalo; Allen Canfield and Mrs. Ethel Schmidt of the Division of Continuing Education, Mrs. Jean Gavin, SUNY/Buffalo.

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INTRODUCTORY REMARKS

G. Alex Mills
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First, I would like to say welcome to both new and old coal research scientists on behalf of the Office of Coal Research, one of the sponsoring organizations of this conference, and to express our appreciation to the State University of New York at Buffalo, and especially to those who have worked so effectively at organizing this workshop.

The objectives of this meeting were set forth in the conference brochure (1) to identify the kind of constructive research projects that can be best carried out in universities (2) to provide some time and financial perspective on these projects, and (3) to develop some guidelines on methods to effectively bring the universtities "on board" and have them contribute both to research and to training efforts.

These objectives can be considered in the context of our national energy research and development program. An essential element of the U.S. Energy Program is to develop technology which will provide greatly increased amounts of energy from coal in a manner which is environmentally acceptable and economically sound.

The United States is fortunate to have enormous coal resources. However, it has been said that unfortunately there are two problems - it can't be mined and it can't be burned (because of environmental restrictions). To learn how to burn, i.e., to utilize coal in a satisfactory manner is the ultimate objectives of this workshop.

It is an essential tenet of the coal research program that the application of suitable technology can provide answers to the problems of coal utilization and further that this technology can be created by appropriate research.

There are several strategy options for U.S. energy. Each involves coal as a major factor both in the near and mid-term. Insofar as coal research is concerned, the strategy adopted is to go forward simultaneously with major research on each of the following elements:

Mining
Conversion to synthetic fuels (gases and liquids)
Combustion with pollution control-stack gas scrubbing
-fluid bed combustion

Power generation - magnetohydrodynamics
- combined power cycles

It is significant that the federal budget for fossil fuel research, especially coal, has been expanded greatly. The Department of the Interior budget for this purpose is in excess of $500 million this year. The synthetic fuels from coal program has increased from $112 million in fiscal year 1974 to a projected $376 million in 1976. Of special interest to the university community is the growth of research in Advanced Research and Supporting Technology, increasing from $7 million to $33 million. Specifically, OCR funding of research in universities is at the $4 million per year level and, under Dr. Paul Scott, Program Manager, is expected to about double this year. Other organizations are also participating in supporting coal research at universities. These include the Bureau of Mines, the National Science Foundation (R.A.N.N.) and the Electric Power Research Institute, and these organizations are represented at this meeting.

Some of the needs for improved technology have been identified previously and will be further discussed at this workshop. Examples are better basic engineering data for fluidized beds under pressure, more active and selective catalysts, improved valves, filters, and other mechanical devices, and better processes to manufacture hydrogen from water using coal as the energy source. The universities have certain unique capabilities - an ability to provide fundamental scientific data, to generate innovative ideas needed for second generation processes, to inform society of the serious facts of the energy situation and to train those scientists and engineers who will be vitally needed. In this last regard, it is interesting to note that the bill which the President has signed creating the Energy Research Development Agency (ERDA) contains authorization to assist in the training and education function for energy research purposes.

The structure of a university coal research program is expected to involve a number of centers with multi faculty participation. Present examples involving OCR are the University of Utah and Penn State. In other instances, participation centered around a single faculty member has a special value.

This workshop will concentrate on the technical aspects of coal research. Perhaps some comments are in order concerning the contracting process for sponsoring work at universities. The time elapsed between proposal and contract is often six months at OCR. During this period some 37 steps occur, including such actions as auditing, justification of sole source, where applicable, and other non-scientific activities. This is mentioned to encourage adequate proposal preparation. Even more important, so that the evaluation process can be favorable, the proposal should specify objectives and reasonable expectations for accomplishments. The proposal should exhibit a critical knowledge of the literature to avoid cuplicating work carried out previously by the Bureau of Mines or German scientists. Frankly, this comment is necessary in the light of a number of the 50 plus proposals received from universtities and currently being evaluated.

At present, good research ideas are the limitation, not dollars.

The opportunities in coal research are many and of great variety. It is our expectations that research related to coal at universtities can be a major and unique factor in solving problems relating to energy, the environment, and the economy which depend upon coal. I look forward to this workshop to be a significant factor in this development.

GENERAL PERSPECTIVES ON COAL RESEARCH

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INTRODUCTION

The quickest way to get perspective on problems likely to be associated with research in coal technology is to define the material with which we would be working.

Coal is a chemically and physically heterogeneous solid substance that contains undesirable impurities, some incorporated in the chemical structure and some distributed as discrete minerals throughout the coal substance.

When some coals are heated they first get gummy. All coals, when heated, give off gases and a viscous black liquid called tar and leave a porous residue known as coke or char depending on the conditions of heating.

Today, most coal is burned as a pulverized solid so that the flue gases contain undesirable gaseous impurities as well as fly ash.

The underground mining of coal is costly, requires intensive attention to insure the health and safety of the miners; to prevent ground subsidence; to prevent contamination of underground and surface waters; and to dispose of mine residues without contaminating the above ground or underground environments.

Strip mining is less costly than underground mining although it too has costly environmental constraints, particulary in the rehabilitation of the surface.

This is some of the bad news associated with the use of coal as a raw material or as the subject of a research program. If you are not already too discouraged, I will tell you some of the good news.

Coal is our most abundant fossil fuel resource. In spite of recent increases in cost brought about by more stringent safety regulations, coal is still the least expensive source of hydrocarbon fuel considering those fuels that are in competition in unregulated markets. This latter caveat is necessary because of the fictitiously low price of natural gas as a result of what some individuals believe to be ill-advised and politically motivated federal regulations.

Coal is reasonably reactive under certain conditions and can be converted to clean but expensive liquid and gaseous fuels through chemical processing. Or as stated above, it can be burned directly if the impurities in the coal are low enough or if the contaminants in the flue gases can be reduced to acceptable levels.

In view of the foregoing, it is apparent that the basic problem in research on coal technology is to devise ways and means of taking an intractable, heterogeneous solid substance and economically converting it to a more desirable and environmentally acceptable form or devising economic ways of using it directly without environmental contamination. This is the challenge for all segments of the technological fraternity in industry, in government and in the university.

EARLY HISTORY OF FUEL SCIENCE AND TECHNOLOGY

In gaining further perspective on research in coal technology, it is helpful to review what has happened in the past. In doing this, we will consider developments in fuel science and technology because this broader outlook gives a better picture of developments of coal technology in relation to other closely allied fuel fields.

In the case of coal, a logical and identifiable starting point is the year 1350 when coal first became a commercial commodity. Gas was first recognized as a state of matter in 1620 and coal was first distilled in the laboratory to yield gas in 1660.

The carbonization of coal to produce metallurgical coke was known in the late 1600's but was not practiced on a large scale until 1730. Coke was a by-product of another process developed in 1792 in which coal was distilled in an iron retort to produce illuminating gas. These two processes initially were considered basically different and this concept persisted until the early 1900's.

With the increasing use of by-product coke ovens in the early 1900's, it became apparent that it was more efficient and economical to produce gas in the by-product coke oven than in the more labor intensive gas retort so the gas retort soon became obsolete. The first by-product coke ovens were constructed in France in 1856. Since that time, they gradually replaced beehive ovens which in 1900 accounted for about 95% of United States production of coke but less than 5% in the late 1930's and an insignificant quantity today.

In 1855 Bunsen invented the atmospheric gas burner which opened the way for gas to expand its markets from lighting to a wide range of heating applications. The need for a high illuminating power for gas was no longer required after Welsbach invented the incandescent mantle in 1884. This need would have been eliminated anyway in a few years when the incandescent electric light was invented and the gas lighting load was eventually lost until its recent resurgence.

The advent of electric lighting opened up a great potential for coal combustion in the generation of steam for power generation. Thus, the combustion of coal went through the stages of burning in open-fireplaces in the early days to burning in the fuel beds of small household furnaces and subsequently large industrial furnaces and power plants and finally to burning as pulverized fuel in large central station furnaces. This latter application was first tried in 1876 but was not successful in the United States until the factors affecting proper furnace design were elucidated in 1917.

As the use of coal gas developed, the production of gas for heating purposes was also developing. The first gas producer making low Btu gas was built in 1832. This principle was not widely used until it was applied by the Siemens brothers in connection with their invention of the open hearth furnace in 1861. The use of producer gas increased from that time, until at the turn of the century it was an important fuel for industrial heating furnaces. But subsequent to that time, its use has declined and in 1920 there were only 11,000 producers in use in the United States. The gas producer has recently been rediscovered as a possible source of clean boiler fuel from coal.

Another development in the field of gas making stemmed from Fontana's discovery in 1780 of the production of blue gas, a mixture of carbon monoxide and hydrogen, when steam was passed over incandescent carbon. This discovery was dormant until the period between 1823 and 1859 when additional experimental work was done on the steam-carbon reaction. This eventually led to the development of processes for producing blue water gas in the period of 1859 to 1875. The first successful commercial process was developed by Lowe in 1875 when he introduced the carbureted water gas set. The increased use of this gasification technology continued until natural gas supplanted manufactured gas.

This brings us to the early part of the present century at which time, we see that the technology of coal carbonization was highly developed in the by-product coke oven. The gas retort was in its last days. The gasification of coke in the carbureted water gas set was becoming increasingly important. The gas producer was in use but its decline was imminent. Coal was burned on grates in various applications but this use was soon to be on the decline. Finally, the combustion of pulverized coal in large boiler furnaces was in its infancy. For example, the boiler heating surface fired in this manner increased from 200,000 sq. ft. in 1918 to 2,000,000 sq. ft. in 1925 just seven years later, an annual growth rate of almost 40%.

Considering now the role of universities in contributing to the development of coal technology in existence at the beginning of this century, we will first have to define "university research." In the period prior to the beginning of the century we will consider arbitrarily the development of basic concepts or basic studies as equivalent to "university research."

In this context, we see that the basic studies which led to coal carbonization dated back to the late 1600's. Similarly, the basic work on the reactions of coal and coke with air, carbon dioxide, and steam dated back also to the period between the late 1600's and the late 1700's. Subsequent to these periods there were refinements in the basic knowledge of coal carbonization, gasification and combustion in fuel beds and significant improvements in commercial processes but no new basic concepts came into being prior to the beginning of this century.

The combustion of pulverized coal did not stem from basic studies because as Orning stated, "The use of pulverized coal has developed largely as an industrial art." This will be discussed in more detail subsequently.

Thus we see that early technology in the field of coal utilization was founded on comparatively few basic concepts and largely evolved through developments in commercial processes.

DEVELOPMENTS IN COAL TECHNOLOGY IN THE PRESENT CENTURY

GENERAL

For purposes of discussion developments in coal technology have been arbitrarily divided into two periods, the period prior to the beginning of the present century which was just discussed and developments in the present century which are about to be discussed.

This division might not be as arbitrary as it seems when it is realized that at the beginning of this century commercial coal technology was in a fairly unsophisticated state evolving as it did into processes in which coal was heated or in which coal was gasified at atmospheric pressure, either continuously to produce a low calorific gas, or under cyclic conditions to produce an intermediate calorific value gas. As stated earlier, the combustion of pulverized coal was in a very elementary state.

In discussing developments in the present century, we will consider them in the general areas of carbonization, combustion, hydrogenation and gasification.

The relation of basic or as we have said before "university studies" to these areas will be illustrated. Inasmuch as these areas involve large-scale commercial operations, it is not always easy to trace the impact or relationship of basic work to these developments. This is one reason for concentrating our discussion on these areas and neglecting such areas as the origin, petrography and classification of coal as well as the chemical constitution and reactions of coal where the contributions of basic research are obvious and direct.

CARBONIZATION

The carbonization of coal involves the interaction of a wide range of chemical and physical properties of the coal itself in a high temperature thermal environment to produce a combustible gas, hydrocarbon liquids or tar and coke. The nature of the tar and its yield as well as the physical properties and reactivity of the coke and its yield are affected by the coal used and by the carbonizing conditions. Thus, an understanding of the complex coal carbonization process involves research on: the plastic, agglutinating, agglomerating and swelling properties of coals; dependence of yields of products on type of coal, temperature and rate of heating; the chemical nature of coal tar; and as stated above, the physical properties and reactivity of coke.

Important related areas include the properties of coke-oven gas; light oil from coke-oven gas; removal of sulfur compounds and miscellaneous constituents from coke-oven gas; the treatment of ammoniacal liquors; and the broad field of industrial coal carbonization.

Basic research has contributed significantly to almost all of the areas just mentioned particularly in basic studies of the plastic properties of coal which led to the development of the dilatometer and the plastometer. The former gives the most complete information on the behavior of coal in the pre-plastic range and the latter measures the "viscosity" of the coal in the plastic range. The development of the free swelling index, also a product of basic studies, provided a means for evaluating the agglomerating properties of coal.

Carbonization tests are not amendable to small-scale basic-type studies and it has been found that a charge of at least 200 lbs. is required to get meaningful data on yields of coke and by-products. Also the quantity of products obtained is adequate for testing by standard methods. The Bureau of Mines has developed such a test in cooperation with the American Gas Association. The agreement of the results obtained in this test with full-scale plant data has been close enough to justify confidence in the test as an indication of the performance of the coal under commercial conditions.

The entire field of the pyrolytic reactions of coal has been studied extensively in the past. This work was predominantly "basic" or "university-type" research and although this field is not covered specifically in the program to be presented, it is a most fruitful area for fundamental work.

COMBUSTION

Studies of the combustion of solid fuels have involved experiments: with graphite, coal and wood charcoal; with sizes ranging from less than 200 mesh particles to 1" spheres; with individual particles, clouds of particles, filaments; and with both stationary and moving fuel beds. This wide range of conditions can be considered as falling into one of two categories--basic studies and studies of combustion processes. The former includes, for example, studies with graphite in filaments or in simple geometric shapes. The latter embraces the use of coal in the more complex systems.

Although basic studies have provided insights into combustion mechanisms in fuel beds as well as on the behavior of individual particles, such studies have had their limitations particularly in the combustion of powdered coal. In reviewing this field, in 1943 Orning stated "The early history of the use of pulverized fuel is vaguely defined. The failure to comprehend the burning of solid fuel while suspended in air, as a distinctive method of firing, as well as the lack of knowledge of the technical requirements, contributed to its slow development. The first important industrial development followed the experiments of Hurry and Seaman of the Atlas Portland Cement Company in 1894. The universal adoption of pulverized coal throughout the cement industry, except where local market conditions favor oil or gas, is evidence of their success, but the reluctance of cement manufacturers to disclose their methods contributed to the continued slow development. It was not until 1900 that it became generally known that they were using pulverized coal."

Basic studies in the general combustion field made early in this century included work that showed that carbon monoxide was the primary product in the reaction of carbon with oxygen at temperatures above 1,000°C. The dependence of reaction rates on gas velocity was clearly demonstrated in tests in which the monotonic effect of increasing gas velocity was used to estimate the absolute reaction rate by increasing the gas flow until no further increase in reaction rate occurred.

Insofar as coal itself is concerned, basic studies demonstrated that the combustion of individual particles of coal is complicated by the formation of cenospheres as a result of the simultaneous softening and evolution of volatile matter which when burned, shows up as a luminous gas flame in photographic studies. As indicated by its name, the cenosphere resembles a hollow spherical particle and it has been shown that its characteristics are vastly different from those of solid particles containing the same weight of combustible.

Easly in this century several basic studies were made to elucidate the mechanism of combustion in fuel beds. Such studies although important at that time, have comparatively little relevance today because the fuel bed and the mechanical stoker have decreased in importance in the combustion field.

In the early development of the combustion of pulverized coal, the successful removal of the ash required that the particles be deposited in a dry or unmolten state. These dry-bottom furnaces were not particularly successful with coals having low-fusion ashes. The problem was solved by going to the other extreme of maintaining the ash in a liquid state and tapping it intermittently or continuously. The wet-bottom furnace was the outcome.

Operation of such furnaces depends largely on the properties of the coal ash and its slag. Here, basic research was able to make a significant contribution by a systematic study of coal-ash slags involving viscosity-temperature relationships as a function of slag composition and other factors.

It is apparent that basic research has contributed significantly to the field of coal combustion. In the case of powdered coal combustion the original development was in commercial applications and the basic studies followed subsequently. This frequently occurs where the commercial scale factor and the configuration are so important to the development of the technology. At the same time, there are aspects of the technology such as operation under slagging conditions just mentioned in which basic research is the most effective and direct way of developing the information required to solve difficult problems encountered in large-scale operations.

HYDROGENATION

In discussing the hydrogenation of coal we will consider first the direct hydrogenation of the coal itself and then the indirect hydrogenation by first converting coal to synthesis gas and then catalytically reacting this synthesis gas to produce liquid fuels.

Direct Hydrogenation of Coal

Coal hydrogenation was first practiced on a large scale in Germany in 1925 and subsequently in France, Great Britain, Japan and the United States. The development of coal hydrogenation technology is an interesting example of commercial operation preceding the publication of the results of fundamental research on the process. In commenting on this Storch stated in 1943, "Except for a relatively small amount of research published by the British Fuel Research Laboratory, little information on the fundamentals of coal hydrogenation is available, despite the voluminous patent literature, which is often more confusing than informative. Unquestionably much more is known by industrial interests, particularly in Germany and Great Britain, than appears in print. However, a study of the development of coal hydrogenation in these countries reveals that the intensive drive made during the past decade 1930-1940 to achieve large-scale production has left little, if any, time and funds for fundamental research."

Subsequent to the commercial development of coal hydrogenation extensive basic work was done by the Fuel Research Station at Greenwich, England; by the

Canadian Bureau of Mines; by the U.S. Bureau of Mines; by the Coal Research Laboratory of the then Carnegie Institute of Technology; and by the Fuel Technology Department of Penn State University. This work covered all aspects of coal hydrogenation, including for example: mechanism of solvation; effect of catalysts, vehicle, type of coal, petrographic constituents, and process variables. This fundamental work led to new concepts in coal hydrogenation which have been incorporated in technology now under development.

Synthesis of Hydrocarbons from Mixtures of Carbon Monoxide and Hydrogen

The catalytic conversion of mixtures of carbon monoxide and hydrogen to hydrocarbons which is referred to as the Fischer-Tropsch synthesis or the gas synthesis process was highly developed and commercialized in Germany prior to World War II. This type of development involving as it does catalytic processes is ideally suited to university or basic research. Up to the present time, most of the research in this field has been done by commercial or governmental laboratories. However, there are some real opportunities for innovation particularly in the production of ethylene and other chemicals used in the petrochemical industry. In previous work on the Fischer-Tropsch synthesis, the objective was the production of liquid fuels and also generally paraffinic type hydrocarbons. However, if we look at the possibility of producing for example ethylene from coal, the characteristics of the catalyst would be entirely different from a Fischer-Tropsch catalyst. This could be a fruitful area for university research.

GASIFICATION

In discussing coal gasification, I think it would be helpful first to give perspective to the many developments in this field in the present century. At the beginning of the century there existed two processes for the complete conversion of solid fuels into gaseous fuels. One of these was the continuous producer gas process in which coal or coke was gasified with air and steam to produce a low heating value gas (140 to 170 Btu/cu. ft.). The other was the intermittent carbureted water gas process in which coke was gasified with steam to produce blue water gas which could be enriched by cracking oil in the checker-bricked carburetor of the water gas set. Each of these processes had its limitations either because it could not use coal directly; because it produced a low heating value gas; because it was intermittent; or because it had a relatively low output per unit of cross-sectional area.

All of the developments in gasification technology in the present century were directed toward overcoming one or more of these limitations. For example, continuous operation was achieved by using oxygen or by heating solids or liquids by burning char with air and using these heated substances as heat carriers for gasification reactions. Higher outputs per unit area were achieved by operation under pressure or under slagging conditions. Enhancement of heating value was realized by the use of hydrogasification. In addition such contacting techniques as fluidization and suspension or entrained gasification came into being. Finally, the technique of ash agglomeration in a so-called "dry" fluidized bed reactor was developed.

Except for the concept of hydrogasification all of the other developments came about in connection with commercial or near commercial processes. Hydrogasification was the outgrowth of work done by the British Gas Council on the autothermic coking of coal by hydrogen in the middle 1930's. Since that time fundamental studies by the British Gas Council, Institute of Gas Technology, U.S. Bureau of Mines and the Australian Department of Scientific and Industrial Research have all contributed to the advancement of the science and technology of hydrogasifying coal.

Although the other developments in this century originated generally in connection with large-scale developments, nevertheless once these developments came into being, fundamental or small-scale studies in such areas as pressure gasification, fluidization, and slagging contributed significantly to advancing gasification technology.

The physics of gasification and combustion reactions are so closely related that basic work of this type in the latter field which has already been discussed is also applicable to gasification. In addition, much basic work has been done on the mechanism and kinetics of gasification reactions. Some of this work has guided commercial developments and some has been useful in sizing reactors.

One gasification area in which university research has taken a leading role is in the catalysis of the steam-carbon reactions by alkali salts. This work has not yet been applied commercially although the use of molten sodium carbonate as a heat transfer medium in a proposed gasification process incorporates the added advantage of catalyzing gasification reactions.

SUMMARY

If we reflect on our discussion of developments in coal technology, it is apparent that basic research has played an important role in refining and extending the technology. However, the complexity of commercial processes for utilizing coal has resulted, in most instances, in technological advances coming first in relatively large-scale operations. In such developments, basic or university-type research did not play a role in the past nor will it play a role in the future.

Universities, particularly in Great Britain, Germany, France, Japan and the United States have added fundamental knowledge to the field of coal technology. Unfortunately, the number of such universities has been relatively small in the past. Their contribution to the field has been multiplied by the many individuals that they educated and who went to work for Government research organizations, private industry and industry-supported research organizations where most of the basic work on coal technology was done in the past.

Coal is not a cut and dried substance to work with - like a pure compound. In attempting to present a general perspective of the field of coal technology, I hope the difficulties of working with coal and its intractability have come through loud and clear in my presentation. Whether we like it or not, coal is going to become a major supplier of energy in the next 20 to 50 years. As a consequence of this fact, we will need all the help we can get from industry, governmental laboratories, trade association laboratories and universities to contribute to the advancement of coal technology which will be so vital to our energy system for many years in the future. Hopefully, as a result of conferences such as this one, the interest of universities in doing work in this field will be stimulated and we will see a much broader participation of universitites in what is going to be a vital field of research.

THE ROLE OF THE UNIVERSITY IN COAL RESEARCH

Harry Perry
Consultant
Washington, D.C.

The topic that Dr. Weller asked me to address today is really much more complex than the straightforward title indicates. It raises not one but a series of questions that need to be addressed. Among them are: What is the real value to society of research on any subject? Assuming that we conclude research is a desirable activity, where does the university fit into the scope of the research activities? Having answered these questions, we ask how, if at all, university coal research differs from research by the universities on other subjects and what the universities should be doing to fill any perceived gaps.

The relationship between R & D and economic growth is difficult to quantify but it appears certain that R & D improves productivity and, through this, economic growth and well-being. In 1971, in a colloquium conducted by the National Science Foundation, it was concluded that "econometric studies do provide reasonably persuasive evidence that R & D has a significant effect on the rate of productivity" and that "the marginal rate of return from an investment in research and development has been very high."[1]

In other studies, attempts were made to trace the various R & D activities that were precursors to the commercialization of new technologies. Such developments as the heart pacemaker, hybrid grains, and the green revolution, video tape recorder and organophosphorus insecticides were analyzed to relate the R & D activities associated with their discovery to the commercial development.[2] Because of the long periods between these two stages, it is frequently difficult to relate them with a high degree of precision, but for the cases examined it was clear that, in part, focused research was responsible for these new technologies.

The factors which influenced the rate of the innovative process for the case studies were quite varied, but the most important of all was the recognition that a technical opportunity existed. The second most important factor was the recognition that there was a "need" for a technological development.

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[1] Research and Development and Economic Growth/Productivity, NSF 72-303, December 197

[2] Science, Technology and Innovation, NSF C-667, February 1973.

Many other factors were also considered important: internal R & D management, availability of funding, and the presence of technological entrepreneurs. It seems appropriate to note here a point to which we will return later: the universities have background and are well-prepared in some of these important areas but not in others. One would expect that a university would be well staffed to recognize the existence of a technical opportunity but would not be as expert as industry at being aware of the "need" for a particular development. In most of the other important elements that have been identified as leading to innovation, most universities do not have any particular advantage over competing research institutions.

Another factor that has been important in the development of new innovations has been the confluence of a variety of new technologies at a particular time. Since the different technologies that must come togehter frequently arise in different fields of science, a deliberate attempt to use an interdisciplinary approach to the development of a new technology appears to be a highly desirable method to follow. Unfortunately, in my experience in dealing with universities, I have found that it is difficult (but not impossible) for them to set up a well-functioning interdisciplinary team. On examination, the reasons are fairly obvious why such teams are not easy to organize or to make operational at universities. The administrative and budget structures, divided as they are, into a school of engineering, a school of business, a law school, etc., cuts the university into units concerned with a relatively narrow field of learning. Moreover, the academic freedom that is the traditional policy of all universities--no matter what its other advantages--works to the disadvantage of functioning interdisciplinary teams. A given university may have all the experts that it needs to assemble an interdisciplinary team to tackle a new problem, but if members of one department do not wish to participate (and their reasons may be valid) it is all but impossible to make the team function well.

The place where the university fits into the spectrum of R & D that ranges from basic research to improvements in the operation of an existing commercial plant has generally been at the basic research end of this continuum. No matter how the term "basic research" is defined, most research at universities falls into this category. Occasionally one finds some applied research being undertaken by the universities. This frequently occurs when funds are available to do this type of work and a particular school needs outside funds to maintain its ongoing activities. Most often it seems to occur where a university professor also happens to have entrepreneurial talents and is anxious to get into more practical fields.

Although I have not seen studies to prove it, university research seems to come off in this field probably no better or worse than the basic research conducted by other institutions. One of the long stated "truths" about the success of basic research seems to be borne out by experience, i.e., the probability of success if very much dependent on the quality of the researcher.

By concentrating on basic research the universities are faced with the inherently long time lag between the research and the time when the results have a practicel value. This makes short-term justification of funds difficult. Moreover, basic research must be regarded as a long-term investment since it becomes a wasteful process if funds are turned on and off. A lower level of support that is steady is better than a higher one that in intermittent. Finally, it has been pointed out in an NSF study[1] that research investments depreciate and become obsolete. They depreciate "because much of the knowledge would be forgotten and rendered useless without continued efforts at exercising, retrieving, and transmitting it. That is what much of higher education is about."

It is this last point that I want to emphasize most. Despite the useful contributions that R & D at universities may make in developing new technologies they must never forget that their main role is to educate. Any activity they undertake that reduces the quality of education should be strenuously resisted. Obviously, R & D activities are essential at a university in preventing "knowledge from depreciating" and to provide the means for graduate students to gain experience in the performance of R & D. The more sophisticated the research opportunities offered, the better will be the students who are attracted to the program. This in turn should lead to a higher quality research product.

Having discussed R & D in general and the role of the university in particular, I want to now turn to just where the universities fit in developing a strategy of coal research. In short, should the role of the university by any different for coal than it is for other research activities? Does coal research have any unique features and, if so, how should the universities respond?

To answer these questions, one must first examine what new problems the nation faces in the energy field and what role coal will play in overcoming

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[1] <u>Research and Development and Economic Growth/Productivity</u>, <u>op.cit.</u>, p. 48.

these problems.

The change in the energy position of the United States from a nation with low-cost, abundant energy resources of all kinds to one faced with shortages and dramatically higher prices for energy has forced the country to re-evaluate its energy future. Since energy availability is so indispensable to economic growth, energy supplies are basic to our future economic well-being. It is not surpring, therefore, that the sudden change from abundance to scarcity has gotten the attention of all segments of society--everyone is interested in improving our life styles. It is also not surprising that lay people and politicians alike have turned to science and technology for answers to the new problems raised by the shortages. In the past, the widespread application of the scientific approach has increased man's productivity and raised the living standards in some countries to unprecedented levels. The underdeveloped countries are still numerous enough to remind us of the difference between living conditions in the technologically-oriented countries and those, which for one reason or another, have not been able to apply science and technology in their economic systems.

However, the use of science and technology to solve man's problems has limitations and these must be recognized. R & D may, under some circumstances, be the best and least costly method of solving a given problem, but this is not always the case. In many instances, other totally different types of activities may prove to be superior. These include such actions as changes in laws and regulations, modification of existing economic incentives, and changes in the tax structure. Moreover, even if R & D is thought to be the best answer to our energy shortages, then the R & D program must be designed to meet certain objectives which in turn, must be well defined if a balanced program is to be achieved. Among the reasons that have been advanced for an expanded energy R & D program are:

1) Reduce the cost of energy
2) Provide flexibility of supply
3) Provide customers with a choice of energy systems
4) Promote competition
5) Expand knowledge
6) Increase energy availability
7) Exploit a resource
8) Promote self-sufficiency

9) Promote environmental quality
10) Provide a product for foreign markets

The optimization of energy policies, given such a diverse set of objectives with unspecified degrees of importance and whose relative importance tends to fluctuate over time, would clearly constitute a mathematical miracle. A major first task for policy makers is to sort out and consolidate these objectives and to attempt to provide a logical, stable weighting system.

The reasons for selecting coal as the specific energy topic of today's discussion is easier to justify, even if the program were not sponsored in part by the Office of Coal Research. If the nation is to solve its energy problems without depending too heavily on resources that must be imported from other countries, then the vast coal resources of the United States will have to become a much more important part of our energy supply than it has been in the recent past. Without the breeder reactor and at U_3O_8 prices up to $15 per pound coal makes up over 80 percent of the total nonrenewable energy reserves of the United States. Moreover, coal research has been badly neglected not only by the universities but by the government and industry alike. Finally, because of some of its objectionable qualities much of the coal will first need to be converted to more convenient forms if it is to be used in greatly increased amounts. And if costs are not to be excessive, this will require the development of new conversion technologies.

The past neglect of coal research activities is easily demonstrated by the limited number of technologies in the development stage that could be accelerated to meet our immediate needs. If a reasonable level of coal R & D had been conducted in the past there would now be an array of technologies at various stages of development on which to draw.

The reasons that coal R & D was neglected are not difficult to understand. The coal industry has historically consisted of a large number of small companies, and throughout most of its history, has been economically depressed. The absence of any significant capital barriers to entry and the vastness of the resources on which to draw kept competition at a cut-throat level, except for wartime periods.

In some fields, if industry did not conduct a reasonable level of R & D, the government responded to fill the gap. For the coal industry, however, there were two reasons why this did not occur. First, the overall energy supply situation for the country appeared to be very favorable and prospects seems very good for this situation to continue. Secondly, after World War II, the nation adopted a policy--partially as a means of atonement for dropping the only atomic bombs that were ever used--to develop peaceful uses for atomic energy. As a result, for many years the government's energy program was heavily concentrated in the development of methods to use nuclear fuels for the commercial generation of electricity. Until the last several years 80 percent or more of the federal energy budget was devoted to nuclear energy.

In the absence of a strong R & D program either by industry or government, the universities were unable to support the type of program that was needed. As a result, coal research has been largely neglected by the universities and the number of graduate students working on coal problems was so small that their contributions were miniscule. Except for a very limited number of universities - and even those have a subcritical mass of talent - there is no tradition or history of coal research in these institutions. This can only mean that we must first concentrate on developing a cadre of experts in the universities who will be able to teach what is needed. To do this, the universities will need support at reasonable levels on which they can depend for extended periods as they gear up to learn a new discipline. After centers of knowledge about coal have been developed - and this will take time - we can then expect the universities to turn out the necessary number of well-trained people to work in industrial laboratories on coal technology. And that should be the first and most important objective of the universities.

At some later time, as the universities develop their own competence, the research should be useful in its own right. Moreover, because some of the funds at the graduate level will be supplied by OCR and others who have particular problems in which they need help, the research will become more focused and of more direct assistance in the development of the new technologies that are needed. Because of the long lead times, under the best of circumstances, between basic research and the practical application of what is learned and the special situation with respect to coal where some "catching up" is also required, those who support the research will have to be more patient than usual while waiting for the research to yield useful results.

To sum up, the most important role of the universities in coal research, particularly over the next five to ten years, is to train the people needed so we will have the manpower to be able to accelerate R & D by industry and the rest of the scientific community. In performing this function, R & D will play an important role in the educational process. Hopefully, some of the R & D will be successful so that some of what is learned will eventually be applied; but even if it is not, the R & D performed would have served its most useful purpose.

RESEARCH OPPORTUNITIES FOR UNIVERSITIES IN COMBUSTION OF COAL

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SUMMARY

Research on the combustion of coal has proceeded in a most erratic manner for historical reasons of century-long, oscillating interest and funding. The traditional pattern of solving the easy problems first and leaving the difficult ones to solve themselves (for the most part) is particularly marked. In many cases, the material studied was not even coal. A classic simplification has been the substitution of the study of "pure" carbon reactions, which are now understood in certain respects to a stunning level of sophistication and detail. At the other extreme: (1) the "structure" of coal is still effectively unknown, making generalizations extremely difficult; (2) there is no clear model for the mechanism of pyrolysis, and there are still differing views on the role of rate of heating on the rate of pyrolysis and on the ignition mechanism; (3) the kinetics of coal volatiles in combustion is virtually unstudied; (4) there are still major ambiguities in the burnout mechanism of the flame-formed coke, both in the solid bed and in the dispersed phase (pulverized coal flames or entrained reactors); (5) there are still unsolved problems governing the flame front location in a plane flame system. This listing indicates the prime areas of research opportunities. However, one need above all is development of an adequate working model of coal structure or constitution that can be used as the basis for generalizing specific results and subsequently for predictive purposes.

1. INTRODUCTION

The revival of interest in coal combustion research is something that has been forecast many times since the end of World War II, and -- with some small trace of residual specticism -- it now appears that revival after many previous false starts may be a fact. We are therefore now faced with the classic situation of demand for investigators and results, with an unbelievably small cadre of investigators with prior experience of coal combustion research to draw on or to build upon. It is indeed fortunate that there was still a handful of university who were prepared to spend the last decade or two being "irrelevant" by continuing such research, generally on shoestring funds, and with much time and energy spent in defending their proposals against their "peer" reviewers who were unacquainted with the precise subject and who were nevertheless convinced that such research had no point. I, personally, abandoned coal research for lack of funding in about 1965, but I was fortunate in being able to continue parallel work on incineration that had much in common with coal. This continued until incineration research was also declared out of bounds about 1970/71 as a result of belief that recycling would solve all solid waste problems.

We are now back in coal research. My task at this meeting is to discuss the problems of combustion of coal. As I understand it, the meeting has two objectives: first, to introduce newcomers to coal research; and, second to identify the problems at the forefront of research. To satisfy these two objectives the format of this material is to provide a description of what is known about coal behavior in combustion, in relatively simple terms, with some additional commentary and listing of problems that assumes a somewhat wider familiarity with the coal research literature. The difficulty in constructing this presentation is that one cannot talk meaningfully about coal research without some knowledge of: the nature of the material; where it is currently used; where it might be used in the future; what is already known about its behavior; what theories of behavior (i) exist, (ii) are generally accepted, (iii) or are disputed, (iv) or have yet to be constructed. The difficulties are compounded by the varied applications where theories developed for one application have little relevance to another, by the highly variable nature of the material under investigation, by the related difficulties of generalization, by the difficulties of unambiguous experimentation, and by need for an awareness of where coal research stands in terms of the "theory" of theories.

Above all, coal research must be "Applied Research." Although this by no means rules out basic research (under the guidelines of applied research at a fundamental level), nevertheless, selection of priorities must be largely -- though not totally -- guided by the current or prospective applications. Fortunately, this procedure from the time of Archimedes onwards has proved to be effective in identifying the most significant fundamental problems and simultaneously most efficient in solving practical problems. (The classic example of this, of course, was the discovery and use of the principle of hydrostatics in solving the problem of the adulteration of the gold crown belonging to Hiero II of Syracuse.)

To set the nature of the research problems in context, a brief look at the nature of coal and some derivative difficulties follows. This includes some pertinent historical background.

2. SOME HISTORICAL PERSPECTIVES AND OTHER BACKGROUND

Research on the combustion of coal can be said to have been in progress for something between a century and a century and a half, with references to coal combustion (explosion) problems going back three centuries. The earliest significant paper was undoubtedly that of Faraday and Lyell in Phil. Mag. for 1845 reporting on the investigation of the Haswell Colliery explosion in which the volatiles theory of ignition was first advanced (the Faraday mechanism). This was also typical of research of the next 60 or 70 years in that the main incentive was safety underground rather than combustion utilization. It was significant that commercial combustion and gasification systems, including grate combustors, shaft gasifiers, and pulverized or suspension firing developed largely by trial and error, with many of the central problems being mechanical or related to ash behavior rather than deriving from combustion.

The impact of fundamental combustion research on utilization has therefore been minimal, and much of the fundamental research applied to utilization was originally derived from the explosion literature. The development of fundamental research was also hampered by oscillating interest that was inevitably accompanied by oscillating funding. It was also a matter of chance that as fundamental interest shifted from explosions to utilization, about 1920, research in the fast developing oil industry became far more attractive and interesting to fuel chemists than continued work in coal. Early research, particularly in the first two decades of this century, was mostly well planned and well executed, the results being largely limited by the relatively primitive experimental equipment, instrumentation, and related techniques available at that time. The investigators were mostly chemists, few in number, but mostly it would seem of high caliber, and some of the work carried out at that time stood as the best work in the subject for the next half century -- indeed, some of the results are still the only available sources on one or two topics.

Between the two World Wars, by contrast, it can only be said that coal research became one of the least attractive research areas, and it has to be recognized that the overall quality of research suffered accordingly. The quantity of research went up, but the quality went down. By 1924 Harvey compiled 5000 titles of papers on pulverized coal firing alone, and by 1930, in a list by Knabner, this had grown to 10,000. What it may be today may be almost beyond reckoning. The literature on coal combustion is staggering; but at the same time, the really valuable content is disproportionately small. However, to dismiss this past literature as valueless would be to throw out, for example, such classical and critically significant papers as the Nusselt diffusion analysis of 1924, and the Tu, Davis, and Hottel papers on carbon sphere combustion.

Research since World War II has also been spotty both in activity and quality of the research. By and large the quality can be said to have improved (which in some cases does not say very much), but it has also become apparent, as research results have amplified, just how complex the problem is and how difficult it is to design unambiguous experiments -- this is compounded by the astonishing ease of performing thoroughly ambiguous experiments. It is possible that in no other research area is it so important to make the critical distinction between correlation and causation. The relevance of this to the newcomer to coal research is that lack of a minimum knowledge of the literature seems to provide ample opportunity for the re-invention of the wheel, and acceptance of unsubstantiated beliefs, and past experience indicates that the most usual re-invention is of poorly defined experiments that increase the body of ambiguous or uninterpretable results. The problem is greatly aggravated when this condition of ambiguity is not recognized and correlations are interpreted as causations. As an example, (out of many): it has been observed that particle samples obtained from pulverized coal flames, and displayed on slides, frequently show a number of so-called cenospheres, and a number of small fragments. This is interpreted as implying that combustion proceeds via cenosphere formation. The conclusion may indeed be correct, but not on that "evidence." It can just as well show that the cenospheres are there because they are not burning -- which is why they can be sampled in quantity, and particularly as true cenospheres are formed in neutral or reducing atmospheres --

and the small fragments that are dismissed because they are present in small quantity could be easily the important fragments: they may be present in small quantities because they *have* been burning! In fact, we must recognize that the results are ambiguous; and unfortunately, the coal research literature is full of such ambiguities.

A second prime source of difficulty that must be emphasized relates to the problem of generalizing research results. Some aspects of combustion research have reached the point that reasonable agreement with existing theory is now possible -- after the fact -- but reasonable prediction of quantitative combustion behavior ahead of time still seems to be impossible. The source of the difficulty is the lack of knowledge of coal structure and constitution that makes quantitative generalization from one coal to another still impossible. The point to remember is that without such generalization at some time in the future, we shall be limited to endless testing of one coal after another for all practical purposes. The prime requirement here is development (7) of an adequate model of coal itself.

Some of these points can now be usefully re-iterated and set in context by what follows.

2.1 The Nature of Coal - This is itself a major area of knowledge and research in its own right. Some minimal acquaintance for combustion purposes is necessary. Some of the more important factors are listed below.

Physical appearance: Hard to friable "black rock"

Gross Composition: (1) Organic matter
(2) Mineral matter
(3) Moisture

Elemental Analysis: Organic - C 65 to 95%
H 2 to 7% (9)
O 2 to 20% (25)
N 1 to 2%
S up to 5% (10)

Inorganic - SiO_2, Al_2O_3, Fe_2O_3, CaO, etc.

Proximate Analysis: Volatile Matter: 5 to 40% (50)
"Fixed" Carbon - (100 - VM) on d.m.f. basis
Moisture: up to 10 or 20% (brown coals, 70%)
Ash: up to 10 or 15%, special cases very much higher

Petrographic Analysis: maceral composition

Molecular Structure: Various models have been proposed; none yet accepted. Essentially involves some variable form of ordered ring structure constituting stacked lamellae or crystallites, with crystallites randomly ordered with respect to each other.

In this listing, the percentage ranges given are the common ones; values outside the ranges can be found. The elemental analyses are for the total coal; elemental analyses for the maceral constituents will vary. The variability of the maceral content, and also of the ash (or more accurately mineral matter, which is ash prior to combustion) makes one suspicious of the implied accuracy of typical coal analyses given in published tables. There are commonly given to two decimal places. Since the oxygen in the earlier analyses, and still often today, was by difference, and also contained the errors, there was no real check on accuracy as would be provided by an analytical closure. The accuracy of the analytical methods is not in doubt, if competently done, but rather the variability of one sample to another of the same coal. It is possible that the implied accuracy of analysis has given a totally spurious idea of the uniformity of coal that is totally false and that can critically affect the way that one does think or should think about design of experiments. The variability of coals cannot be over-emphasized. This variability is responsible for the:

PRIME INTRINSIC SOURCE OF DIFFICULTY IN COAL COMBUSTION RESEARCH

This is: UNCONTROLLABLE INHOMOGENEITY WITH RESPECT TO VIRTUALLY ALL CHARACTERISTICS.

e.g.
1. Irregular shape (usually approximated as spherical)
2. Irregular breakage (usually ignored)
3. Size and shape variations even in a "narrow" sieve cut
4. The inhomogeneity of a given particle or lump
   - notably distribution of macerals and minerals
5. The variation of "average" particle properties between particles
6. Random variations in swelling behavior and ash formation

Briefly:

1. No two lumps or particles are alike
2. No two seam samples are alike
3. No two seams are alike

Such variations cause appreciable scatter in experimental results and generate the following question: How do you know when scatter is due to poor experimentation or due to natural inhomogeneities?

The question of experimentation leads to specification of the:

PRIME EXTRINSIC SOURCES OF DIFFICULTY

1. Ease of executing poor experiments of low information yield and high level of ambiguity
2. Difficulty of designing and executing well designed unambiguous experiments yielding high quantity of high quality information that can be explicitly interpreted

2.2 Experimental Methods - Some of the more reliable experimental methods are as follows:

1. Single captive particle - limited to crushed size range
2. Isothermal furnace - very dilute phase, crushed or fine size, narrow size cut
3. "Plane" flame furnace - dilute phase, fine size, size controllable within limits
4. Explosion volume - uniform density cloud in fixed volume, fine size and narrow size cut
5. Combustion pot - dense phase, fixed bed; coarse or crushed size, and narrow size cut
6. Smoke Tube - liquid particulates (volatiles)
7. Shock Tube - dilute phase, fine size, narrow size cut

Details of these methods are out of place here on account of space, but they are considered to be methods that with care, can yield interpretable results. Even so, the emphasis should be on the core required. However, what should be avoided is the type of experiment used, for example, for many decades in which clouds of particles are dispersed upwards against gravity. This was long a popular method for measuring the so-called "ignition temperature" of the dust cloud. What, in fact, was measured was the temperature of the igniting source under the conditions of experiment, and the relation of the igniting source temperature to the ignition temperature was never explained or discussed (and it was noteworthy that the original experimenters between 1900 and 1920 carefully noted the difference by the use of "relative" ignition temperature for the ignition source, a distinction that was improperly dropped in later usage).

The prime objections to the method, however, were that the dust concentration was not accurately defined, and neither was the direction, local fineness, and velocity of the cloud at the moment of ignition. Apart from urgent ad-hoc testing, that such devices were originally designed for, the deficiencies for research experiments should be obvious. It is difficult therefore to understand their continued use over several decades for research. Unfortunately they contributed quite massively but uselessly to the combustion literature.

3. GENERAL PROBLEMS IN COAL COMBUSTION SYSTEMS

As a framework for a more detailed specification of problems relating to coal combustion, the problems can be set in a general perspective, starting from the applied point of view of engineering interest. The major industrial use of coal is for steam raising in industrial boilers (mostly pulverized coal firing, but with smaller units still grate fired). In these systems, the dominant problems are other than combustion, at least so far as current use is concerned. Prospective use will require more knowledge of combustion and kinetics.

3.1 Engineering Problems - These can be summarized as follows

A. CURRENT
- Heat Transfer (model development)
- Slagging
- SO_2 Control
- NO_x Control
- Particulate emissions control

(Note: Interest in combustion characteristics is minimal to zero).

B. PROSPECTIVE
(1) Use of ultra-fine coals in very limited space as substitute for oil or gas
(2) Use of low volatile fuels - notably chars - and other low grade solid fueld of potential commercial interest
- Flame Stabilization
- Reactivity (burn out)

The point is made here again that emphasis has not been on kinetics needed for practical reasons, although better knowledge of the combustion behavior might provide routes to better boiler and burner design. In contrast, knowledge of kinetics could and should be central to understanding, design, and control of fixed bed reactors (grate combustors or shaft gasifiers). Incentives for continued coal research have come rather from gasification studies on the practical side, and otherwise from intellectual curiosity (generally coupled with the expectation that understanding will also provide a practical pay-off in applications). Separate from this has been massive continuing research on carbon reactions, deriving mostly from concern with physical and chemical stability of carbon moderators in nuclear reactors, but with additional interest in carbon as a structural material (including heat shields) and in regeneration of catalysts in petrochemical operations (by chemical engineers). The Chemical Engineering literature, however, has mostly reinvented previously established results with a lag time of about 10 years). For the future, however, the needs of new devices and applications, or such requirements as use of char, are likely to depend for success on the more fundamental knowledge of combustion kinetics. These prospects provide a basis for continuing fundamental research on coal combustion mechanisms of the type that combustion engineers have had relatively little interest in to date. The point is amplified by considering the following uses:

<u>Current Uses</u> - Boilers: Mainly p.c. (large units), some stoker firing
(small units: generally less than 250,000 lb/hr. steam).
Varied other "minor" uses.

<u>Prospective Uses</u> - Recovery of part of industrial process heating
market for firing furnaces. (Thermal process industries: ferrous,
non-ferrous, refractories, lime, cement, etc.).

<u>Methods</u> - (1) Direct firing - particularly attractive if ultra-fine,
clean coal is available.
(2) "Indirect" - some form of gasifier.

<u>3.2 Scientific Problems</u> - Research on the different practical systems, however, will be influenced by the scale of the equipment used and the particle or lump size involved. These partly determine the nature of the "scientific" problems of interest. More generally, there are four parameters who values vary over several orders of magnitude with the result that different mechanisms are important over different ranges of the four parameters. The four parameters are: particle size, particle density, temperature, and rate of temperature rise. Table 1 provides a particle size and density classification that yields four different combustor system groups of importance or potential importance.

For the four parameters, the ranges of importance are roughly:

Particle Size: 10^{-4} cm to 10^{2} cm

Particle Density: 1 gm/cc to 10^{-4} gm/cc

Temperature: 300°K to 3000°K

Temperature Rise Rate: 10^{-3} degC/sec to 10^{6} degC/sec
(or as high as 10^{8} C/sec in some instances)

Of these parameters, only temperature does not exceed a coverage of more than one order of magnitude. However, temperature has its corresponding influence through the variation of reaction rates in consequence of the Arrhenius group. Overall, including the region of diffusion dominance for which the temperature coefficient can be approximated by E = 1500 kcal, E varies from 1500 to 50,000. Including the effect of coal rank, we then have to consider the possible permutations of these parameters within the context of the following list of problems or considerations:

(1) Breakage Mechanism - shape, size and size distribution.
(2) Analysis - Ultimate (elemental)
  - Proximate (V.M., H_2O, ash)
  - Petrographic (macerals)
(3) Ash Slagging Characteristics.
(4) Pyrolysis Mechanism (depends on coal type, size, T, and $\dot{T}$)
(5) Ignition Mechanisms and Criteria.
(6) Combustion Mechanisms and Kinetics
  - Volatiles (homogeneous)
  - Solid residues (heterogeneous)
(7) Total Flame Characteristics
  - flame stability (kinetics and mixing)
  - flame emissivity (banded and continuous radiation)
  - flame length

The specifically combustion aspects of this list are amplified in the following section.

4. AN OUTLINE OF MECHANISMS

Amplifying the list at the end of the preceeding section, we are now in a position to focus more closely on the concepts and mechanisms involved; first, in the combustion of a coal particle in different circumstances, and, second, on aspects of flame speed and propagation.

4.1 Combustion of a Coal Particle - Although there are still arguments over details of behavior, particularly with regard to numerical values of reaction order and their interpretation, there is believed to be general agreement over the qualitative sequence of events when a coal particle burns. What is presented here can be regarded as the sequence on the prevailing Best Evidence, and subject therefore to modification if better evidence so warrants. With these provisos, the behavior of a coal particle in a fixed bed, or a fluid bed, or an appropriately dispersed phase - with specific variants to follow - is as follows:

1. The coal particle starts heating and loses moisture.
2. At pyrolysis temperature, volatile matter is generated that screens the solid surface from oxygen attack (mostly).
3. The volatile matter flowing out into hot air will ignite (Faraday Mechanism) - into cold air generally will not ignite: the system becomes a copious smoke generator.
4. If the particle is large enough, a thermal wave accompanied by a pyrolysis wave progresses into the particle interior.
5. Some outflowing volatiles will probably crack in particle pores or on other particles.
6. As the volatile flow declines, the screening effect diminishes, oxygen reaches the carbon surface, and reaction starts.
7. The carbon reaction proceeds to completion with the following sequence:
    1. Oxygen diffuses to the particle surface,
    2. Oxygen is either (i) chemisorbed on the external surface or (ii) diffuses down pores into the interior and is chemisorbed on the internal surface.
    3. After a "characteristic" residence time, the oxygen is desorbed as CO or CO_2 (ratio is temperature dependent),
    4. The desorbed products diffuse back to the main stream, completing the reaction.

This general description is modified by certain differences in values of specific parameters. These can be listed as variants on the general behavior, as follows:

1. *Small Particles* - d < 100 microns
    1. Pyrolysis is volumetric: no thermal wave is created
    2. Reaction generally chemically controlled
       Boundary layer diffusion not important
2. *Large Particles*
    1. Reaction *controlled* by boundary layer diffusion
    2. No internal reaction
3. *High Heating Rate* ($\dot{T} > 10^4$ deg.C/sec)
    1. No pyrolysis before ignition (not Faraday mechanism)
    2. Coal particles ignite heterogeneously
4. *High Heating Rate and High Temperature* (explosion flame)
   ($\dot{T} > 10^4$ deg.C/sec.; $T > 3000$°F)
   Heterogeneous ignition *and* burn out

What can now be mentioned briefly here, with more specific reference later in the list of Research Questions, is the point that the above descriptions represent current best belief. However, in many cases, the experimental evidence for part of the description is still relatively small, with maybe one investigator reporting a result but no additional and independent substantiation as yet. This, therefore, provides some basis for further research on similar lines to that already carried out in such cases.

4.2 Flame Speed, Propagation, and Stability - Looking next at the total flame system and characteristics, we identify the problems of flame stability and propagation. Concerning propagation, we recognize first that stability refers only to those flame systems that involve stationary reactions; this excludes explosions. Concerning flame speed and propagation, however, this includes explosions. Amplifying first the problem of flame stabilization, we recognize two classifications, as follows:

1. *Plane Flame* - Radiation stabilized: generally consistent with radiation theory
2. *Other* - Generally mixing determined (introducing combustion aerodynamics)

At this point, we should recognize that the mixing stabilized flames now introduce many other factors beyond those of just the combustion mechanisms of coal. For total flame systems, these are important. However, in the context of the requirements for better understanding of coal combustion mechanisms, introduction of combustion aerodynamics adds little or nothing but further complexity. What indeed has to be guarded against is the use of a mixing-stabilized flame for studying combustion kinetics, except where the specific objective is to determine the effect of mixing on some previously-established kinetics without mixing.

With this exclusion of mixing-controlled flames, we can now consider a comparison of flame speeds and burning times for different flame propagation mechanisms and heating rates. These are listed in Table 2. For the radiation propogated flames the values of flame speed and rate of heating are mostly consistent with all appropriate theory (with some discrepancies involving char combustion to be resolved). For the conduction flame the conclusion is believed to be incorrect; a radiative re-interpretation is more consistent with other behavior. Data for the turbulent convection explosion flame are considerably speculative, but are consistent with other considerations of behavior. Nevertheless, reliable data here are sparse to non-existent, and additional data are badly needed.

4.3 Source of Theories - In all the preceeding, mention has been made periodically to existing theory. There are now theories of varying degrees of acceptability for: the rates of production of pyrolysis products; the rate of combustion of pyrolysis products; the rate of combustion of char or total coal combustion; and the rate of propagation of flame through solid beds and pulverized coal clouds. For reasons of space these will neither be reviewed nor summarized in this article. However, articles listed in the Bibliography provide adequate sources for all appropriate theories. What is of importance to emphasize at this point is that, good or bad, theories do exist, in some instances with little adequate testing, but in some instances, with substantial agreement developing between theory and experiment. One missing theory, however, of crucial importance is a general model of coal constitution that can be used for prediction.

5. OPPORTUNITIES FOR UNIVERSITY RESEARCH

On the basis of the foregoing, we can now start to identify those problems that are specifically suited to university research. There are two general problems to consider first of all: the question of scale; and the question of scope. Both points can be illustrated by Fig. 1 which is designed to represent the relationship of the basic sciences involved to the engineering applications. This also illustrates the so-called "Hierachy of Models" with each stage in the diagram representing a different level in the hierarchy. It will also be evident that the higher stages in general will require larger, more elaborate, and more expensive equipment. For university purposes, the research should be restricted to the lower regions of the diagram, including a reasonably scaled furnace or research reactor only where there is adequate operational competence for such equipment. On the question of scope, the core of any work should be reactivity and combustion studies but studies of heat transfer and mixing that are not integral parts of a total flame system would not seem to be appropriate at present. These can be added in later as needed by outgrowth of the reactivity and combustion studies. Within these limitations there is more than sufficient work for numerous investigators. Following is a brief list of what are considered to be the outstanding research requirements. Development and test of:

1. An adequate model of coal constitution or structure.
2. An adequate model of coal pyrolysis.
3. An adequate model of pyrolysis products combustion - or extensive experimental test of the two-component mass model.
4. Accurate, unambiguous determination of the dominant char combustion mechanism(s), reaction orders, activation energies and frequency factors for coal reaction:
    1. In a solid bed.
    2. In a fluid bed.
    3. In a pulverized coal flame.
    4. In an explosion flame.
    5. With ash-catalytic effects.
5. An adequate total flame model of the plane flame furnace system and of the explosion flame system.
6. Test of and/or independent substantiation of specifics:
    1. Pyrolysis delay at high heating rates (Juntgen).
    2. Heterogeneous ignition at high heating rates.

3. Hetrogeneous ignition and total coal burn out at high heating rates and high temperatures.
4. Desorption reaction dominance of char burnout (zero order).
5. Delayed hydrogen loss from char in p.c. flames.
6. Solid bed kinetic equations.

Above all, the thrust of future work should be towards generalization of results in such a way that adequate prediction of experimental behavior, before the fact, can be satisfactorily accomplished. This it would seem, must depend largely on development of an adequate model of coal. Until this point is reached, we are faced with the prospect, as observed earlier, of having to test every coal individually in every experimental device of interest if we are to be sure of knowing accurately the desired behavior.

6. CONCLUSIONS

In conclusion we may consider some specifics and some generalities.

6.1 Selected Problems - In the foregoing, we may identify five general categories of research related to coal combustion problems. Following are problems of principal argument and ignorance in the five categoeis, partially reiterating and partly amplifying some of the preceeding discussion.

1. Investigation of the structure of coal (Ref. 1-3 in Bibliography) is not a topic that should be supported by combustion funds; there should be support for this elsehwere. However, better understanding of the influence of coal constitution on combustion properties (e.g., Ref. 28 in Bibliography) would greatly increase the generality of all research results and reduce the need for individual testing of each separate coal.

2. Kinetics of the combustion of coal volatiles is probably the greatest gap in knowledge of coal reactions. What little is known is reviewed briefly in Ref. 21. What is primarily needed here is data accumulation (the "natural history" description as basis for further theoretical and experimental work.

3. A useful basis for pyrolysis studies exists in Ref. 16 and 17 (identification of further problems is given in Ref. 15). Best evidence is that particles heating at less than 10^3 deg. C per sec. will pyrolyse before igniting, with ignition starting in the volatiles (Faraday mechanism). With

heating rates above 10^4 deg. C per sec., significant pyrolysis is delayed and ignition occurs at about 1000°C, by direct heterogeneous attack by oxygen on the solid surface. Subsequent pyrolysis quenches the heterogeneous reaction for larger particles (roughly greater than 10 microns), until most of the "normal" volatile components have been evolved. There is marginal evidence that after the devolatilization has effectively stopped and solid combustion resumed, the solid being burned still contains a small weight percent but significant mole percent of hydrogen. At heating rates in excess of 10^5 deg. C per sec., (explosion flames), if the temperature rises to 3000°F or higher, the subsequent rate of heterogeneous reaction, in competition with pyrolysis, is fast enough for almost complete burn out by the heterogeneous reaction. Since the reaction is a hydrocarbon solid, it can be expected to be significantly more intrinsically reactive than any char or coke. This would reduce burning times from the usual one second, or thereabouts, in pulverized coal flames, to the order of 0.1 sec., estimated for explosion flames.

This general pattern of pyrolysis delay from rate of heating is considered by some to be arguable or erroneous. The evidence on which the picture outlined is based is "best evidence," but still very limited. The principal scope for research here would be independent confirmation or refutation of the picture outlined. A complicating factor is the so-called "Q factor" (ref. 17) which is most probably a valid phenomenon, but which has been used, probably erroneously as the basis for objection to the heterogeneous ignition conclusion at high heating rates. Indications are that the VM production is increased under such experimental conditions that high rates of heating are involved. The more likely explanation for the (Q factor) increase is that the experiments are also in dilute phase which reduces probability of volatiles cracking and re-capture. The details of the problem are discussed in Ref. 15. Nevertheless, further investigation of the problem is warranted.

A related problem of capture of cracked volatiles occurs in the case of pyrolysis of large particles (greater than about 100 microns). Pyrolysis of such particles occurs with pyrolysis waves travelling into the solid, with the outflowing volatiles stream being filtered by freshly formed coke. This can be important in fixed beds (grate fired boilers, or shaft gasifiers). The heat and mass transfer fluxes can also couple, to generate temperature plateaus at unexpected temperatures. This was explained theoretically by Henry (Ref. 30). Also related are such results as those by Juntgen (Ref. 16) which indicate that the escape of some pyrolysis products is controlled by chemical pyrolysis and some by activated diffusion. There is substantial information here, but it needs experimental re-check by independent investigators, and mathematical analysis for generalizing to other coals and systems.

4. A massive base for reaction and burn-out studies exists in the carbon and related literature (Refs. 7 through 15). Nevertheless, there are still certain specific problems outstanding. Some are influenced by particle size and by use (dispersed phase or fixed bed), but some are general. Further details are discussed in Ref. 15. The principal general problem is the dominant reaction mechanism at flame temperatures at the solid surface whether it is the adsorption of oxygen atoms or molecules, or the desorption of the absorbed layer. The majority view is the latter, but the best evidence in logic as discussed in Ref. 15 is the former. This affects whether the reaction in the bulk of the flame is first order with respect to oxygen (adsorption dominance), or zero order (desorption dominance), or half order (pore diffusion dominance, or possibly adsorption dominance with dissociation), or some other. There is sufficient ambiguity in all published results, and reanalyses, for the question of reaction dominance still to be considered open. (Also discussed in Ref. 14.)

In pulverized fuel flames, the reaction rate is dominated by kinetics; diffusion is fast. There is also evidence that the same coal (anthracite) burned under slightly different conditions can give temperature coefficients characterized by activation energies of either 40 kcal. or 20 kcal. This change is consistent with change from total reaction throughout the particle to pore diffusion dominance (partial penetration). The conditions producing one or other in the flame, however, are obscure. Clarification is likely to be significantly revealing regarding the progress of opening the pore structure during reaction.

In solid beds, the first question of mechanism has yet to be resolved. For single particles above 100 microns, the reaction is strongly influenced, or dominated, or controlled by boundary layer diffusion, depending on the ambient velocity. In fixed bed, the equivalent system is a porous block with channels. What is not entirely clear is the Reynolds Number in the pores (assessments depend on arguable assumptions). Best, though marginal, evidence is that it is most usually below 2000 so that reaction is diffusion dominated (see Ref. 23). However, this needs re-examination. There are also outstanding problems of the effects of gas velocity in the pores (for a brief discussion see Ref. 11).

5. Finally, total flame or system studies require elaboration since adequate ability to predict flame location is still incomplete in spite of improving agreement between flame speed theory and experiment. "Anomalous" behavior has been found recently with chars that generate high flame temperatures but low flame speeds. The source of the problem appears to be related to reactivity, but there is scope here for substantial further investigation.

6.2 Status of Coal Research in Terms of "Theory" of Theories - If we accept the views generally expressed in the so-called theory of theories, that theorizing about any particular problem or subject generally goes through a number of different stages, these are illustrated in Fig. 2. This general plot is presumably familiar: the curve is drawn according to the view that theories tend to proliferate in the early stages of research, although starting of course from zero when the field opens up, with a progressive peaking followed by decay in the number as deductive prediction accompanied by crucial testing by experiment progressively destroys inadequate theories. The plot includes the four "development" stages:

1. The "Natural History" period in which the investigations are primarily directed towards developing phenomenological information about the problem (Initiation).

2. The stage of inductive development of concepts on which to base the subsequent deductive, mechanistic theories (Youth).

3. The stage of development of deductive, mechanistic theories used to predict previously unobserved phenomena whose investigation is used to test the validity of the predictive theories (Maturity).

4. Finally the stage of consolidation of the finally accepted theory (Old Age).

Within this scheme, it is notable that no specific topic can yet be said to have passed into the Deductive state (3, Maturity), although flame propagation and carbon combustion in some aspects may be close to it. Otherwise, pyrolysis is still at the stage of inductive development of concepts, and volatiles combustion is still at the early "Natural History" stage.

This classification again reinforces the prime need for combustion research to advance beyond the point of development of concepts and to start the process of development of predictive theories for testing.

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TABLE 1

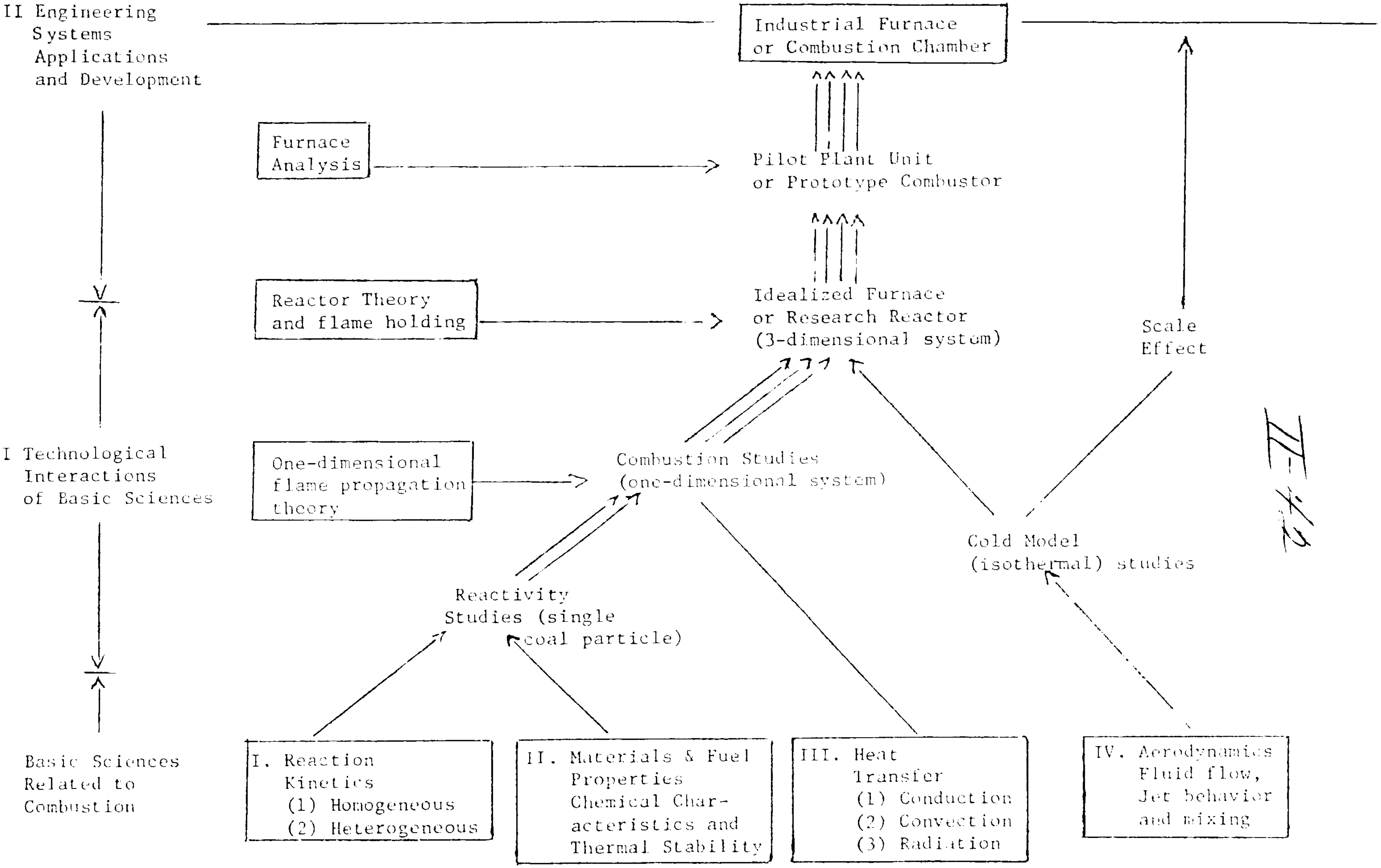
Particle Size and Density Classification of Practical Systems

PARTICLE SIZE	Particle Density	
	Dense phase order of grams per c.c.	"Dilute" phase order of grams per liter
Lump (<100 cm)	"fixed" bed (grate or shaft)	–
Crushed (<1 cm)	unballasted fluid bed	ballasted fluid bed
Pulverised (<100 m)	–	P.F. or p.c. burners

TABLE 2

Approximate Flame Speeds and Burning Times For Different Ignition Flame Propagation Mechanisms and Heating Rates

Rate of Heating deg C/sec	Conduction	Radiation	Turb. Conv.	Burning Time (sec)		System	Ignition Mechanism
	Flames Speed m/sec			Vols	Coal/char		
$10\text{-}10^2$	-	10^{-5}	-	10^2	10^3	Solid Fuel Bed	Pyrolysis (Faraday)
$< 10^3$	-	0.5-1.5	-	0.1	1	Plane Flame	Pyrolysis
10^4	-	0.3-0.5	-	0.1	1	Plane Flame	Heterogeneous
$> 10^5$	0-0.3(?)	-	10 to 10^3	(?) 0.1 (total coal)		Explosion Flame	Heterogeneous (ignition and combustion)



ig. 1 - Schematic breakdown to illustrate the information flow required for a complete understanding of industrial furnace or combustion chamber behavior. Understanding rests on the four basic sciences: I, Reaction Kinetics; II, Materials properties; III, Heat Transfer; IV, Aerodynamics. The diagram also illustrates the general relationship between science, technology, and engineering.

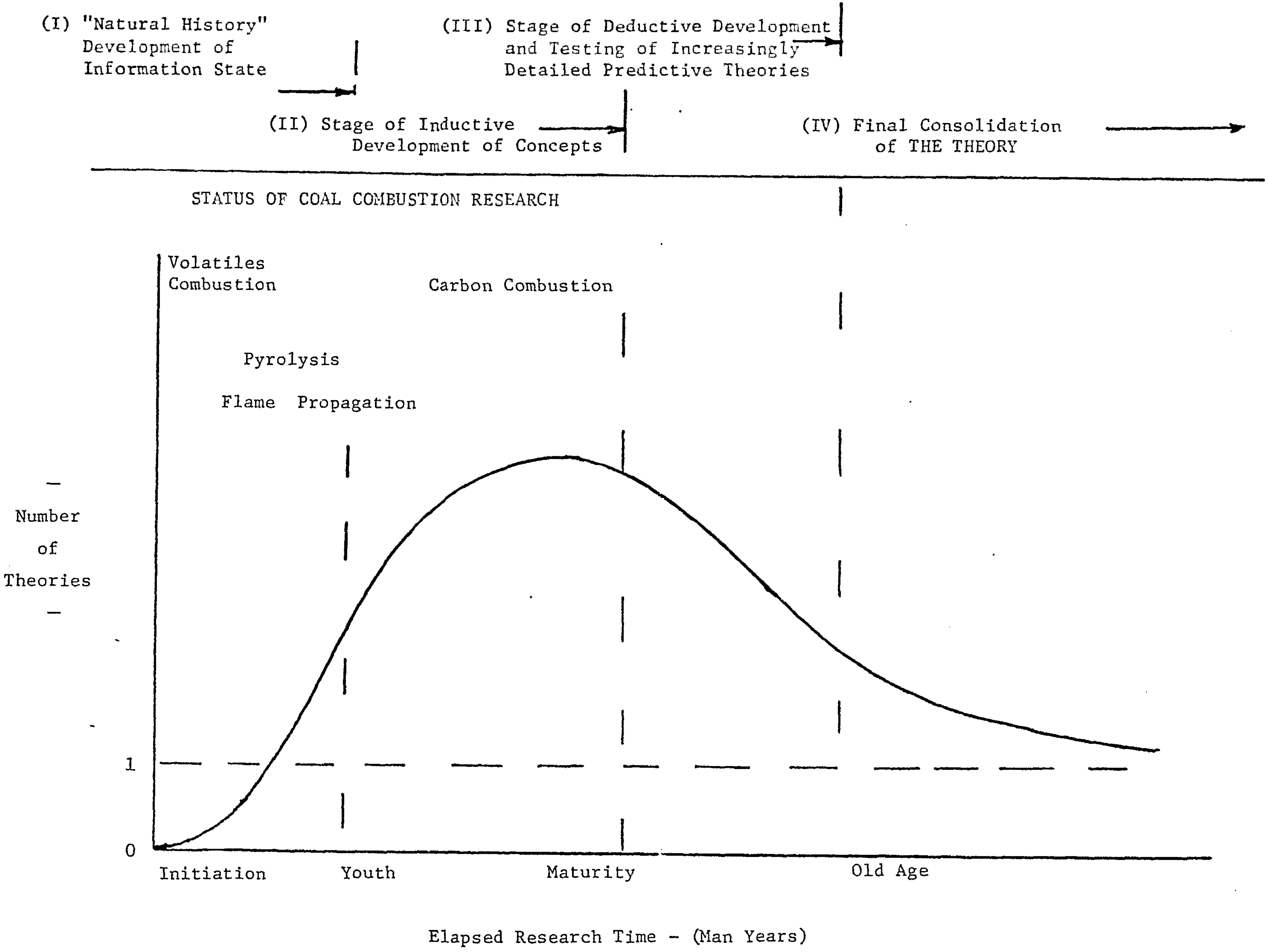


Fig. 2 - STATUS OF COAL RESEARCH IN TERMS OF "THEORY" OF THEORIES

UNIVERSITY RESEARCH IN COAL GASIFICATION

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University research in coal technology can

- turn out a flow of talent,
- contribute toward a flow of fresh ideas,
- provide deeper insight into critical or difficult steps under development,
- create visibility for long range options not yet under serious commercial study and develop information that will speed such options when commercial work begins, and
- help to create a consistent point-of-view toward fluidization, an important unit operation for coal technology, for which art is far in advance of scientific understanding.

Talent dedicated toward solving the problems of supplying energy from coal is the most important of these products. Our Nation urgently needs a first-class cadre of fuel technologists that can respond flexibly and imaginatively against the recurring crises of the next 30 to 50 years as we pass from an era in which energy was almost a free good to an era in which energy will be prized and husbanded and expended with utmost care.

Universities will not be able to create the needed flow of talent if other important roles are denied. In the past generation, physics and nuclear energy and aerospace science did not attract their superb supply of talent solely because these activities were glamorous. They were glamorous in part because budgets were large and because headlines recorded a steady parade of public spectaculars that marked the serious purpose of agencies funding work in these fields. Research in coal technology will need similar treatment if talent is to be forthcoming.

There is a connection, then, between the first product of university research in coal technology and the other benefits of the research.

These other benefits might be summed up as providing results and considerations that the community cannot expect commercial interests to produce. Commercial considerations are inevitably taken in a time frame that looks only a very few years ahead, and unfortunately, are often taken in an institutional setting that takes in only a narrow range of society's needs.

I will leave to the Sub-Group open discussion tomorrow morning a consideration of detailed topics that deserve attention in university research in coal gasification. I have provided a tentative list of topics for the discussion.

In this paper, I will concentrate upon:

a need for large-scale experimentation with fluidized beds, especially beds for high fluidizing gas velocity;

a need for long range planning to provide energy supplies that are resilient in face of decline in Worldwide availability of natural gas and oil; and

the related need for a vigorous cadre of alert fuels technologists with strong ties between men in industry and in universities.

Large-Scale Experiments on Fluidization:

For the practical man, university research in fluidization has in the past had mainly heuristic value. This is not to depreciate the importance of the early phenomenonological studies at M.I.T. or Princeton, nor the importance of Zenz's extension and organization of the phenomenonological data, providing important connections between data for fluidization and those for standpipe flow and for solids conveying and especially between data for these systems and the flow of a liquid. This is also not to depreciate the importance of the brilliant researches of Rowe and the Cambridge school in the early 1960's on the physical behavior of the single, isolated bubble and more recently, of bubble clusters. Although such study has led to an ample literature on bubbles in fluidized beds, its practical value, as Rowe himself is quick to point out, is small.

Most industrial fluidized beds operate well beyond velocities at which individual bubbles can be recognized. It is unfortunate that it was left to P.W.K. Kehoe and J.F. Davidson [Institution of Chemical Engineers (London) Symposium Series, no. 33, pp. 97-115 (1971)] to recognize clearly for the first time the breakdown of the bubbling regime with formation of a turbulent regime for the fluidization of a fine powder (Geldart's type A) as the velocity surpasses about 1 to 1.5 ft/sec. The practical man has long suspected that the regenerator of the fluid catalytic cracker, operating at about 2.5 ft/sec, performs better than a model based upon bubbles might reasonably suggest. We still lack a scientific description of the fluidization regime in a large catalytic cracker regenerator. (Is is turbulent in the sense suggested by Kehoe and Davidson's paper? If so, on what scale of turbulence?) Even an eyeball glance at a 6-inch turbulent bed of fluid cracking catalyst in the laboratory makes the good performance of the regenerator intuitively credible.

W.K. Lewis and E.R. Gilliland (U.S. Patent 2,498,088, Feb. 21, 1950) clearly recognized what we at The City College have dubbed the fast fluidized bed condition: "If one will operate at a gas velocity sufficient to blow all or substantially all of the [particulate] solid material out of the reactor in a relatively short time, provided no fresh solid material be introduced during this time, but will feed into the reactor simultaneously solid material at a sufficiently high rate, one can maintain in the reactor a high concentration of solid granules approaching that of the "liquid state" ... [of the slow, stationary fluidized bed], and yet be blowing the solid particles out of the top of the reactor at a corresponding rate." They reported a fast fluidized density as high as about 8 lbs/ft^3 for a pulverized clay catalyst at a superficial fluidizing gas velocity of about 8 ft/sec. It is worth noting that the Lewis and Gilliland patent of 1950 was a division of an application filed in 1940!

In light of the wartime urgency to build cracking capacity to provide aviation gasoline, there is no problem in understanding why the industry adopted in 1940 the slow, bubbling fluidized bed for this purpose, and not the fast bed. The slow bed was the conservative choice, and indeed, the capability to engineer a fast bed in a reasonable time was probably lacking. Lewis and Gilliland's patent did not disclose a practicable arrangement, and the chemical engineer's knowledge of both cyclones and standpipe flow was primitive.

The fluid cracker evolved toward a turbulent bed in the regenerator and developed the riser reactor at about 50 ft/sec for the cracking step. It is unfortunate that the petroleum industry did not later see in Lewis and Gilliland's early teaching the opportunity for a revolutionary change that would have substituted a fast fluidized bed for the regenerator. My colleagues and I at The City College have little doubt that this could now be done easily if a sufficient number of new crackers are yet to be built to justify the development expense.

The fast bed was not entirely neglected. A reactor for Fischer-Tropsch synthesis built at Sasolberg, South Africa, by M.W. Kellogg in the early 1950's fluidizes an iron catalyst of about 30 microns at about 7 ft/sec. This almost certainly provides either a turbulent or a fast fluidized bed. Lurgi of Frankfurt, Germany, has had a commercial success with a fast fluidized bed for calcining aluminum hydroxide, and it was this success that brought the fast bed to our attention. With our grant from the RANN Program, we are creating visibility for the fast bed opportunity, and we consider this aspect of our work to be an important example of how university research can contribute in the fourth way listed in the opening paragraph of this paper. We are also obtaining data that can help industry when the fast bed catches on for more applications, as it surely will.

We have recently observed, for the first time so far as we are aware, what appears to be a transition from the turbulent regime of Kehoe and Davidson to the fast fluidized condition. The difference between these conditions is that the fluidized density in the turbulent regime is not a function of solid input to the bottom of a fluidized bed zone, while the fluidized density in the fast fluidized condition is a strong function of solid input. Our tentative conclusion is that there is a critical velocity, about 6.4 ft/sec for fluid crack catalyst, below which fluidization is turbulent and above which it is fast.

We have 1,200 ft^3/min of air at 10 lbs/in^2g, giving us the capability of operating a 12-inch fast bed at about 25 ft/sec. We can learn much at this scale of effort about:

fluidized density as a function of gas and solid rates,
the transition from turbulent to fast fluidization,
the transition from dilute-phase conveying to fast fluidization,
thermal conductivity of the fast fluidized state,
gas backmixing and eddy diffusivity,
solid mixing,
heat transfer, and even
chemical reactions of several orders.

It should be noted that work on this scale, even at atmospheric temperature, is inevitably expensive. I should point out to other university researchers that there has been one item of expense, that is also a factor for delay, that we did not fully appreciate in planning the work. This is simply the maintenance and servicing that is needed to keep our large rigs in working order.

Our costs, however, are almost as nothing in comparison with the cost of a large pilot study of a fluidized bed for a process at elevated temperature and especially at elevated pressure, such as many of the opportunities for gasifying coal. It might be noted in passing that the costliness of subsequent hot work is of course a major justification for getting as much supporting data as possible from an atmospheric rig such as ours before planning the hot work.

One cannot help feeling that opportunities have been missed during the past twenth-five years because the petroleum and chemical industries were not organized in a relationship toward academic and scientific establishments in quite the same way that the nuclear and aerospace industries have been. No doubt this is because of the far larger role played by government funding of work in support of the latter industries. More than twenth years ago, it would have been logical, directly following expensive failures of two large fluidized-bed developments, one for Fischer-Tropsch synthesis and another for fluid hydroforming, for someone to have said, "Hey! We need a large laboratory in which to conduct large-scale experiments on fluidized beds." Such a laboratory could have played as useful a role toward certain petroleum or chemical process developments as experimental nuclear reactors and wind tunnels have played toward nuclear energy and aircraft development. Indeed, the parallel with the aircraft industry is very close. Something of the same empiricism and intractableness toward theoretical prediction, something of the same kinds of surprises, stand in the way of understanding the design of both a fluidized bed and an air frame. A large laboratory for study of fluidization might have meant that some processes now conducted in fixed beds would have gone fluid instead.

In considering today's requirements for development of fluidized-bed gasification for our energy industries, I believe we have today at least a rough analogy with the needs of nuclear engineering 25 years ago. There are too many options for gasification today, as there were then for the configuration of a power reactor, for intellectual exercises alone to pick a sure winner. Experiments on reactor proposals had to be big, and they had to be backed up with heavy support facilities. Meaningful fluidization experiments at high temperature and pressure must move quickly to vessels approaching 30 inches in internal diameter, simply because access to the interior is important lest intolerable delays arise from changes dictated by experience. Big vessels mean big supplies of gas, and these are costly.

The late F.J. Dent, whose last ten years of service for the British Gas Council before his retirement in 1966 were marked by so much commercial success with processes for substitute natural gas, put the matter well:

> "The cost of operating on ... [our] scale calls for a fairy godmother and ours has been the Gas Council.... It is significant too, that we usually had reason to regret any protracted period of exploratory investigation. Small-scale experiments have often been time-wasting even when large-scale conditions have been reproduced as faithfully as possible.... Operation on a reasonable scale at an early stage is most desirable to throw difficulties into their proper perspective. Laboratory work was of most value after the problems had been recognized in this way."

In the Fall of 1971, I sent Dent our research proposal to the National Science Foundation for high-velocity fluidized bed studies. He replied:

> "... of course, [your proposal raises] that old problem in my mind re: the use of high fluidizing velocities. In spite of your advice, we never got round to doing it, and simply because our gas supplies were limited to 1 million cu. ft. per day. This gives a very small diameter reaction vessel when compressed 20-50 atoms. if used at a velocity of 10 ft/sec. We may have missed a lot."

These words came from the boldest, best financed and most successful researcher in the technology of coal and oil gasification and fuels conversion of the past generation, and they sharply point up the required scale of the funding necessary if fluidization studies on a large scale are to be useful.

I believe that the electricity industry, the gas industry, and, yes, even the petroleum industry will have to look to institutions such as the Office of Coal Research and the Electric Power Research Institute for major process development. There are many signs that United States industry has largely lost its appetite for major process development that involves a radical change in procedure. The collaboration between Standard Oil Development Co. and Lewis and Gilliland of M.I.T. that led to fluid catalytic cracking is a model that we may not see again. The scale of industrial operations is now so large that a radically new procedure may require a decision to embark upon a course that could lead to expenditures running into the scores or even hundreds of millions of dollars before the adventure reaches black ink. In such an enterprise, there is of course great risk that it will fail after many millions have already been spent. The Standard Oil-M.I.T. collaboration occurred in a simpler time, when the likelihood of a profitable outcome could be established with reasonable certainty and quickly and cheaply. Moreover, a first commercial, profitable plant was tiny by today's standard.

The university community should display more skepticism toward industry's development plans when they touch upon vital needs of our culture in the future. There is a tendency to accept such plans as the products of sure minds who have weighed all alternatives carefully. Often, I have the impression that all that has been weighed is the question of what course is absolutely the safest and most likely to reach some degree of technical success and operability. One can be sympathetic with such thinking when one considers the enormous sums at stake, but someone somewhere should at least pay attention to what may be missed if all decisions for our energy future are made from an ultra-conservative point of view.

The developments now underway for fluidized-bed gasification of coal are conservative in the extreme. The known proposals contemplate slow fluidized beds with velocities on the order of 1 ft/sec and sometimes considerably less! The boldest proposal is that of Union Carbide with Chemico Corp., with a parallel effort at Battelle Memorial Institute, that calls for an ash-accreting fluidized bed combustor at a velocity considerably beyond 1 ft/sec to burn char and to provide heat in the form of a circulating burden of hot ash beads to a bed of coal fluidized by steam at a lower velocity.

A laboratory for hot studies of fluidization on a large scale, organized to provide a broad service to the nation, could inject a note of greater boldness into our program for coal gasification, as well as for other applications of fluidization. The laboratory would, of course, examine bubbling and turbulent beds as well as the fast fluidized bed of a fine powder that interests us at The City College. There will be great interest, too, in learning more about the bubbling fluidization of large sticky particles. We have made good progress at The City College in experiments on a small scale that open up the study of such sticky fluidized beds. Other questions abound. Can large particles be put into the turbulent or fast fluidized state? From discussions with experts on the formation of hailstones, who seem to believe that nascent hailstones in a storm cloud move in patterns resembling the City

College movies of the fast fluidized state, we would suspect that the answer to this question is, yes. Will there be a practical use for such beds? Indeed, is the fluidized bed gasifying coal in the lower part of the Ignifluid boiler a turbulent bed? This operates at 40 to 70 ft/sec, which is from about 10 to 15 times the minimum fluidization velocity of the coke particles undergoing air gasification. This is the highest multiple of minimum fluidization for a bed of coarse solid known to us, and the Ignifluid bed might well prove to be turbulent at its deep end.

I do not need to belabor the point that there should be close ties between universities and a national laboratory for fluidization development. Many Ph.D. researches could profitable be conducted on large, hot fluidized beds of the national laboratory.

The laboratory should not set up for the limited objectives of just one of the three major energy sectors, but should serve equally the country's needs for electricity, gas, and liquid fuel. It should not be set up for study of just one feedstock, but should cater to processes for residual oil, pitch, bitumens, tar sands, and oil shales as well as coal. Its interests should range over a wide variety of process steps where fluidization can serve, and a variety of ways in which it can serve, and should not be bound to the development of some specific flowsheet that happened to appear attractive at the time the laboratory was set up.

I do not wish these remarks to sound too critical of present programs or the present quality of the decision-making in our large corporations. I am keenly sympathetic to the position of a man who is responsible to thousands of stockholders who look up to him for income. The fluidization research center should of course supply support for programs that are now ongoing, as well as display opportunities for more radical change in procedure.

In general, university research in coal gasification should strike a balance between studies that support current programs and studies that look toward better opportunities.

Resiliency in Energy Supplies

The December 1972 issue of the Journal of the Institute of Fuel carried an obituary of Sir Harold Hartley,* who died that September at 94. Sir Harold worried about the energy crunch that now concerns us at least 25 years ago. A passage in his obituary evokes a picture of the fuel economy of Great Britain just before World War II:

> "In 1938, the Mines Department set up a committee, with Sir Harold as its Chairman, charged with designing a small, portable gas producer to be used for fuelling motor vehicles if supplies of petrol became short in the event of war. This task was successfully accomplished, and led to the design and development of the Government Emergency Producer which was to give, in the Second World War, such valuable service in fuelling furnaces producing vital munitions when supplies of town gas suffered serious interruption by enemy air raids."

Behind the Emergency Producer were two factors that lent great strength and resiliency to British energy supply: (1) a cadre of fuels technologists performing vital and varied functions and thoroughly familiar with gas-producer art; and (2) widely dispersed stocks of gas coke, an ideal fuel for a fixed-bed gas producer yielding low-Btu gas.

Present inflexibility of United States energy supply is, of course, due in part to our insistence upon what substantially amounts to instantaneous clean-up of emissions from combustion, an insistence that has removed coal and high-sulfur oils from competition. In contrast to the Great Britain of 1938, however, the rigidity of our fuel supply stems also in part from the greatly increased scale of all of our energy operations, from the smallness of the community of fuels technologists who have sufficient breadth of knowledge to

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*Sir Harold was amazing. His appetite for knowledge in an extraordinary range of subjects put hundreds of his "younger" colleague -- none younger in spirit -- to periodic inquisition as to progress of their studies. Sir Harold reciprocated with timely intervention at sticking points in many careers. I personally am deeply in Sir Harold's debt for his gentle insistence that Hydrocarbon Research, Inc. permit me to report in early 1960 to the Institution of Chemical Engineers upon the operation in early 1958 of the 26.5-inch, 20-atm fluidized-bed gasifier at H.R.I.'s Trenton laboratory, that was reactived recently with good effect on behalf of the Bureau of Mines' Synthane gasification program.

keep in view a wide range of options, and from inflexibility of our combustion equipment, and, often, fuels distribution facilities as well. Pressure on our energy net at one point produces a chain of effects. Propane shortages are caused by large purchases of propane to replace gas. Heating oil also becomes short because of purchases by former users of gas. Gasoline becomes short because of demand for heating oil. And so on.

I believe that systems studies of our energy supply should concentrate upon measures that will restore resiliency and flexibility rather than upon the narrow concern of optimizing costs. The more options that can be developed, at reasonable costs, the better off we will be.

The university community could well take the lead in a skeptical discussion of the future of the various sectors of our energy supply industry. There has not yet been a serious discussion of the relative amounts of energy that ought to be supplied in the form of electricity, gas, liquid fuel, and byproduct heat in the year 1990. There has been no serious discussion of a topic that the gas industry seems to wish to avoid altogether: What is the logical mix of the various kinds of gas that can be made from coal? It is not sensible, in my opinion, to convert Illinois coal to methane at a location near the large power stations of this state, and then burn the methane in the stations. It may perhaps be sensible to ship synthetic methane from Wyoming to Illinois, but even this proposition might fairly be set down for consideration alongside other alternatives. My own view is that the gas industry will make a great mistake if it lets its present industrial customers, particularly the steel industry, set up equipment for converting coal to low-Btu gas or intermediate-Btu gas. The gas industry should, in my opinion, broaden its product line to include all of the gases, and thereby avoid the slow decline that seems inevitable if it insists on marketing methane and nothing else.

I would like to hear this proposition debated, with an input to the debate from spokesmen other than representatives of the gas industry. No doubt economists must contribute to the debate, but I have found economists, as a whole, sadly ignorant of the methods of technological change and especially of the time scale required for major change. One benefit of the debate might simply be the education of economists in this respect.

It surely goes without saying that these questions, important to our future, will not be answered by one or two funded studies of a year or two each, but only after many ideas have emerged and have gone through the refining fire of controversy.

Community of Fuels Technologists

I would first make a broad point. I believe that the avenues that conduct a nation's prime talent into whatever it is that the nation prizes most can have a profound effect upon its future history and future welfare.

I love to read history, and I have been struck by the way in which Spain blew its opportunities in the 16th Century. It began the Century with a vigorous agriculture, lively and promising business and manufacturing communities with the makings of a middle class, with a number of fine universities -- in all of these respects, far in advance of the contemporary England, for example. I do not think the expulsion of the Jews or the Inquisition was the prime factor in Spain's downfall. Rather, it was Spain's misfortune to acquire American gold and silver in what seemed limitless amounts and at the same time to acquire a dynasty with interests in Middle Europe, which thought that gold and silver could buy anything. Spain's prime talent in the 16th Century went to colonial administration and military enterprise, and Spain ended the Century not only far behind in the real-world activities that make a nation strong but also deep in debt, its silver fleets mortgaged for decades.

I believe England's troubles in recent years have stemmed at least in part from neglect of its real-world business after World War II -- especially steel and ship-building -- and its investment of prime talent into aircraft and nuclear enterprises that have neither yet afforded England any substantial earnings.

Surely part of our trouble in the United States today is that too little talent has been recruited for fuels technology in our recent past. Much prime talent needs to be recruited for this field as quickly as possible. I have already made the point tlat talent was recruited for aerospace and nuclear enterprise through a judicious application of money. I do not see how we can expect to recruit an adequate supply of first-class people for fuels technology without similar treatment. Money talks.

I had not appreciated just how low engineers stand in the academic pecking order until a meeting of the Curriculum Committee of the School of Arts and Sciences at The City College at which our coal research team proposed a course in fossil fuel technology for non-engineers. We have much work ahead to establish fuels technology at a significantly higher level in the community's esteem.

I wonder if our enterprise does not require some adjustment of the way we teach chemistry and chemical engineering. We have turned out for some time now a student who is strong in analysis but weak in synthesis. Often, he is especially weak in those aspects of chemistry and chemical engineering that have to do with art rather than science. Descriptive chemistry has long been out of fashion. Engineering educators often appear to have little interest in the accumulated wisdom of the human species, but only in what problem can be answered by a computer. Much cannot be done by the computer. My own career has involved me heavily with both fluid-particle systems and the chemical behavior of coal. How often I have been surprised that either the particles of the coal were too dumb to realize what my intelligence told me perfectly well they ought to do. We should teach our students to expect and value and, yes, enjoy such surprises. Students should appreciate the wonder of so much that chemists and engineers know but cannot yet explain in mathematical terms. It is important for students to appreciate that many great scientists, notably Faraday, have not been mathematical but thought in pictures and images and a kind of phenomenonological logic of their own. I do not wish of course to depreciate efforts to provide the mathematics, but it does seem to me that many recent efforts by academic researchers in engineering have concentrated upon problems selected because they were tractable to computer analysis rather than because they were interesting to the practical man. There has seemed to me to be a tendency to avoid phenomena that are not yet well enough understood, or sufficiently measured, to be ready for analysis.

How many more important surprises are left? How many are vital to our development of the economic gasification of coal? We need much more experimental work in our university research, and more work simply looking at phenomena with the real chance that a sensible mathematical description of the phenomena may be too hard to find in the span of a research grant.

It would be well, too, if we turned out students who have a broader appreciation of technological history and the wide range of successes of the past. This is particularly true, perhaps in fuels technology, where the rich alternatives that the 19th Century possessed are largely forgotten, yet still contain matter of great value.

I cannot emphasize strongly enough my personal view that our national health may depend upon prompt action to establish a first-class cadre of fuels technologists. It is pleasant to dream of the golden age in which our energy needs will be met by some inexhaustible energy source, and I would not wish to reduce budgets for development of the exotic energy sources. But it is also important, even far more important for the short run, to worry, how do we get there from here? Our fossil fuel supplies are the bridge, and the way we use these supplies in the next 50 years may make us or break us, for it is easy to imagine a delay in appearance of the ultimate energy source and a gap that our reserves of coal would be hard pressed to fill.

COAL CHEMISTRY - THE UNIVERSITY's ROLE

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ABSTRACT

Research projects in coal chemistry are discussed that may best be carried out at universities. Guidelines are suggested on methods to effectively bring the universities "on board" and have them contribute both to research and training efforts.

INTRODUCTION

These are exciting times for coal chemistry. Just like Cinderella and the Ugly Duckling, coal chemistry has become glamorous. This is a good time for universities to get involved in coal chemistry. Not only because there is money available for coal research but because there are challenging problems waiting to be solved in coal chemistry. But before we get carried away too far by this new-found glamor, let us ask a sobering question: Is research in coal chemistry really necessary?

WHY COAL CHEMISTRY

One answer that comes to mind immediately is, of course, that coal gasification and liquefaction will have to make up for our dwindling gas and oil supplies. And what methods of coal liquefaction we shall use and how economical these methods are going to be will certainly depend to some extent on our research into the nature and reactions of coal. But let us assume, for the sake of argument, that the problem of stack gas removal of SO_2 has been solved and that the most economical way to use coal were to burn coal in powerplants and to save our gas and oil reserves for other needs. Now, we certainly do not have to know much about coal structure or coal chemistry in order to burn coal. But even in that case, there is, I believe, a good reason for research in coal chemistry. Because, even if we decide to just burn coal, we still have to mine the coal. And the possibility of underground solubilization or liquefaction (just like underground gasification) of coal merits consideration in vew of the hazards and environmental damage connected with conventional mining methods. So, even if the economy of the energy situation should favor only combustion of coal, it would still be worthwhile to study coal chemistry with regard to underground solubilization and liquefaction.

There is still another reason why coal research is important. Sooner or later, coal will replace petroleum as our main source of chemicals. The more we know about the nature and chemical reactions of coal, the better our chances will be of producing chemicals directly from coal rather than from petroleum or coal tar.

Now, what are the types of research projects that can best be carried out at universities? From what I have said so far, it should be obvious that coal solubilization and coal liquefaction are high on the priority list.

A GLANCE AT COAL CHEMISTRY

Let me give you first a brief overview of the state of coal chemistry as it pertains to coal solubilization and coal liquefaction and then mention some projects suitable for university research.

The primary objective of coal liquefaction is to produce a low-sulfur, low-ash fuel. This is achieved by treating coal at elevated temperature and hydrogen pressure. This treatment is carried out either in the presence or in the absence of an added catalyst, depending on the type of coal used and the type of product desired.

It is generally agreed that the conversion of coal to oil in the presence of hydrogen proceeds essentially in two steps:

$$\text{COAL} \xrightarrow{\text{fast}} \text{ASPHALTENES} \xrightarrow{\text{slow}} \text{OIL}$$

A fast step in which coal is converted to asphaltenes and a slow step in which asphaltenes are converted to oil.

I should like to point out here that this mechanism was first proposed and supported by experimental evidence (1,2) by Dr. Weller over 25 years ago when he was working at the Bureau of Mines on the problem of coal liquefaction.

The asphaltenes which are formed as intermediates in the liquefaction of coal are operationally defined as material soluble in benzene and insoluble in aliphatic hydrocarbons such as pentane or hexane. Oil, on the other hand, is defined as material soluble in pentane or hexane. The conversion of coal to asphaltenes takes place at about 400°C in the presence of hydrogen or a hydrogen donor solvent. For the conversion of asphaltenes to oil to take place at a reasonable rate, the presence of a catalyst and higher temperatures and hydrogen pressures are required.

What happens in the first step is essentially this: Coal, which is a solid and insoluble in benzene is converted to asphaltenes. Now asphaltenes are also solid materials, but in contrast to coal are soluble in benzene, anthracene oil and other solvents.

The conversion of coal to asphaltenes is often all that is needed to produce a low-ash, low-sulfur fuel. The asphaltenes are dissolved in a suitable solvent such as anthracene oil and the solution is filtered or centrifuged to remove all the mineral matter, particularly pyrite (FeS_2), a major source of sulfur in coal. When the solvent is removed, there remains an ash-free, low-sulfur material which is a solid at room temperature. This solid is known as solvent refined coal (SRC) and the process by which SRC coal is obtained is known as the SRC process.

The SRC process works fine with coals that have a low organic sulfur content. But coals with high organic sulfur content present a problem, because only a portion of organic sulfur is removed in the SRC process. To remove the bulk of organic sulfur we have to convert coal to oil and that, as mentioned above, requires the use of a catalyst and higher temperatures and hydrogen pressures. Examples of processes that convert coal to oil are the H-COAL and the SYNTHOIL process (3).

So much for the mechanism and technology of coal liquefaction. Now what do we know about the chemical structure of coal and of asphaltenes? The answer is: Very little. It seems that we know much more about how to convert coal to oil, than about the chemical reactions that are involved. While Dr. Weller was able to shed some light on the mechanism of coal liquefaction, we are still in the dark about the structure of coal and asphaltenes. However, recently we have made some inroads into the jungle of coal and asphaltene chemistry.

Let me start with the structure of asphaltenes. All that was known about asphaltenes was that they were operationally defined as material soluble in benzene and insoluble in pentane or hexane. We now have found that asphaltenes consist of hydrogen-bonded acid-base complexes and that the acidic and basic components can be separated by dissolving the asphaltenes in toluene and passing dry HCl gas through the solution (4). The basic component precipitates as an insoluble HCl-adduct while the acadic component remains in solution and can be recovered by evaporation of the solvent. Experiments including Thin Layer Chromatography (TLC), Thin Layer Electrophoresis (TLE), Nuclear Magnetic Resonance (NMR), D_2O exchange, and determination of sodium replaceable hydrogen suggest the composite structures for the acidic and basic components shown in figure 1.

The essential features of these structures are as follows. The oxygen in the acidic component is present as phenolic hydroxyl and the nitrogen as acidic nitrogen, as in pyrrole. The oxygen in the basic component is present as ring or either oxygen and the nitrogen as ring nitrogen, as in pyridine. Complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups, as indicated in figure 1.

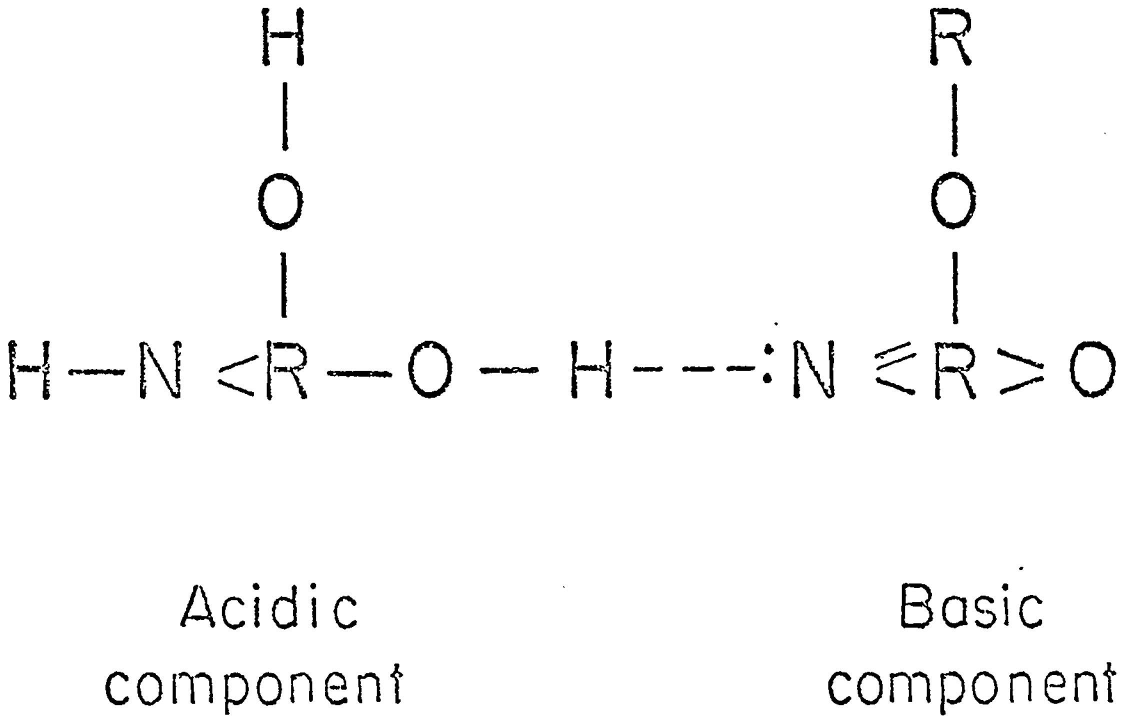
The hydrogen bonded structure of asphaltenes is compatible with their solubility characteristics. In moderately polar solvents such as benzene, the asphaltenes are soluble because the acidic and basic components are separately solvated. When the polar solvent is replaced by a nonpolar solvent such as pentane, hydrogen bonding takes place, a large complex is formed, and the asphaltenes precipitate as hydrogen-bonded acid-base complexes.

Whereas more work will have to be carried out to confirm the structural details in figure 1, our experimental data leave no doubt that the acidic component contains all, and the basic component none of the acadic (proton exchangeable) hydrogen present.

We now come to the structure of coal. The structures that have been suggested for bituminous coal are based on ultimate and functional group analysis, spectrometric and x-ray data and chemical reactions (5,6,7). An example of such a structure (7) is shown in figure 2. This structure has some good features and some bad features.

First, the good features. This structure has something of everything. It contains aromatic and naphthenic hydrocarbons; almost every type of oxygen, i.e., oxygen in rings, in carbonyls, in ethers and in phenolic hydroxyls; basic nitrogen as in pyridine and acidic nitrogen as in pyrrole; and sulfur, predominantly as dibenzothiophene sulfur. You get the impression that you could carry out with coal every reaction described in a textbook of organic chemistry. And, strange as it may seem, your assumption would be correct.

If you are an organic chemist and have some experience in the chemistry of aromatic hydrocarbons, you can reduce the aromatic hydrocarbons in coal



$$\mathrm{H{-}N{<}\overset{\begin{array}{c}H\\|\\O\\|\end{array}}{R}{-}O{-}H{-}{-}{-}{:}N{\leqslant}\overset{\begin{array}{c}R\\|\\O\\|\end{array}}{R}{>}O}$$

FIGURE 1. - Acidic and basic components of asphaltenes. The hydrogen attached to the nitrogen in the acidic component represents an acidic hydrogen as in pyrrole.

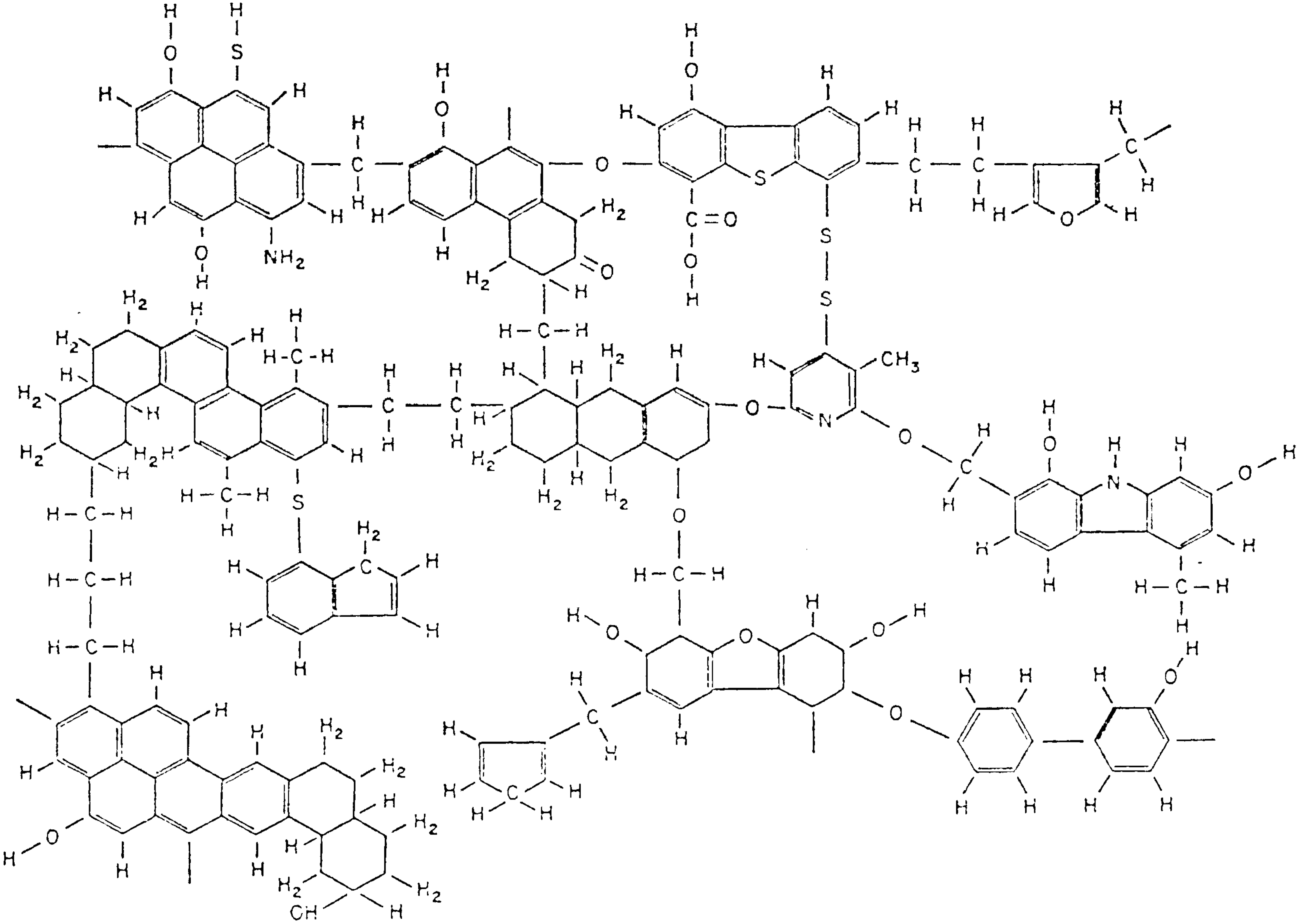


FIGURE 2. A REPRESENTATION OF BITUMINOUS COAL STRUCTURE

chemically (8) or even electrochemically (9) to naphthenic hydrocarbons. If you prefer to convert the naphthenic hydrocarbons in coal to aromatic hydrocarbons, you can do so by using classical organic methods. For example, when coal is treated with palladium on calcium carbonate in a suitable solvent, hydrogen is split off and the naphthenic hydrocarbons in coal are converted to aromatic hydrocarbons (10,11). If you like oxidation reactions, you can oxidize coal with sodium hypochlorite and draw some conclusions as to the amount of sp^3 and sp^2 type carbons present in coal (12). Or, if your Ph.D. thesis was on the structural elucidation of alkaloids, you may try your luck and find out something about the nature of the nitrogen compounds in coal.

Furthermore, using again classical organic methods, you can introduce alkyl groups into the aromatic hydrocarbons of coal by reductive alkylation (13,14). This reaction is particularly useful because the alkylated coal is soluble in benzene. We now have a method available that converts coal into a benzene soluble substance without breaking any carbon-carbon bonds. This should enable us to obtain some information about the carbon skeleton of the original coal molecule. Moreover, we can now, for the first time, determine the molecular weight of the original coal molecule. This molecular weight turns on to be in the 3000-4000 range, the same as that of the petroleum asphaltenes (13).

Now with regard to the bad features of the proposed coal structure. This structure gives the impression that the coal molecule is sort of an amphoteric molecule with acidic and basic functional groups randomly distributed over the whole molecule. I do not believe that this amphoteric structure is correct. I believe that coal has an acid-base structure similar to that we found in asphaltenes. It certainly seems extremely unlikely that the conversion of coal to asphaltenes could change such a random distribution of acidic and basic functional groups into one where these groups are segregated, i.e., where acidic and basic functional groups are attached to different molecules as in the case in the asphaltenes. It is reasonable to assume, therefore, that coal has an acid-base structure and not an amphoteric structure as it generally assumed.

An acid-base structure of bituminous coal is compatible with earlier experiments (15) that showed that bituminous coal can be solubilized by aromatic compounds at elevated temperatures. The solubility of coal in high boiling aromatic compounds, like that of asphaltenes in benzene, may be attributed to solvation of hydrogen bonded acid-base complexes.

The acid-base structure of asphaltenes and the possibility of coal having an acid-base structure are examples of what I meant when I said at the beginning of this talk that coal chemistry is exciting and full of challenging problems.

I think it is safe to assume that further significant advances in coal solubilization and coal liquefaction techniques will depend in a large measure on how much progress we shall make in our understanding of the essential features of coal structure. For example, we have to know more about the amount and type of bonds that are broken in the conversion of coal to asphaltenes and of asphaltenes to oil and also about the mechanism by which these bonds are broken. Such knowledge may lead to savings in hydrogen consumption and perhaps to radically new methods of coal liquefaction and coal solubilization. Much of this badly needed research and development work could be carried out at universities, and I have listed a number of research projects that may be attractive to university based investigators. This list is not arranged in any order of priority, is not exhaustive and should merely serve as a sample and as a basis for further discussion.

SOME RESEARCH PROJECTS IN COAL CHEMISTRY

1. Determine the changes that take place in the conversion of coal to asphaltenes.

2. Determine the changes that take place in the conversion of asphaltenes to oil.

It will be desirable to divide project 1 into two parts:

a) Chemical changes in coal to asphaltene conversion where asphaltenes are the end products, as for example, in the SRC (solvent refined coal) process.

b) Chemical changes in coal to asphaltene conversion where asphaltenes are intermediates in the conversion process as, for example, in the H-coal or SYNTHOIL process.

The reason for this subdivision is that asphaltenes obtained under part (a) are formed under milder conditions than those formed under part (b) and that these two types of asphaltenes may be significantly different.

To achieve the objectives of projects 1 and 2 will require the efforts of several investigators and a certain amount of analysis and separation acrobatics. From molecular weight determinations and ultimate and functional groups analyses of the starting coal, asphaltenes and oils, it should be possible to answer questions such as how many carbon bonds are broken, where is the hydrogen added, what happens to ring and phenolic oxygen and how much and what type of sulfur and nitrogen is eliminated in each of the two conversion steps.

The investigator need not and should not carry out these conversions in his laboratory. Instead, he should be provided with the starting coal used in one of the pilot plants now in operation and with samples of the conversion products obtained in that plant. Results obtained in this way will yield basic information on the chemistry of the coal liquefaction process and at the same time provide data useful to the chemical engineer concerned with trouble-shooting, process design or scaling up of pilot plants.

3. The catalytic effect of mineral matter on the liquefaction and desulfurization of coal.

This research project is long overdue. It has been known for a long time that the mineral matter in certain coals acts as a catalyst in the liquefaction of coal. But only recently, attention has focused on the fact that during liquefaction of these coals a significant percentage of organic sulfur is eliminated. This elimination of organic sulfur as well as the liquefaction of the coal may be catalyzed by metallic iron formed from the pyrite in the coal at elevated temperatures and hydrogen pressures (16), a possibility that should be further investigated.

Organic chemists should be delighted to try their skills on project 4.

4. The nature of the acidic and basic components of asphaltenes.

As mentioned before, we have shown that asphaltenes have an acid-base structure and that the acidic and basic components can be separated. Much more work will have to be done to pin down the structural details of these two components.

Knowledge of the structure of the acidic and basic components in asphaltenes may be helpful in designing a better catalyst for the conversion of asphaltenes to oil. For example, we found (4) that the acidic component by itself is about 50 percent soluble in pentane and much more fluid at relatively low temperature than the original asphaltenes. A catalyst designed to eliminate nitrogen from the basic component may lead to a more efficient asphaltene to oil conversion. As in the case of project 1, project 4 should be subdivided into projects 4a and 4b. Project 4a would deal with asphaltenes obtained in

SRC type processes and 4b with asphaltenes obtained in SYNTHOIL-type processes.

There is another interesting point that should be investigated in connection with the proposed acid-base structure of asphaltenes and coal. What would happen if the acidic and basic components were pyrolyzed separately? Would pyrolysis of the acidic component produce only tar acids and pyrolysis of the basic component only tar bases? If that were the case, much could be learned about the mechanism of coal tar formation and about producing chemicals directly from coal.

5. Nature and strength of hydrogen bonding between acid and basic components in asphaltenes.

Project 5 deals with what is perhaps the most important aspect of the acid-base structure. NMR measurements of acidic and basic components at different concentrations and temperatures should give some information on the nature and strength of hydrogen bonding in various solvents and why certain solvents are better than others.

Project 5 covers the ground work that has to be done before project 6 can be tackled.

6. Coal solubilization and extraction methods in light of a possible acid-base structure of coal.

Earlier work has shown (15) that bituminous coal can be solubilized at elevated temperatures by aromatic hydrocarbons with an angular arrangement of rings such as phenanthrene but only poorly by aromatic hydrocarbons with a linear arrangement of rings such as anthracene. The difference between the solubilizing power of phenanthrene and that of anthracene is quite impressive. Phenanthrene dissolves 95 percent of the coal and anthracene, only 24 percent. It would be interesting to obtain some information, perhaps with the help of model compounds, on hydrogen bonding between nitrogen bases and phenols in phenanthrene and anthracene solutions. Another interesting result of these earlier experiments was the discovery that coal can be converted to a benzene soluble material by treatment with long chain fatty acids in the presence of phenanthrene. If coal contains basic components similar to those present in asphaltenes, then passing HCl gas through the benzene solution of the treated coal should precipitate the basic component as an HCl adduct.

7. The nature of pyridine soluble pre-asphaltenes, their formation from coal and conversion to benzene soluble asphaltenes.

Project 7 deals with an important but neglected problem of coal liquefaction and that is the nature of the so-called benzene insolubles.

The efficiency of a coal liquefaction method is measured by the percent coal to benzene solubles conversion on a moisture- and ash-free basis. Very often in laboratory experiments and plant operations, coal conversion in terms of benzene solubles is less than 100 percent. It is generally assumed then that the benzene-insoluble material is unreacted coal. We have shown that this assumption is not justified and that the benzene insoluble material is pyridine soluble and closely related to the benzene soluble, pentane insoluble, asphaltenes. Moreover, the pre-asphaltenes, as we may call these pyridine soluble, benzene insoluble materials, are soluble in and impart a high viscosity to the coal liquefaction product (17). This causes problems with ash removal by centrifugation or filtration. It would be interesting to learn more about the chemistry of these pre-asphaltenes, their relation to the original coal, their acid-base structure, their formation from coal and conversion to asphaltenes. Pre-asphaltenes form very rapidly on heating, with little or no hydrogen consumption. The problem with pre-asphaltenes is solvent recovery. Pre-asphaltenes, probably due to their acid-base structure retain a comparatively large amount of solvent that cannot be recovered, particularly if the solvent contains basic or acidic groups such as in pyridine or phenol. A better understanding of the chemical nature of the pre-asphaltenes should lead to better solvent extraction and recovery methods and improved SRC processes.

8. The sensitivity of lignite to oxidation.

Project 8 has two aspects. One has to do with the economy of shipping lignite, the other with the liquefaction of lignite. Lignite, as mined, contains a large amount of water (up to 45 percent). Shipping all this water is expensive; it would be much cheaper to dry the lignite prior to shipping. However, lignite when dried often ignites spontaneously and therefore it is not possible to ship lignite with too low a water content. The sensitivity of lignite to oxidation has still another consequence (18). Whereas freshly mined lignite can be readily liquefied at elevated pressures of CO and H_2, lignite exposed to air is more difficult to liquefy. This, a study of the reactivity of lignite towards oxygen may solve the problems of spontaneous combustion and the problem of the detrimental effect of weathering on liquefaction.

THE VIRTUE OF TYING RESEARCH PROJECTS TO ONGOING PROCESSES

This list of projects, as I mentioned before, is by no means exhaustive and may be modified and amplified according to needs. However, there is one common denominator to all these projects, and that is that they are all tied in one way or another to certain coals used in existing ongoing processes and to products obtained in those processes. This, in my opinion, is an extremely important consideration when planning first-generation research projects in coal chemistry. In the past, time and effort were lost in coal research due to dissipation of efforts. Analyses and reactions of subbituminous and bituminous coals must be interpreted differently, and even within the same rank, analyses and reactions are seldom comparable. Ten or twenty years ago this dissipation of effort was perhaps unavoidable because there were no urgent, well-defined problems to be solved. But today the situation is entirely different.

Today, you have a number of pilot plants in operation, pilot plants that use certain representative coals and make certain products. Any research work carried out on these coals, processes and products has a good chance to be of immediate value. I think that it would be cruel and unusual punishment to allow a prospective investigator who does not have considerable background and experience in coal chemistry to choose the coal or the process he wants to work on. I think this idea of offering to the universities a multiple choice of clearly defined research projects is excellent and avoids the extremes and pitfalls on the "throw the bone to the dogs" and "hat in hand" approach. The "throw the bone" approach is to let the universities fight for grants offered for some vaguely defined research problems. This approach does not work too well, even in the case of dogs because it is not necessarily the smartest dog that runs away with the bone, but the biggest or the hungriest. The "hat in hand" approach is to ask a well known scientist if he would honor the sponsoring agency by accepting a research grant without any strings attached.

HOW TO SELL COAL RESEARCH TO UNIVERSITIES

Now that we know how to avoid these extremes and pitfalls, how do we go about selling these research projects and get the universities involved in coal research? To answer this question, we first must decide on the type of university that we want to "bring aboard." There are already some universities that are centers of competence and excellence in coal research, and work at these universities will continue to be funded. The university we have in mind is one where nobody knows or has even heard anything about coal research. And here is how I would go about bringing such universities "on board."

First, I would circulate a list of research projects such as the one we discussed before and then I would visit the universities and explain and discuss these projects in detail. And this is roughly what I would say to a prospective investigator.

This list of projects is designed to help you choose a promising area of research in coal research. The literature in coal chemistry is so vast and diffuse that without some prior experience in coal chemistry is it almost impossible to come up with a viable proposal. This list of projects is intended to save you time in writing elaborate proposals and to get you started as quickly and as painlessly as possible. I said "as painlessly as possible" because some pain and perhaps even shock cannot be completely avoided if one was used to working with pure compounds. Do not apply for coal research money unless you are prepared to make a wholehearted effort. This may require some autohypnosis and mediation on the subject: Why should I get involved in coal research? And here are some suggestions to help you along. You have made your reputation in the field of kinetics of aromatic halogen substitution. Your papers XXII and XXIII have just appeared in JACS and you are preparing to send in paper XXIV. And now you are worried. Should you drop your work on the kinetics of aromatic halogen substitution where you have become an expert and start in coal chemistry where you'll be a novice? Who knows how long it will take you to gain the same reputation in coal chemistry that you had in the field of aromatic halogen substitution.

But consider now your situation from a different point of view. Your 23rd paper on halogen substitution really did not have the novelty and zip your first three papers had. Except for a few specialists, nobody will be interested in paper XXIV. Coal chemistry, on the other hand, is uncharted territory, full of problems that are very challenging from a scientific point of view and whose solutions are most urgently needed.

Don't worry too much about following the work plan to the letter. The research contract is flexible enough to allow you to change the course of your investigations if you want to follow a new lead. If you run into difficulties, don't hesitate to call X at laboratory Y and discuss the problem with him. If he can't help you, he will find somebody who can.

And this, roughly, we be the extent of my sales talk.

URGENT NEED FOR A LABORATORY MANUAL ON COAL CHEMISTRY

And now we come to the most difficult and most urgent problem of all. How to get the universities involved in a training program. We might as well call this "operation vicious circle" or, if you are an optimist, "operation boot strap." Universities do have laboratories and know how to teach laboratory courses, but with few exceptions have not the slightest idea about coal chemistry. To remedy this situation, I suggest that the highest priority be given to writing a laboratory manual on coal chemistry. If coal chemistry is ever to be practiced on a larger scale, this will only be possible after a good laboratory manual has been made available. A laboratory manual, when properly put together, is a thing of beauty and inspiration. It has a magic, soothing effect on one who desperately needs a quick introduction into a new field. Just reading about the kind of experiments that can be carried out gives you a sense of security. A good manual not only teaches experimental techniques but also contains the relevant theoretical background for each experiment.

The manual I have in mind would contain chapters on each of the following subjects: Sampling, coal preparation, coal petrography, coal ranks, coal analysis, coal chemistry, coal liquefaction, coal gasification, combustion and carbonization. The manual should be written with a 2- or 3-month intensive graduate laboratory course in mind. Such a manual must, of course, be written by experts in the field in cooperation with the universities.

The compilation of such a laboratory manual on coal chemistry would fulfill these needs. First, it would force the expert to compact the theoretical part into a few pages. This compaction, if rigorously adhered to, will do wonders for coal research because it will cut out most of the dead wood that has accumulated in the past and make room for new ideas. Second, this manual, when avaiable, will help train many more technicians and scientists than would be possible otherwise. Finally, this manual would show the interaction between the various topics treated. To do coal research one must be acquainted with problems of sampling and petrography and all the other topics treated in the manual.

Of all the project proposals mentioned, producing a manual deserves the highest priority.

CONCLUSIONS

Have experts in the field define problem areas and research projects.

Assist university investigators at the beginning and throughout their studies with technical advice on handling coal and coal products. Allow for flexibility of work plan to permit investigator to change course of investigation.

Tie in coal research projects with ongoing processes.

Issue a first class laboratory manual on coal chemistry.

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CONVERSION OF COAL TO LIQUIDS -- RESEARCH OPPORTUNITIES

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Coal represents about 80 to 85 percent of the known fossil fuel energy reserves of the United States. Bituminous coal and lignite constitute the great bulk of these vast coal reserves. Experience at the University of Utah indicates that high volatile bituminous coal lends itselt best to liquefaction.

Bituminous coal as well as products to be derived from it may be represented on a graph relating hydrogen and carbon. Such a representation on an atomic hydrogen to carbon basis is shown in Figure 1. One observes from this figure that the conversion of coal to any liquid product involves the addition of hydrogen to that portion of the coal substance which is to be thus converted.

Bituminous coals cover a rather wide range of atomic compositions. Utlimate analyses for two bituminous coals at opposite extremes of atomic hydrogen to carbon ratio are given in Table I. Western U. S. coals being generally younger than Eastern coals tend to have higher hydrogen to carbon ratios. Examination of the ultimate analyses reveals that to produce a satisfactory refinery feed stock one has other problems to solve in addition to increasing the hydrogen to carbon ratio. One must reduce the very large oxygen content as well as the nitrogen and sulphur contents to essentially zero values. In a hydrogenation environment, these operations will all consume hydrogen.

Any liquefaction process represents an attack upon the "molecular" structure of the coal. For any process other than pyrolysis alone, this attack involves diffusion of the reactant into the porous structure of the coal and for all processes, including pyrolysis alone, it involves diffusion of products out of the porous structure. Whether or not these diffusion processes are rate controlling, they are important. A very brief summary of some of the things we know about the structure of bituminous coal, partiularly how it is put together and the things we have to do to it to convert it to fluid fuels, liquid or gaseous, would appear to be in order.

The primary structure of bituminous coal is principally aromatic in nature, with generally about 70 to 75 percent of the carbon being aromatic carbon. Six membered aromatic rings predominate although significant quantities of five membered configurations exist. The basic ring positions are mostly occupied by carbon atoms although there are many of the rings with a sulphur atom, a nitrogen atom, or an oxygen atom in ring positions. A substantial amount of hydro-aromatic structure also exists where a part of the structure is saturated with respect to hydrogen. In general about 15 to 25 percent of the carbon in bituminous coal is associated with hydro-aromatic structures.

As seen from the ultimate analyses, the three hetero-atoms, sulphur, oxygen and nitrogen, are present in significant quantities. These three hetero-atoms appear in a very large number of types of compounds. Figures 2 to 4 attempt to illustrate the most important of the kinds of structures in which these hetero-atoms occur in coal. On an average about one-half of the sulphur found in bituminous coal is inorganic in nature. It is possible by certain techniques to remove essentially all of the inorganic sulphur without chemical interaction. The balance of the sulphur, on an average about 50 percent, exists principally as thiophenes, sulfides, disulfides, and mercaptans. Of these types of sulphur compounds, the thiophenes are by far the most difficult to remove. It should be noted that the percentage of sulphur existing as inorganic sulphur as well as the percentage existing as thiophenic sulphur varies widely among bituminous coals.

Oxygen also occurs in a very large number of types of structures in coal. Principal among these are phenols and other compounds containing the OH radical, ether-type compounds, ketones, quinones, etc. Oxygen has also been identified occupying ring positions within the structure. Similarly, the types of structures in which nitrogen occurs in coal are represented.

The principal types of structures, namely; aromatic and hydro-aromatic, are joined together to yield the fundamental coal structure. At the present state of knowledge, it seems quite impossible to accurately represent this structure. However, it is observed that these ring structures are joined together in various types of patterns with the basic structure consisting of single rings, condensed double rings, condensed three ring structures, etc. From x-ray data as well as diamagnetic susceptibility data one concludes that the average size of a cluster making up the fundamental coal structure contains about three condensed rings actually ranging from single rings to several condensed rings per cluster. Short side chains appear on some of the rings. These clusters are joined in a network in two dimensions relative to a particular cluster with interatomic distances in the range of chemical bonds, generally less than two angstroms. This is not to be interpreted to imply a perfect two dimensional network without holes however. The minimum distance between atoms in the third dimension is of the order of 3.5 angstoms, too long for ordinary chemical bonds.

The clusters are joined together by connecting bridges principally of the types indicated in Table II. Short aliphatic groups, principally methylene and probably not longer than four carbon atoms, seem to constitute the principal connecting bridges. Ether linkages, sulfide and disulfied linkages and biphenyl linkages also appear in significant numbers.

One might appropriately conclude that bituminous coal should not be thought of as a three dimensional solid but rather as being composed of stacked layers. A layer may be thought of as a number of clusters joined together with the possibility that a particular cluster may be randomly oriented in a different plane than its nearest neighbor to which it is attached. One may then think of bituminous coal as a random stacking and orientation of micelles. Figure 5 is an attempt to represent bituminous coal structure in a single plane representing the aromatic and hydro-aromatic structures as well as principal hetero-atom configurations, illustrating the manner in which these are joined together and showing cavities between the clusters. As a consequence of the coalification processes and the resulting stacked and randomly oriented lamellae, a rather extensive internal pore structure exists in bituminous coal, thus generating large internal volumes and internal surface areas. These areas are associated mainly with a capillary system having passages of width of 40 angstroms or less which passages are linked by constrictions even smaller, down to 5 to 8 angstroms in width. Most of the internal surface area is contained in the ultra fine region of the porous structure.

The "holes" in the ultra fine structure range from gaps a few angstroms wide caused by random packing of the large molecules to comparatively large openings up to 100 angstroms wide. In addition, there are still larger capillaries and cracks which in bituminous coals contribute from 20 to 50 percent of the total internal free volume.

The internal capillary structure of the coal particles is a very important feature in coal liquefaction. Success of the conversion operation depends upon rapid and efficient contacting of the coal surface by reacting gases where reactants are involved and also by the catalyst where a catalyst is involved. Satisfactory and practical conversion rates demand availability of more surface than the external particle surface. Rates of diffusion of reactants to these surfaces and products away from the surfaces are largely determined by the diameter and lengths of the diffusion channels.

If one examines the representation of the coal structure as indicated in Figure 5 one senses the magnitude of the task confronting us if we would convert this coal structure to liquid fuels. One finds only a very small amount of material existing naturally in the coal which is liquid at room temperature. For example, it has been noted that the average size of a fused configuration in bituminous coal is about three rings. Since some of the rings are single rings, others of the configuration must consist of more than three rings. A majority of the configurations must contain at least three rings. When one observes that the normal boiling point of anthracene (a three ring fused structure) is 350°C, and the solubility of naphthacene (a four ring structure) in benzene is 0.057 grams per 100 grams solvent, one concludes that the amount of three ring material in a product which is liquid at room temperature must be limited and practically none of configurations of four or more rings may be present in such a liquid. Specifically, any process which would yield a liquid and gaseous product consisting of say, 70 to 80 percent of the original coal, the product to be liquid at room temperature, must not only rupture essentially all of the connecting links between clusters but must also accomplish reduction in size of a very large number of fused configurations. Such fused aromatic structures cannot be ruptured by thermal means alone in the temperature range of interest in producing liquids. Practically speaking, these processes consume a considerable amount of hydrogen.

Although varying amounts of coal liquids can be produced at temperatures below the softening temperature of bituminous coal, the yields generally are too low, or the rates of liquefaction too slow, for this to be a practical temperature regime for coal liquefaction on an industrial scale. Bituminous coal begins to soften or become "plastic" at temperatures in the general range of 325-350°C. The initiation of plasticity is associated with, and undoubtedly the direct result of, thermal rupture of bonds within the coal structure. At these temperatures the bonds affected are principally connecting links between clusters (a single ring is here included in the term "cluster"), bonds joining a side chain to a cluster, and other bonds of similar energies. Bond rupture within the aromatic structures does not occur at these temperatures. Dehydrogenation of the hydroaromatic structures to yield molecular hydrogen is not significant at the lower temperature of plasticity (but may become significant at temperatures above about 500°C). However, the hydroaromatic structure is involved in the production of volatile material (tar) liberated throughout this temperature range. It will be assumed that rate considerations demand temperatures above those required for the initiation of plasticity. Hence, pyrolytic processes are active and important contributors to the overall processes.

A great many studies have been made and processes suggested in relation to the conversion of coal to liquids. (Varying amounts of gases are also produced, but the processes considered here have as a principal objective the production of liquids.) The processes which to date have exhibited enough promise, either technologically or economically, to have passed beyond the small bench scale of the laboratory may be grouped under four general headings:

1) Pyrolysis
2) Solvent refining of coal, yielding either a solid or heavy liquid ash-free, low sulfur product
3) Production of a CO-H_2 misture from coal and steam, followed by catalytic synthesis of hydrocarbons (Fischer-Tropsch variations)
4) Direct pressure catalytic hydrogenation of coal, using H_2 or CO-H_2O mistures;
    a) Coal slurried in a vehicle oil
    b) Coal "dissolved" in a hydrogen donor solvent

c) Coal fed dry to reactor

1. Pyrolysis

When bituminous coal is pyrolyzed, thermal rupture of the bonds in the "connecting links" between clusters becomes appreciable to temperatures in the range 325-350°C (introduction of plasticity) as illustrated in Figure 6. Bonds connecting side chains to the clusters and other bonds of similar energy may also be ruptured. The extent of the bond rupture increases as the temperature increases. Each bond rupture results in two free radicals which are extremely reactive and probably of very short life at these temperatures. If the fragments thus produced by the bond rupture are small enough, and if they can be stabilized by addition of an atom (e.g., a hydrogen atom) or small group (e.g., a methyl group) thus becoming stable gaseous molecules at the existing temperature, they may be evolved as part of the tar. If the fragment is too large, it will remain with the char. If no small entity (e.g., H atom or small radical group) is available to perform this stabilization of the "radical end," polymerization of the fragments will occur, yielding char or coke. Some fragments (e.g., a hydroaromatic fragment) can provide stabilization within themselves through rearrangement of atoms. A fully aromatic fragment must interact with another entity from outside itself to achieve stabilization. A small aromatic fragment may collide with a hydroaromatic portion of the coal structure, abstracting a hydrogen atom to achieve stabilization. Liberated side chains may be stabilized in like manner.

In this connection it has been observed that a quantitative relationship exists between the hydroaromatic content of a bituminous coal and the tar yield upon pyrolysis of that coal. If one reduces the hydroaromaticity of the coal a corresponding decrease in tar yield is observed, the tar yield becoming zero when all of the hydroaromatic structure is eliminated. One should not conclude from this observation that only hydroaromatic carbon can appear in the tar, but rather that the hydroaromatic structures may also contribute to the stabilization of radicals which later appear as molecules in the tar.

In the range of temperatures of interest for the production of liquids from bituminous coal (generally below about 550°C) total yield of volatile material is generally below 40-45% by weight. Of this amount, about one-half is usually gases. It is observed that as the residence time in the reactor is decreased, the liquid yield can be increased with lower gas yields. To maximize liquid yields it is essential that the coal particles be heated to the 500°C range very rapidly and the products be removed quickly from the heated zone.

2. Solvent Refining of Coal

Bituminous coal can be dispersed in a solvent, as for example a hydrogen-donor solvent such as tetralin. It is then possible to remove the ash by filtration and with it essentially all of the inorganic sulfur. Up to 50% of the organic sulfur may also be removed in the process. For essentially complete dissolving or dispersion of the coal temperatures in the range of 450°C are usually required. The maximum temperature is often determined by the boiling point of the solvent at the pressure of the system.

The kinetics of the dissolution process essentially demand that the process be carried out at temperatures about 350°C. At these temperatures thermal bond rupture within the coal structure becomes rather extensive. The bond rupture may be promoted by the action of the solvent. As in the case of coal pyrolysis, the thermal rupture of a bond produces two free radicals, which are highly reactive and of short life. The free radicals seek stabilization by such means as are available to them, namely; addition of an atom or small group, arrangement of atoms within the fragment, or polymerization. The extent of bond rupture within the coal structure increases as the temperature increases. Hence dispersion is more complete and the average "molecular weight" of the dispersed material decreases as the temperature increases.

A hydrogen-donor solvent, if brought into intimate contact with the coal, readily yields hydrogen atoms to stabilize the free radical fragments, as illustrated in Figure 7, thereby inhibiting polymerization and yielding "molecules" or particles small enough to be carried in solution of suspension by the solvent. At temperatures in the 425-450°C range bond rupture accompanied by hydrogen stabilization is extensive enough to release most of the inorganic matter trapped in the coal structure and to permit essentially complete solution or suspension of the organic matter. A very substantial portion of the organic material thus dissolved is of low molecular weight, up to two or three hundred, and is removable as a gaseous or liquid product. Of course, since bond rupture of connecting bridges between condensed configurations is not nearly complete, some rather large configurations still exist, although dispersed in the solvent. In this condition, most of the inorganic material can be removed by filtration.

The average molecular weight of the liquid product of dissolution of coal in solvent, excluding the solvent itself, has been reported to be of the order of a few thousand (dissolution occurring in the 350 to 450°C temperature range). The solvent evidently is not too effective in producing rupture of the connecting links between clusters, and apparently accomplishes very little if any breakdown of the fused configurations, through hydrogen saturation or otherwise.

In studies involving dissolving coal in a hydrogen-donor solvent, for example tetralin, the solvent is observed to become more aromatic as the dissolution process proceeds. If one wishes to preserve the hydrogen donor capability of the solvent, or of the coal-produced liquids which also contain hydro-aromatic materials, this may be accomplished by the addition of molecular hydrogen to the system. It is possible, and indeed quite likely, that the mineral matter in the coal functions as a catalyst for the reactions of the molecular hydrogen in this system.

3. Conversion to CO-H_2 Mixture Followed by Hydrocarbon Synthesis

Coal may be reacted with oxygen and steam to produce an appropriate mixture of carbon monoxide and hydrogen. Under carefully selected conditions of temperature and pressure, and with the aid of a catalyst, hydrocarbons in the liquid range may be synthesized. The best known process utilizing this reaction sequence is the Fischer-Tropsch Synthesis. Commercial plants in Germany during World War II and the Sasol Plant in South Africa today have demonstrated the technical feasibility of the process. However, the cost is high by American standards and the process has not been considered to be economically feasible in the United States. However, the decisions regarding the economics of the Fischer-Tropsch process were made two or three decades ago and the very extensive catalytic know-how which has been developed in the petroleum industry during this period has not been applied to the Fischer-Tropsch-type of synthesis. There is now considerable interest in such an application.

4. Direct Hydrogenation of Coal

Processes involving direct hydrogenation of coal currently in use within the limits of this discussion may appropriately be divided into two groups:

1. Dissolving of coal in a hydrogen donor solvent, followed by or in association with catalytic hydrogenation of the extract.
2. Catalytic hydrogenation of the raw coal.

The kinetics of a practical coal hydrogenation process demand temperatures generally above 400°C, hence, thermal bond rupture in the coal substance is a significant phenomenon, as it is in coal pyrolysis and coal dissolution in solvents. Figures 8 and 9 show a comparison of product yields as a function of time, and a comparison of the rates at which the three processes proceed toward completion, for the same coal at similar temperature, which emphasize the similarities of the three processes. The hydrogenation data appearing in the figures involved coal dissolved in a coal-derived solvent prior to hydrogenation. It is suggested that thermal bond rupture, yielding free radicals which are then stabilized by the addition of hydrogen atoms detached from the catalyst, plays an important role in the hydrogenation process. The catalyst must necessarily be very near to the sight of bond rupture.

While the product yield per unit time is very similar in hydrogenation and dissolution, the average molecule in the hydrogenation product is much smaller than the average "molecule" in dissolution. It is probable that the catalyst in coal hydrogenation (absent in coal dissolution) significantly promotes the bond rupture in the hydrogenation process.

It has been observed that to obtain a high yield of liquid product from bituminous coal, one must rupture a very high percentage of the connecting links between clusters and stabilize the resulting fragments. This cannot be accomplished in the appropriate temperature range without the aid of a catalyst. Further, considering that a majority of the coal substance must consist of three or more fused rings (in order for the average to be 3 rings) and considering the melting points and boiling points of the condensed aromatic compounts, the conversion of 70% or more of the coal substance to liquids and gases must involve reducing much of the miltiring structure to smaller configurations. Again this cannot be accomplished in the appropriate temperature range without the aid of a catalyst. In a practical sense in the production of liquid fuels where a fully aromatic cluster is concerned, this latter process involves addition of hydrogen to at least one of the rings, producing saturation of the ring, before ring opening and size reduction will occur, and this is a catalytic operation.

In order for any substance to catalyze a chemical reaction, there must be an interaction of a chemical nature between the catalyst and at least one of the reactants. In the case of a solid catalyst, this means chemisorption of at least one reactant. If a second reactant is involved it must be brought into very close proximity of this catalyst-reactant complex for reaction to occur. (This is the Eley-Rideal scheme for catalysis.) In some systems apparently both reactants must undergo chemical interaction with the catalyst before reaction can occur. Equilibrium is established and maintained for these adsorption or chemical interaction processes, and the overall rate of reaction is determined by the chemical reaction between the two reactants. (This is the Langmuir-Hinshelwood scheme for catalysis.) It is now known which scheme applies to coal hydrogenation, but both schemes require intimate catalyst-coal-hydrogen contact.

The mixing of a powdered catalyst with dry coal does little to promote the subsequent hydrogenation of the coal in the temperature range desirable for production of liquids unless the catalyst has a low enough melting point and high enough vapor pressure to permit the catalyst to extensively and intimately cover the internal coal surface. Otherwise the extent of contact between catalyst of low volatility and the coal by first dissolving the coal in a hydrogen-donor solvent or other agent (such as in the Consol. Proc, H-Coal Process or Bureau of Mines Process) which disperses the coal substance in the solvent and through mechanical mixing, brings it into intimate contact with the catalyst surface. Final conversion yields can be high in such a process. However, the liquid which then surrounds the catalyst impedes the diffusion of hydrogen to the catalyst surface and greatly reduces the rate of hydrogenation. Thus, residence times in the reactor become long (generally of the order of minutes) compared with hydrogenation of dry coal (a few seconds).

Direct hydrogenation of coal with no solvent present as in the University of Utah Process permits the hydrogen to diffuse rapidly to the reaction sites, within the microporous structure of the coal as well as the external surface. This can provide for very fast reaction, and hence, very short residence times in the reactor. However, for this to be beneficial the catalyst must also reach these internal sites rapidly or be there in advance. To achieve this, the catalyst has been dissolved in a solvent (such as water) impregnated throughout the porous structure of the coal and the solvent evaporated leaving a film of catalyst over the surface, internal as well as external. A catalyst such as $AnCl_2$ with melting point of 262°C and boiling point 732°C has a rather high vapor pressure at temperatures of interest in coal liquefaction. Studies indicate it may not be necessary to impregnate the coal with this catalyst, but rather one may take advantage of the vapor pressure and permit the catalyst vapor to diffuse to the reaction sites.

Dissolving the coal in an appropriate solvent prior to feeding reduced the difficulty of feeding finely powered coals. However, feeders have been developed which seem to have solved the severe problems formerly associated with this operation. Dissolving the coal in solvent prior to exposing it to liquefaction temperatures also eliminates many of the problems associated with agglomeration.

Feeding a strongly caking coal dry to a reactor where temperature are above the plastic temperature of the coal presents the possibility of char build-up and plugging in the reactor. High gas velocities sufficient to ensure turbulent flow in the reactor appear capable of preventing build-up to cause plugging, although at modified Reynolds numbers in the lower range of the turbulent region some build-up begins. There appears to be a somewhat complex relationship between coal feed rate, gas flow rate, reactor tube diameter and reactor temperature which affect the tendency toward char build-up.

With the rapid penetration of the hydrogen to the inner microporous structure of the coal, accompanied by impregnation of the catalyst on the coal, heat transfer within the coal particle appears to control the required residence time of the coal in the reactor. Experiments involving free fall of coal particles through the reactor revealed that at the short residence times being considered here the outside of the char was essentially completely hydrogenated while the innermost part was essentially like the original coal. This char could then be passed through the reactor again without further addition of catalyst and extensive hydrogenation occurred, indicating that catalyst contact inside the coal particle was not the limiting variable.

Studies concerned with the catalytic hydrogenation of multiring aromatic compounds (for example, anthracene or phenathrene) reveal that one wears the molecule down by saturating one end (at least) followed by ring opening and scission, then saturation of another ring, yielding a single ring compound (but only one) from the multiring compound. In this temperature range, hydrogenation of the ring must precede ring opening, and a hydrogenation catalyst is necessary for this to occur.

Considering the increasing demand for single ring aromatic materials, for example, as additives in gasoline to improve the octane rating, as raw materials for the manufacture of conventional explosives, as solvents and chemicals, etc., it would be very useful to increase the yield of these compounds by splitting, for example, three ring structures in the coals, yielding two single ring compounds.

One would expect that the addition of hydrogen to the 9 and 10 positions on the anthracene molecule would reduce the resonance energy surrounding these positions and weaken and therefore lengthen the bonds on either side of the 9 and 10 carbon atoms, thus permitting cracking in these bonds to yield two single ring compounds. This was not accomplished in the studies in our laboratory. Calculations made in our laboratory involving some approximation methods, because thermodynamic data are lacking in the literature, indicated that the free energy change associated with cracking the bonds with which we are concerned is slightly negative in the amount of a few kilocalories per mole. However, the free energy associated with the transfer of hydrogen from the 9 and 10 positions to adjacent positions on an end ring is also slightly negative in the amount of a few kilocalories per mole. While these calculations do not offer strong encouragement relative to the possibility of selectively cracking these multi-ring aromatic compounds in a center ring position, it does appear to be possible. This could prove to be a fruitful area for research.

RECOMMENDATIONS FOR RESEARCH ON COAL COMBUSTION

Panel Chairman Robert H. Essenhigh

General:

1. The focus for university research should be on coal structure and reactions, with necessary concern for the fate of mineral matter (ash), fuel nitrogen, sulfur, and other factors that may circumscribe engineering design.
2. The thrust of the research should now be on developing, and testing experimentally, models of total systems and parts of systems -- on a step by step basis.
3. Engineering systems of concern existing or proposed at present include:
   a) Pulverized coal firing (mainly steam raising).
   b) Grate firing (mostly steam raising).
   c) Fluid bed - ballasted (under commercial development).
   - unballasted (commercial).
   d) Coal-fired MHD combustors involving high temperatures and pressure.
   e) Direct firing of process furnaces, perferably utilizing ultra fine coal.
   f) Direct firing of gas turbines, preferably utilizing ultra fine coal, and operating at pressure.
   g) Rotating fluid bed.
4. The thrust of total system analyses and model constructions should aim first at identifying gaps in the more fundamental knowledge required for necessary descriptions.
5. Parts of system can include, for example, the full behavior of a one-dimensional flame, at one extreme, or the initial steps of pyrolysis of a single coal particle, at the other extreme.
6. Support of heat transfer research, or combustion aerodynamics or mixing research, where these are not integral parts of a total system is not recommended.
7. The focus should be in general on the materials properties and structure of coal, and on the relevant kinetic behavior, under the varied conditions of particle, size, temperature, rate of temperature

rise, pressure, oxygen enrichment, velocity fields, and so forth encountered in the practical systems, or foreseen for future systems.

8. It is, of course, understood that the sponsoring agents will so adequately monitor proposals that a balanced coverage of coal types is maintained, if necessary by direct specification of coals to be included as a requirement for an award.

Details: Outstanding research questions are agreed to embrace the following:

1. An adequate model of coal constitution or structure is required. This should incorporated all possible analytical knowledge.
2. An adequate model of coal pyrolysis is required either as an independent development or as a derivative of the coal structure model. Particular attention should be given to the effects of rapid rate of heating.
3. The combustion behavior and kinetics of the volatiles (liquid partiulates) is virtually unstudied. This now needs attention.
4. Models for char and total coal combustion now exist with some degree of definition. Definitive work that will test arguable points is now required with particular attention to more exact values of activation energies, frequency factors, reaction orders, reaction zone locations, etc. particularly for the specified practical systems:
   a) The solid fuel bed.
   b) The fluid bed in both configurations.
   c) In the pulverized coal flame -- including high pressure, temperature, and oxygen regimes.
   d) The explosion flame (safety in mining).
   e) With ash -- catalytic effects.
5. Models of total systems should now be considered for definitive experimental test where the models are sufficiently advanced. Special attention to the following is required:
   a) Stability limits.
   b) Flame speed.
   c) Fate of pollutant elements, notably fuel N and S.
   d) Mineral matter behavior and volatile emissions relevant to corrosion/pollution.

6. Specifics: focus on the following is recommended:
   a) Pyrolysis delay at high heating rates.
   b) Ignition mechanism at high heating rates.
   c) Explosion flame combustion mechanism (believed to be total coal combustion).
   d) Reaction orders of char burn out with respect to oxygen concentration.
   e) Fate of hydrogen through a flame and the question of volatiles residue in the flame tail.
   f) Extension and experimental test of the solid bed kinetic equations.
   g) Pressure, oxygen enrichment, high temperature and high relative velocity effects on burning of particles.
   h) The fate of nitrogen in char.
   i) Coal/limestone interaction in fluid beds, including specific attention to calcination, SO_2 sorption, and absorber/ash interaction at pressure.

Combustion Related Behavior: Problems of concern to the combustion engineer that require attention or urgent attention:

1. Ash behavior and slagging -- notably the behavior of the mineral matter and including fly ash control by combustion modifications.
2. Pollution control -- notably sulfur and ash -- by benefication and flue gas cleaning.
3. Mechanism of SO_2 control/removal by absorbers, in or out of the flame; also mineral matter interaction with limestone.
4. Breakage and breakage mechanism, and particularly means of reducing power consumption for ultra fine grinding.
5. Special methods of ultra fine coal cleaning.
6. Physics of behavior of fast flowing dust streams.
7. Heat transfer to the particles and inside particles, particularly at high temperature rise rates.
8. Corrosion/errosion/slagging.
9. Waste disposal of pollutant control materials (absorbers, etc.).
10. Development of valid and acceptable sampling methods.

In addition consideration should be given to the following:

1. The creation of a fuels engineering center.

2. Study of general coal behavior with a view to development of new combustion devices.
3. Retrofit requirements of existing or new equipment in novel configurations.
4. As a separate subject, steps should now be taken to develop all information available on the nature of, and combustion properties of, coal-derived gases and oils and solid combustibles such as char.

RECOMMENDATIONS FOR RESEARCH ON COAL GASIFICATION

Panel Chairman Arthur M. Squires

The sub-group on coal gasification identified worthwhile university research objectives

a) in support of ongoing development work in industry,

b) to provide a showcase for new development opportunities and supportting data for them, and

c) to supply fundamental information with a reasonable expectation that at least some of the information will prove useful to future development work or will reveal future development opportunities.

The order in which the objectives are presented here does not imply an ordering of priorities, and the sub-group did not address economic and other factors that must be considered in implementing any work objective.

The discussion took place in the context of the following chemistries for gasifying coal:

1. Anthracite of coke + air
 + steam
 + steam/oxygen
2. Raw bituminous coal or raw coals or lower rank
 + air
 + steam
 + steam/oxygen
 + hydrogen
 + hydrogrn/carbon monoxide/steam
 + hydrogen/steam
3. Pretreated caking bituminous coal + all of those listed in 2.
4. Lignites and peats (and wood) + steam at pressure and at temperatures generally below about 1,200°F to yield methane and carbon dioxide (a catalyst is probably required).
5. Pyrolysis.

The sub-group developed the following check list of work objectives. Little time was spent in discussing relative priorities. A few items in the following list are starred (*) to indicate a broad attitude of the sub-group that these items are especially important. In the case of some items, definite objectives are noted, and this can sometimes be taken as an indication that the sub-group felt the areas to be well developed industrially and that university research might not be welcomed unless it rests upon a relatively radical idea for a change in the present procedure. For some items, explanatory notes are provided to point up as area where research is needed or to illustrate the need.

I. Unit operations aspects of coal gasification

1. Comminuting coal

   [Note: Some processes need control of particle size.]

2. Drying and heating comminuted coal

   [Note: A method with recovery of water would be useful for Western coals.]

3. Conveying comminuted coal (both hydraulic and pneumatic)

   [Note: Little is yet known of effects of cohesiveness of various coals on conveying, and coals differ dramatically in this respect. A test rig for hydraulic conveying (like that at the Research Council of Saskatchewan) might be justified, as well as a rig for pneumatic conveying.]

4. Feeding coal to zone at high pressure

   [Note: There are opportunities for materials development in valve seats; also, opportunities for radical ideas.]

5. Injection of coal into process zone

6. Pretreatment to destroy caking properties

   [Note chemistries would be useful that do not destroy valuable chemically bound hydrogen; otherwise, it would be better to move in process directions that do not require oxidative pretreatment.]

7. Bin flow

   [Note: This is still mostly art; there are problems arising from size segregation; effects of the cohesiveness of comminuted solids are little understood.]

8. Behavior of dust in clouds

9. Standpipe flow

   [Note: The art is well advanced for circulating fine powders (Geldart's type A) in standpipes and risers connecting several process zones. Little is known for the reliable circulation of sandy or coarse solids (Geldart's types B and D), and a large university test rig might be appropriate.]

*10. Contacting coal with gasification medium and fluid dynamic modelling of reaction systems

*[Note: Special attention should be given to developing reaction systems with better control of the rate of heating of raw coal introduced therein to and also better control of vapor product residence times. Systems capable of receiving raw caking bituminous coals are in general to be preferred over those requiring pretreatment. Systems that do not yield tars or a large condensate containing phenols will also in general be preferred. Although the gasification reactor in general represents only a relatively small fraction of the investment in gasification systems now under development, there are opportunities for major savings in cost if the first coal-treating step yields a gas whose subsequent processing requires fewer steps.]

(a) Dilute-phase contacting

(b) Cyclone or vortex contacting

*(c) Gravitating bed

*(d) Slow fluidized (bubbling or turbulent) bed

[Note: Slow beds of fine, sandy and coarse solids (Geldart's types A, B, and D respectively) all have a place in coal gasification. University research has not yet sufficiently recognized the striking and important differences among beds of the several solids.]

*(e) Fast fluidized bed

[Note: The usefulness of the fast bed is probably, but not certainly, limited to fine solids.]

(f) Underground (in situ) gasification

(g) Gasification in presence of an inorganic liquid

(h) Gasification of coal is a slurry of oil

(i) Pulsed systems

*11. Large facility for hot fluidization studies including the possibility of studies at high pressure, with strong ties to universities and access for university researchers

12. Supply of heat to endothermic gasification reactions

(a) Air-blown gasification

(b) Steam/oxygen-blown gasification

(c) Moving burden gasification and the problems of circulating large quantities of solid reliably

[Note: See (9) above.]

(d) Acceptor processes

*(e) Directing reaction paths to reduce endothermic heat requirements

[Note: See III below.]

*13. Discharge of ash matter

[Note: A guide to properties of ash would be helpful.]

(a) As dry ash, with or without much carbon remaining

(b) In form of molten slag

(c) As ash agglomerates (e.g., the Godel phenomenon)

*14. Cleaning gas of dust.

(a) At low temperature

(b) At high temperature

(c) When tars are present

*(d) Rethinking gasification systems to make cleaning easier, especially devising systems without tar

*15. Ridding gas of sulfur species

(a) At low temperature

(b) At high temperature

(c) When tars are present

16. Ridding gas of nitrogen species and other minor constitutents such as trace elements

17. Discharge of a coke byproduct

(a) As powder

(b) As lump coke

(c) As coke beads from a coke-accreting fluidized bed

18. Water gas shift

[Note: A low temperature shift catalyst insensitive to sulfur poisoning would be useful.]

19. Carbon dioxide removal

20. Methanation

[Note: A methanation catalyst insensitive to sulfur would be useful.]

21. Gas drying

22. Concentration of hydrogen from mixtures of hydrogen and carbon monoxide or methane

23. Waste disposal

24. Control of gasification systems, particularly when integrated with gas consuming equipment such as a gas turbine, and especially when the gasification system must follow a varying load
    [Note: Sufficient attention to control was not paid in the design of the STEAG combined-cycle installation at Lunen.]
25. Overall systems thinking for gasification plants
    [Note: This was sadly neglected at the STEAG installation with consequent serious problems with tars and dust in the fuel gas.]

II. Process aspects of coal gasification

1. Markets for clean fuel gas from coal
   - (a) For power gas (i.e., low-Btu gas or utility gas)
     [Note: Load following is a problem. Gasification for baseload with a liquid or coke byproduct for peaking equipment should be considered. Other ideas would be welcomed.]
   - (b) For industrial gas (i.e., intermediate-Btu gas)
     [Note: Is there a role for new pipe networks distributing 300 to 500 Btu/ft^3 gas, say, in heavily industrialized districts?]
   - (c) For synthetic methane
   - (d) For hydrogen
2. Markets for hydrogen made from coal or synthesis gas from coal
   - (a) For fuel hydrogenations
   - (b) For ammonia
   - (c) For methanol
3. Synergisms between coal processing and a large onsite consumer of gas made from coal
4. Source of hydrogen for coal hydrocarbonization or hydrogasification
   - (a) Gasification of char residue
   - (b) Reforming part of a methane make-gas
   - (c) Nuclear energy and electrolytic or "chemical" hydrogen
5. It is time to revive the idea of chemical oxygen?
6. Markets for carbon dioxide gas byproduct
7. Markets for coke byproduct and consideration of role for coke fuel in the community
   [Note: In this connection, some attention should be paid to small-scale devices for gasifying low-sulfur coke of anthracite:

for small industry? for specialized transportation needs? Attention should also be paid to small-scale devices for burning such fuels, such as shallow fluidized-bed combustors.]

8. Overall systems examination of the supply of energy to the entire community

   [Note: See VI below.]

III. Chemical and kinetic aspects of coal gasification

1. Support information and services for experimentation done on a small scale

   [Note: The small-scale experiment faces problems in the sizing of the coal, the feeding of coal at low rates (especially into hot systems), the retention of a swelling coal in a batch experiment, and the preservation of coal from oxidation. The problem of obtaining well-characterized and representative samples should also be noted.]

*[General explanatory note: The sub-group recognized that very little data on the treatment of raw coal exists where the rate of heating of the coal has been varied systematically and especially at rapid heating times. Also, there are little data where the residence time of a vapor product at reaction conditions has been varied systematically over a wide range and especially at short residence times. A few centers are beginning to obtain such data, but the sub-group felt that more work of this kind, in more different types of experimental arrangements, might turn up development opportunities, especially in the direction of reducing tars and phenols and of, hopefully, providing valuable byproducts of gasification. This note is broadly applicable to objectives (2) through (7) below. Each objective should receive research attention over a wide range of the heating time of the raw coal and also a wide range of the residence time of vapor product.]

2. Reaction of raw coal with steam
3. Reaction of raw coal with hydrogen
4. Reaction of pretreated coal with steam and/or hydrogen
5. Reaction of raw coal with mixtures of steam/carbon monoxide/hydrogen
6. Reaction of raw coal with mixtures of steam/hydrogen
7. Reaction of raw coal in presence of a "nonreactive" gas such as nitrogen

   [Caution: Nitrogen may interfere, and other gases such as helium should be used to control the experimentation.]

8. Vacuum pyrolysis of raw coal at slow and fast heating times
9. Reaction of cokes and chars with steam in presence of reaction products of raw coal with steam
10. Reaction of cokes and chars with steam in absence of reaction products of raw coal with steam

    [Note: This objective has already received much attention, and a new research would have to be carefully thought out. A difficult area arises from the fact that we are a long way from an unambiguous connection between differential kinetics for this reaction and the gasification performance of a fluidized bed.]
11. Reactions of cokes and chars with hydrogen

    [Note: These reactions are generally slow and would appear to have limited process usefulness, although their speed undoubtedly depends strongly upon the origin of the char, its age, and its history. Here is an area where a radical idea involving a catalyst (necessarily very cheap or cheaply recoverable) might be useful.]
12. Sulfur content of cokes and chars of varying origins and histories
13. Nitrogen (and oxygen) content of cokes and chars of varying origins and histories
14. Reactions of cokes and chars with carbon dioxide, and the temperature level for gasification with air versus that for gasification with steam or steam/oxygen
15. Origin and behavior of tars

    (a) Temperatures at which tars appear in make-gas from fluidized-bed gasification of raw or pretreated coals

    (b) Times and temperatures needed to crack tars virtually to destruction, and as a function of gas atmosphere
16. Low temperature reaction of coal with steam to yield methane and carbon dioxide

    [Note: This reaction probably requires a catalyst, although success in a non-catalyzed version would represent a striking advance.]
17. Catalytic effects on all of the above, with special attention to catalytic effects of constituents in coal ash

IV. Physical behavior of caking coals (viscosity versus time, "stickiness," swelling, etc.), as a function of

(a) gas atmosphere,

(b) gas pressure,

(c) Heating rate

(d) final temperature

[Note: The classic work in this area, which is voluminous, has been performed on behalf of the producer of metallurgical grades of coke. Note much information is available to guide the developer of a gravitating bed or fluidized bed process, for example, that must handle a coal that melts as it is heated. A recent observation at the Research Council of Alberta, that a subbitumionous coal melts under a high pressure of helium, is a warning that surprises may lie ahead.]

V. Physical and chemical character of cokes and chars (porosity, surface area, pore size distribution, and reactivity) as a function of

(a) the process of their formation, and

(b) percentage carbon burnoff and by what gasification medium

*VI. Broad systems thinking about

(a) resource allocation (including water),

(b) means of distribution and the form of the supply,

(c) environmental aspects, and

(d) other considerations

in respect to the entire group of energy service industries, in respect to interactions and opportunities for synergisms among the intrudies, and in respect to the entire range of the community's energy needs, with special emphasis upon the planning needed soon for energy supply several decades from now.

RECOMMENDATION FOR RESEARCH ON CHEMISTRY OF COAL

Panel Chairman Heinz W. Sternberg

1. Make available samples of several widely representative reference coals that could serve as a basis for the inter-comparison of the work of different groups.
2. As a group of long term projects, we recommend the funding of quantum mechanical and phenomenological calculations aimed at constructing a working model of the molecular structure of coal. In addition, similar work should be conducted to elucidate the reaction mechanisms of coals and the nature of the various reaction intermediates.
   Such a program should also include experimental investigations by: a) Chemical techniques (kinetics, thermodynamics, etc.) and b) Physical techniques (light scattering, optical spectroscopy, etc.) aimed at furthering our understanding of the molecular structure of coals and their reaction intermediates.
3. Re-investigate the assumption that the reaction sequence

$$\text{coal} \xrightarrow{\text{fast}} \text{asphaltenes} \xrightarrow{\text{slow}} \text{oil}$$

   is a reasonable working model for the conversion of coal-to-oil. Define the role, if any, of pre-asphaltenes in this reaction scheme.
4. Determine the changes that take place in the conversion of coal to asphaltenes.
5. Determine the changes that take place in the conversion of asphaltenes to oil.
6. Study the catalytic effect of mineral matter on the liquefaction and desulfurization of coal.
7. Study the nature of the acidic and basic components of asphaltenes.
8. Study the nature and strength of hydrogen bonding between acidic and basic components in asphaltenes.
9. Investigate coal solubilization and solvent extraction methods in light of a possible acid-base structure of coal.
10. Study the nature of pyridine soluble pre-asphaltenes, their formation from coal and conversion to benzene soluble asphaltenes.
11. The sensitivity of lignite to oxidation.
12. Study the chemical structure of coal(s) using techniques such as

reductive alkylation and other chemical procedures that make coal soluble under mild reaction conditions.

13. Study the thermal agglomeration of coal(s) and its inhibition as a chemical phenomenon.
14. Study the chemical comminution of coal(s).
15. Study the nature of the chemical interaction between coal(s) and catalysts in coal conversion, including for example, unusual catalysts such as $SnCl_2$, $PbCl_2$, $(NH_4)_2 Mo O_4$, $ZnCl_2$, etc.
16. Study the nature, occurrence, and role, if any, of organometallics present in coal (for example iron porphyins) for their effects on coal conversion and sulfur elimination.
17. Study the chemical enhancement of coal preparation procedures via froth flotation and related techniques.
18. Study chemical procedures (solvent extraction, froth flotation, etc.) for removing ash, mineral matter, and unreacted coal residues from coal-derived liquids and solvent-refined coals.
19. The establishment of a "Sample and Data Bank: on all key substances related to the chemical molecular structure of coal and the byproducts of coal liquefaction and gasification, which will include the necessary synthesis, purification and certification of samples coupled with necessary physical, thermodynamic and spectral property measurements.
20. Publish a laboratory manual on coal chemistry along the lines suggested in the paper "Coal Chemistry - The University's Role."
21. Investigate improvements in the catalytic dehydrogenation of coal to produce H_2 gas. New solvents and catalysts are needed, and procedures must be developed to recover these solvents and catalysts.

RECOMMENDATIONS FOR RESEARCH ON COAL LIQUEFACTION

Panel Chairman Wendell H. Wiser

Coal liquefaction has developed somewhat more as an art than as a science. A number of coal liquefaction processes have been developed on an experimental basis, in some cases with very little understanding of the chemistry of the liquefaction process. As an industry develops without a high level of funding, it is natural that viable processes should be sought with economically acceptable yields of product without the expenditure of money to obtain fundamental and theoretical data, the cost of which may not be recoverable through increased yields in the short term. Universities are particularly suited to pursue research into the fundamental and theoretical aspects of such processes, inasmuch as this type of study is most suitable for the theses of graduate students and most of the experimental work will be accomplished by graduate students and postdoctoral fellows.

A number of areas for research will be listed. Only a brief comment will be made relative to each. The list is not intended to be all inclusive nor should it be interpreted to be in the order of priority. It is recommended that all of the following areas be funded for research. Those with a "T" are designated top priority areas.

A. Fundamental Understanding of Processes and Concepts

Number of "top priority" votes in parentheses*

1. Structure of Lignite and Bituminous Coal. Since liquefaction represents an attack upon the basic structure of the coal, it would be helpful to understand what must be attacked. Such studies require the development of new and sophisticated chemical methods and techniques. (9)T

   Relationships between structures and liquefaction, certain "chemical sensitive" structures, and some sort of index or classification of coal properties might be included.

2. Mechamisms of Coal Liquefaction Operations. It is strongly believed that one will only develop the optimum coal liquefaction processes after the (18)T

fundamentals of the liquefaction operations are understood.

a. Mechaniam of Hydrogenation. As an example, in coal hydrogenation a major and necessary operation is to establish intimate contact between the coal and the catalyst. Hydrogen at elevated pressures must then be brought into contact with the coal-catalyst system. If one understands the mechanism of the hydrogen-catalyst interaction, one may know how to promote these processes. One may also be led to catalysts which are less expensive or perhpas more active for the reaction concerned. Other facets of the mechanism should be studied also, such as termination of free radicals, reductive alkylations and development of a polymer to serve as a "model" coal.

b. Mechanism of Pryolysis. The quantity of liquids produced in a pyrolysis reaction is very dependent upon the length of time at elevated temperature in the reactor; the shorter the residence time the greater the liquid yield if other conditions are right. The hydrogen already present in the coal, particularly in the hydro-aromatic structure, plays an essential (14)T role in the production of pryolytic liquids. If one can understand the fundamentals of the coal pyrolysis reaction it may be possible to increase the liquid yield by pryolysis, which basically is a rather simple system for production of liquids from coal.

c. Mechanism of Dissolution. An understanding of the processes involved in solvent extraction of coal might lead to a more (16)T truly liquid product of much lower molecular weight than is usually obtained. What new unique conditions or solvent mixtures will give higher yields at lower temperatures or change the chemical nature of the extracts?

d. Investigate the physical transport phenomena. (6)

3. It has been observed that the interaction of coal with a carbon monoxide-steam mixture is often more rapid than the interaction of coal with hydrogen even in the presence of an appropriate catalyst. There is need to understand the fundamentals of the carbon monoxide-steam interaction with coal. Such understanding may possibly lead to a new technology which may be economically very attractive. (16)T

4. Lewis acids, especially zinc chloride, are considered by some to be some of the most promising catalysts for the conversion of coal to primary liquids. However, the actual role of zinc chloride in coal hydrogenation is very little understood. Understanding the actual function of zinc chloride may lead to cheaper catalysis or to catalysts which are more readily recovered. (16)T

5. As one attempts to maximize the liquid yield in coal conversion operations, short residence times help to give maximum liquid yields. The rates of mass and heat transfer to the coal particles then become of great importance. Fundamental studies of heat trasnfer to finely divided coal, as well as within the coal particles, seems to be very important. The characterization of physical structures and their changes during short residence time reactions should be investigated. (12)T

6. In a practical sense, the liquefaction of bituminous coal occurs after coal has entered the plastic stage. Investigations of the plastic phenomenon of coal as controlled by the processing (8)

environment seems to be quite important.

7. Studies need to be conducted relative to the fundamentals of solids-gas contacting. (5)

B. Improvement in Process Technology

8. Two or three decades ago the Fischer-Tropsch synthesis was set aside as economically unattractive in this country. There is now a need to re-examine the economics of the Fischer-Tropsch synthesis in light of the catalytic technology which has developed during the last two or three decades, in addition to any new technologies. (16)T

9. Coal liquefaction operations generally will yield some solid product, namely char. There does not exist any very satisfactory technique for the continuous removal of the char from a high pressure reactor. Greatly improved processes need to be developed. (11)T

10. Since short residence time in the reactor generally favors production of liquids and since heat trasnfer may be a controlling factor relative to short residence times, one may wish to feed the coal to the reactor in a very finely divided form in order to enhance the heating operation. There is need for the development of new techniques for feeding very finely ground coal into high pressure, high temperature areas. (5)

11. Catalyst-coal contacting for efficient and rapid reactions in coal liquefaction seems to be very important. Some coal liquefaction systems currently under development inpregnate the catalyst on the coal prior to introduction into the reactor. There are obvious disadvantages to this. Some systems use adaptations of a fluidized catalyst bed while others use a fixed catalyst bed. Perhaps better methods than any now known for establishing rapid and intimate contact between (9)T

catalyst and coal can be found.

12. Extensive research could profitably be conducted into the development of new coal liquefaction catalysts for the primary conversion of coal to liquids. Such catalyst development seems to be in its infancy. (16)T
13. While zinc chloride remains a promising coal hydrogenation catalyst, improved techniques for its recovery need to be developed. (9)T
14. A great need exists for the development of sulphur resistant catalysts for use in upgrading the coal liquids to a refinery feed stream. (11)T
15. There is need to develop improved techniques for the removal of particulate matter from coal-derived liquids. Current filtration techniques leave something to be desired. (20)T
16. There is need to develop sulphur resistant, high temperature, stong metal alloys for use in coal liquefaction processes. (9)T
17. There is a need for the development of innovative chemical and mechanical approaches to coal liquefaction. For example: in situ liquefaction, laser applications, sonic techniques, photochemistry, etc. (22)T
18. Inasmuch as a fundamental part of the conversion of coal to liquids is the addition of hydrogen to the coal structure, most of the liquefaction operations will involve the use of molecular hydrogen. There is a real need for innovative approaches to the production of hydrogen with a principal objective of reducing the cost of hydrogen. Considerations must be given to the high priority uses of hydrogen such as in coal liquefaction, as compared to fuel use of hydrogen in direct combustion. (17)T

19. Coal-derived liquids are unstable during storage, undergoing very significant color changes and viscosity increases. Techniques must be developed for prevention of polymerization reactions in these liquids. (3)

20. Investigations should be conducted into the toxicological properties of coal-derived liquids and their interactions with people and the environment. (19)T

21. System studies which detetmine the comparative economics, social and environmental impact and desirable plant locations should be carried out to assist in planning and optimization of various liquefaction process alternatives. (9)T

22. Refining, separation, testing and analyses of coal liquefaction products for fuels, refinery feeds and chemicals should be investigated and developed. (16)T

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*Voting Priotity Details

At most we had 24 people attending the liquefaction session.

At the end of this session, a vote was taken to distinguish top priority items. Many people indicated their lack of knowledge and, therefore, their inability to vote intelligently.

A vote of 9 or more was considered to move a topic into a top priority voting. Note that a vote of 9 could be a rather high percentage of those feeling qualified to vote on a topic. Generally only 16 voted except in a few very popular areas.

The resultant votes are shown as follows:

Topic	Vote	Priority
1	9	T
2a	18	T
2b	14	T
2c	16	T
2d	6	
3	16	T

Topic	Vote	Priority
4	16	T
5	12	T
6	8	
7	5	
8	16	T
9	11	T
10	5	
11	9	
12	16	T
13	9	T
14	11	T
15	20	T
16	9	T
17	22	T
18	17	T
19	3	
20	19	T
21	9	T
22	16	T

Summary

1. Top vote was item 17 with 22 votes. Note that this is a rather general topic which many people could vote for.
2. The lowest vote for any item was 3.
3. Average vote was 12.5 for the 25 individual topics.

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