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RECOMMENDED RESEARCH AREAS FOR CATALYSIS OF COAL GASIFICATION

The use of catalysts to enhance the gasification of carbonaceous solids has received considerable experimental attention during the last fifty years. The great majority of investigations, however, have been conducted at low pressure, using relatively low reactivity solids without volatile matter, and there has been little work done up to the present time related to catalysis of gasification of actual coals. Due to the obvious potential improvements that the use of catalysts may bring about in the performance of processes currently being developed to convert coal to gas, and due to the urgent need to develop such processes, an intensified broad program to study coal gasification catalysis is justified.

This report considers potentially useful areas of research for coal gasification catalysis as it relates to one of the several current needs for gasifying coal; namely, the conversion of coal to a high-methane content gas. In this consideration, it is helpful to briefly review certain aspects of currently conceived processes being developed to convert coal to a high-methane content gas, which generally would favor improved performance in terms of increasing thermal efficiency and decreasing gas costs.

- "Maximum Formation of Methane Directly in the Gasification Step"

  It is generally favorable to operate the gasification process under conditions which favor the exothermic formation of methane, rather than the endothermic formation of carbon oxides, since this tends to minimize the fuel requirements of the process. Any oxygen or electrical energy used as fuel requires additional coal feed and therefore increases thermal efficiency. Exothermic heat of methanation is not available at a sufficiently high temperature to be very useful in any system.

- "Minimum Reactor Sizes"

  Rates of coal gasification reactions usually increase significantly with increasing temperature. Thus a simple approach to minimizing reactor sizes (thereby decreasing capital costs) is to operate at high temperature. This approach, however, has the disadvantage of resulting in decreased methane production during direct gasification, and, therefore, increased fuel requirements.

- "Technical Operability"

  Most coal gasification processes currently being developed for the production of methane are designed for relatively high pressure operation, and involve massive gas and solids transport operations. The technical feasibility of controlled handling of such large amounts of materials at relatively severe conditions is, however, one of the main practical concerns in development of these processes, due to the lack of adequate available technical information. Although this suggests that it would be desirable to conduct a gasification process in a single stage reactor to minimize gas and solids handling, with such an approach it is difficult to simultaneously achieve the desired objectives of maximum methane production, favored by low temperatures, and minimum reactor sizes, favored by high temperatures. Most process concepts tend to compromise these objectives by consisting of a series of reactor sections through which gas and solids flow in a general countercurrent pattern, with reaction temperatures increasing in the direction of solids flow.

- "Minimum Coal Pretreatment"

  Some of the processes currently being developed for gasification of coal require pretreatment of caking coals with oxygen to inhibit agglomeration during the initial stages of gasification. One of the main disadvantages of such a pretreatment step, particularly when it is conducted with air separately from the gasification system itself, is that it is usually necessary to operate at about 700°-800°F in order to achieve the desired reduction in free-swelling index in a reasonable length of time. This condition, however, results in a significant loss of volatile matter and as much as 10 percent of the feed carbon of the process, which cannot be efficiently utilized. The net effect is a significant loss in thermal efficiency.

In view of the above considerations, several specific objectives for the use of catalysts in coal gasification systems can be summarized:

Improvement of Methane (or light oil) Yield During Direct Gasification

This objective applies in part to gasification during initial stages of coal gasification in the presence of gases containing hydrogen, when devolatilization occurs concurrent with significant hydrocarbon formation during a short-lived, high reactivity period, prior to the formation of relatively low reactivity char. For processes concerned solely with the production of a high methane-content gas, it would be desirable to utilize catalysts to increase the yield of methane during this step as much as possible in order to decrease subsequent char conversion requirements, and increase the thermal efficiency of the process. There is also some interest in maximizing light oil yields during initial gasification stages, which has been demonstrated to be significantly affected by catalysts.[3]

It is also desirable to preferentially increase the rates of methane formation relative to carbon oxide formation during gasification of the residual char resulting from the initial gasification step, with gases containing both steam and hydrogen.

Improvement of Kinetics of Gasification Reactions

For any gasification system, improved kinetics can result in decreased reactor sizes, or alternatively, lower operating temperatures and/or pressures. It should be kept in mind, however, that a catalyst which effectively increases gasification rates, may also effectively alter the product gas yields with respect to carbon oxide and methane formation. It could be undesirable, for example, to increase reaction rates but also increase the ratio of carbon oxide to methane formation. It is of interest to point out, in this respect, that whereas lignites tend to be significantly more reactive than bituminous coals for gasification in steam-hydrogen mixtures, which results in reasonable gasification rates of lignite chars at relatively low temperatures (e.g., 1500°F), with many lignites the ratio of carbon oxide formation to methane formation increases at such a lower temperature, contrary to expected behavior from thermodynamic considerations. This behavior does not occur with bituminous coals, although uncatalyzed gasification of bituminous coal chars at temperatures as low as 1500°F is not very feasible.

Improvement of Oxygen Pretreatment Step for Caking Coals

Pretreatment of caking coals with oxygen or air should be conducted at as low a temperature as possible consistent with acceptable kinetics, to minimize the effective loss of carbon and volatile matter. The use of a catalyst is therefore indicated to permit pretreatment at lower temperatures than have been found necessary for uncatalyzed pretreatment.

Although the recommendations of detailed research programs to study coal gasification catalysis with respect to the objectives discussed above is a very imposing task, there do appear to be certain features that would be desirable in the conduct of a variety of programs.

A. Selection of Catalyst Material (and support material where applicable).

Initial selection of catalyst materials which might be potentially effective in the catalysis of specific coal gasification reactions would be aided by information obtained in previous experimental studies reported in the literature. As indicated previously, however, the value of this information may be somewhat limited since the vast majority of work conducted to study catalysis of gasification of carbonaceous solids has been done at low pressure, and with materials which do not contain volatile matter.

B. Method of Addition of Catalyst to Coal Mass

There are at least three methods of incorporating a catalyst material into the coal mass:

1) Simple Mixing - The catalyst material in the form of powder, crystal, or supported on some other material, may be physically mixed with the coal particles. With this method physical factors related to the nature of mixing of the catalyst and coal particles during the actual gasification step would be of prime importance in affecting overall catalytic performance. For example, if gasification was conducted in a dilute solid phase system, such as an entrained or free-fall reactor, the catalyst would not be likely to significantly affect primary gasification reactions, but could be effective in promoting desirable secondary reactions. For a fixed or moving bed system, the catalyst is more likely to affect direct gasification reactions, in addition to affecting secondary reactions. Behavior in a fluid bed would be intermediate to that in a fixed bed or dilute solids phase system. With any of these contacting systems considerable care would be required to avoid non-uniform gas-solid contacting, or catalyst and coal mixing. One of the major advantages of this method of coal/catalyst mixing, however, is that ultimate recovery of the catalyst is facilitated. One of the major disadvantages of the method is the lack of intimate contact between coal and catalyst which tends to decrease possible effects on primary gasification reactions.

2) Deposition on Internal Coal Surfaces - One method of obtaining an intimate contact between coal and catalyst is to precipitate the catalyst onto the internal pore surfaces of the coal by evaporation of a solution containing the catalyst substance. This procedure would even be suitable for use of catalyst combinations where it is found that different catalysts favor different reaction steps, i. e., pretreatment, initial gasification, and gasification of residual, non-volatile coal char. With this method very intimate contacting between catalyst and coal is possible, which would tend to favor catalyst effects on direct coal gasification reactions. Study of the effects of the actual method of precipitation would be required, however, since these methods would affect the distribution of catalyst deposition within the coal pore structure, and also affect the physical condition of the deposited catalyst (e. g., crystal size).

A possible disadvantage of this method is in recovery of the catalyst substance. In any experimental study using this method, therefore, it would be necessary to determine the physical nature of the catalyst during the course of gasification, with a view to the practicability of ultimately recovering the catalyst substance, assuming, of course, that this is an economic necessity.

3) Chemical Combination of Catalyst Substance with Organic Coal Structure - At the Institute of Gas Technology we have recently been studying catalytic effects of exchangeable cations (sodium and calcium) on the reactivity of some lignites for gasification in hydrogen at 1700°F and 35 atmospheres. Samples were prepared by demineralizing the raw lignite with acid, and then treating the demineralized coal with a solution containing the desired cation (e.g., sodium acetate). A sample was then washed and dried prior to gasification. Apparently this procedure is only suitable for low rank coals due to the requirement for carboxy groups in the raw coal. The postulated reaction for cation exchange is:

$$\text{-COOH} + \text{Na}^+ \rightarrow \text{-COONa} + \text{H}^+$$

No exchange occurred with a subbituminous A coal or with coals of higher rank, apparently due to a lack of carboxyl groups in these materials. With the lignites, however, as much as 5 percent by weight of sodium could be added to the coals, and as high as a 5 fold increase in reactivity was obtained when compared to the reactivity of the demineralized coal. With calcium the catalytic effect is only about one-third as great as that obtained with sodium, at corresponding mass concentrations, and for hydrogen gasification. This relative relationship, however, is only applicable for the gasification conditions employed. Researchers at the Consolidation Coal Company apparently used a similar procedure to catalyze gasification of lignites at 1500°F with steam/hydrogen mixtures, and found that calcium was much more effective than sodium in increasing gasification rates (personal communication). It is, therefore, obvious that in any study to determine catalytic effects, a range of operating conditions pertinent to commercial application would be required. The procedure described for adding catalyst to the coal mass has the same qualitative advantages and disadvantages that apply to precipitated catalysts.

C. Experimental Determination of Gasification Rates (With or Without Catalyst).

A variety of experimental systems have been used to study catalytic effects for gasification of various carbonaceous solids. As in any kinetic study of a gas-solids reaction, however, the best experimental systems are those in which results do not reflect effects due to the particular nature of gas-solids contacting, but rather permit determination of reaction kinetics under known local conditions, e.g., gas composition, pressure, temperature, and solids composition. In this sense, systems in which measurements are made only of overall reactions which result from interactions occurring within a range of gas and solids compositions, and possibly temperatures, are difficult to interpret in terms of fundamental effects. Many of the investigations reported in the literature concerning catalysis of gasification reactions of carbonaceous solids have been conducted with such integral systems, and results of these investigations are primarily useful in terms of qualitative screening of various catalysts.

One of several experimental devices which appears to be particularly suitable for study of gasification kinetics of catalyzed coals, is the thermobalance. The thermobalance is an apparatus which is capable of continuously measuring the weight of a sample of coal or coal char in a desired gaseous environment at constant pressure. Temperature may either be varied or kept constant. Such an apparatus has been successfully used at the Institute of Gas Technology during the last several years to study fundamental gasification kinetics of a variety of coal chars.[4,5] More recently, this type of experimental system has also been employed by investigators at the Case Western Reserve University to study the kinetics of catalyzed coal char gasification at elevated pressure and temperature.[1]

The thermobalance is suitable primarily for study of a single step reaction in which gravimetric changes can be related to reaction stoichiometry. In this sense, it is suitable for study of gasification kinetics of coal char with hydrogen or hydrogen-methane mixtures, carbon dioxide or carbon dioxide-carbon monoxide mixtures, and pure steam. With gases containing both steam and hydrogen at elevated pressures, however, only total gasification kinetics can be simply measured, and to obtain information on the individual formation rates of methane and carbon oxides, other analytical techniques are required. This is because the thermobalance is most effectively utilized when very small gas conversion occurs, since this permits definition of the gas composition existing for gasification. Thus, in order to use the thermobalance to study gasification kinetics with gases containing steam and hydrogen, some techniques to measure essentially differential changes in gas composition would have to be employed.

An alternate experimental system which might be suitable, although not necessarily ideal, for study of the gasification kinetics of coal char in steam hydrogen mixtures, is a "back-mixed" reactor. Such a reactor, currently being used at the Institute of Gas Technology to study kinetics of catalyzed water gas shift, and methanation reactions, consists of a heated isothermal chamber in which feed gases are essentially "perfectly" mixed by a series of rotating impellers which themselves contain solids particles in a wire screen enclosure. With this system feed gas is continuously introduced to the reaction chamber and product gases are continuously withdrawn. The product gas composition, which is the same as the gas composition within the reaction chamber, is continuously measured using infra-red and gas chromatographic equipment, and periodic product gas samples are taken for mass-spectrographic analysis. This experimental system is particularly suitable for gas-solid catalytic studies where negligible changes in catalytic reactivity occur, since steady-state behavior then results, and reaction rates can be determined from the feed and exit flow rates of individual gaseous species, which correspond to the known reaction conditions in the reactor. For catalyzed coal-char gasification, however, product gas compositions will vary with coal char conversion. Although this variation requires a more complex interpretation of the experimental data, nevertheless, reaction rates can be evaluated at known gas compositions, pressures, temperatures, and levels of carbon conversion.

Neither the thermobalance nor the back-mixed reactor is particularly suitable for detailed study of gasification kinetics during the initial stages of coal gasification involving devolatilization and hydrocarbon formation, due to the relatively extended periods required with these systems to initially heat coal samples up to reaction temperature. During such heat-up, when actual particle temperatures are effectively undefined, reactions of interest essentially go to completion. A more suitable system for study of this gasification stage is a dilute-phase transport reactor. With such a system relatively rapid heat-up rates (10^3-10^4°C/sec), can be obtained by using small particles, and solids and gas residence times at temperature can be controlled to range from less than a second to several seconds or greater if desired. Although, with this type of system, reactions occur under integral conditions, reactions during the initial stages of coal gasification must occur under integral conditions with essentially any reactor system, due to the rapidity of individual reaction steps. If lower heat up rates, up to 10^2°C/sec are of interest, a dilute-solids phase entrained reactor can be used under controlled heat-up conditions. Such a system is currently being used at the Institute of Gas Technology to study reaction kinetics of low rank coals during the initial stages of coal heat-up. This experimental system consists of a 200 foot long, 1/16 inch I. D. helical coiled reactor, in which the reactor tube itself serves as a resistance heater.

The reactor tube, although continuous, is divided into nine separate zones (each zone is 22.2 feet in length) and the electrical input to each zone is independently controlled. This permits establishment of essentially any desired temperature profile along the length of the tube. With this system, the use of sufficiently high gas velocities and small coal particle sizes, results in plug flow of gas and solids, with negligible solids slippage. This is a particularly desirable feature since it permits the design of an experimental series of tests which defines rates of gasification of individual coal components, and rates of reaction of individual gas phase species, along the length of the tube for a given combination of reaction conditions. Suppose, for example, that an initial test is conducted at 35 atmospheres with a feed gas flow rate of 0.7 g-mole/min, a gas/solids feed ratio of 0.2 g-mole/g, and the temperature profile along the length of the tube is adjusted to provide a constant heat-up rate of 100°C/sec for gas and solids along the length of the tube. The initial temperature at the entrance of the tube is 300°C, and the final temperature at the exit of the tube is 800°C. Data from this single test define the total conversion of solid components in the feed coal, as well as the net formation rate of individual gaseous and liquid products. To obtain similar information at points within the reactor coil for the conditions employed in this single test, it is possible to conduct additional tests maintaining in each test the same gas/solids feed ratio as was employed in the initial test, but using a different final temperature in each test between 300° and 800°C, and adjusting the temperature profile and feed gas flow rate in each test to maintain the same heat up rate as was employed in the initial test. Thus, with such a series of tests, gas and solids conversions can be determined as function of temperature, at a constant heat-up rate, and feed gas/solids ratio.

Data have been obtained at IGT thus far using a Montana lignite as the feed solids for gasification in hydrogen at 35 atmospheres, for constant heat-up rates of 50 to 100°C/sec. These data (unpublished) have been used to formulate initial kinetic models to define rates of evolution of individual coal components, and formation rates of individual condensible and non-condensible gas phase species, during the initial period of devolatilization and hydrocarbon formation. This particular type of system would, therefore, appear to be suitable for study of catalysis of coal gasification reactions during this phase of reaction, subject to the limitations of controlled heat-up rates discussed above. An additional possible limitation of this experimental system, not yet evaluated, is that use of only non-agglomerating coals may be possible due to the small diameter of the reaction coil.

RECOMMENDED RESEARCH PROGRAMS FOR COAL GASIFICATION CATALYSIS

1) Gasification of Coal During Devolatilization Phase

The objective of this program is to determine the effects of different catalysts and conditions of catalyst-coal combination on gasification kinetics during the initial stages of coal gasification. Particular emphasis in characterizing the performance of a specific catalyst should be placed on methane or light oil formation. Actual gasification reactions should be conducted using a dilute solids phase entrained reactor, possibly of a type similar to that currently being employed at the Institute of Gas Technology for use with non-agglomerating coals. For agglomerating coals, a larger diameter reactor would probably be required.

It would generally be desirable to study a range of catalysts, catalyst concentrations, coal types, heat-up rates, temperatures, pressures, and gas compositions. It is recommended that for this stage of reaction, precipitated catalysts be used to enhance the potential catalytic effects on direct gasification reactions. The significant catalytic effects that can occur with this method of catalyst incorporation has already been demonstrated in a previous limited study using a dilute phase entrained reactor system.[3] It will be necessary, however, to include methods of precipitation as a variable in the proposed study. Possible catalysts which have previously been shown to have significant effects on reaction kinetics during the initial stages of coal gasification are ones precipitated from ammonium molybdate[6], and stannous chloride solution.[3] Other possible catalysts may be suggested from the literature, particularly if other catalysts are desirable for subsequent stages of gasification.

In this study the form and distribution of the catalyst should be investigated as a function of precipitation conditions and reaction conditions, using microscopic techniques. It would also be useful to obtain pore volume and surface area distributions to aid in interpreting the effects of different catalysts. Catalyst stability should be evaluated, particularly for catalysts which appear desirable in terms of general reactivity criteria. This should be done by simulating feed gases which contain some of the minor species present in typical offgases from gasification processes. Such species include hydrogen sulfide, phenols, cyanogen, and ammonia. Recovery of apparently suitable catalysts should also be investigated. To accomplish this it would be desirable to simulate further conversion of the catalyzed coal char resulting from the initial gasification step. This could be done using whatever type of reactor system is considered as a final step to gasify the coal char in the process concept of interest. One system commonly considered in several of the programs currently being conducted for development of commercial coal gasification systems, is a steam-oxygen fluid bed gasifier. Lacking other incentives, such a system is therefore recommended to reduce the carbon content of the coal char down to about 5-10 percent of the carbon in the raw coal. Studies of the residues from this treatment should then be made to evaluate potential methods for recovering the catalyst from the reaction mass, and reactivating it, if necessary, for subsequent addition to raw coal.

Although the experimental program outlined above is quite extensive, it could be broken down into a number of subprograms conducted by several cooperating research groups. Taken as a whole, however, with a fairly intensive effort the program should take at least two years after construction of necessary equipment. Assuming that about 10 coals of varying rank will be used, 10 catalysts will be generally screened, and about 2-3 catalysts will be extensively investigated, I estimate, very roughly, that annual operating costs will be about $150,000/year. Thus, the two year operating costs will be about $300,000. If a reactor system must also be built, then an additional 6 months to a year might be necessary, at an additional cost of about $100,000.

II) Gasification of Coal-Char With Hydrogen and Hydrogen-Methane Mixtures Using Precipitated and Chemically Combined Catalysts.

The objective of this program is to study the effects of different catalysts and conditions of catalyst/coal combinations, on gasification kinetics of devolatilized coal char in hydrogen and hydrogen-methane mixtures. It is recommended that this study be conducted using a thermobalance apparatus for determination of gasification kinetics, and that the study be limited to use of precipitated catalysts, and catalysts that are chemically combined with the organic coal structure (for suitable coals). Physical mixtures of coal char and catalyst are not recommended when using the thermobalance due to the difficulty in defining the nature of gas-solids contacting pertinent to secondary reactions.

Variables to be studied include catalyst type, catalyst concentration, conditions of catalyst addition to the coal-char, gasification temperature, pressure, gas composition, and coal type. For particularly suitable catalysts, additional studies should be made to determine effects of hydrogen sulfide and ammonia concentrations on catalyst stability. In addition, with such catalysts, studies should also be made to evaluate recoverability and reactivation of the catalyst material. For this purpose, the char resulting from gasification in hydrogen should be further gasified in a steam-oxygen fluid bed gasifier to a total carbon conversion of about 90-95 percent relative to the carbon in the raw coal.

As in the previous program (I), catalyst distribution and form should be determined during the course of gasification using microscopic techniques. Porosity and surface area distributions would also be helpful. Alkali and nickel type catalysts have been found to promote the gasification of coal char with hydrogen at elevated pressures.[1,2,7]

The recommended experimental program should take about two years after construction of necessary equipment, at an annual operating cost of $100,000. If the reactor system must be constructed, then an additional period of about 4-6 months would be required, at an additional operating cost of about $50,000.

With this program about 10 coals of varying rank could be used, and about 10 catalysts screened. About 2-3 of the more effective catalysts would be more thoroughly studied.

III) Gasification of Coal-Char with Steam/Hydrogen Mixtures Using Precipitated and Chemically Combined Catalysts

The objective of this program is to study the effects of different catalysts and conditions of catalyst/coal combinations, on gasification kinetics of devolatilized coal char in steam/hydrogen mixtures. The apparatus recommended for determination of gasification kinetics is a back mixed reactor of the type described previously. It is further recommended that the study be limited to use of precipitated catalysts, and catalysts which are chemically combined with the organic coal structure. The general approach in this investigation should be the same as that described above (Program II), except that consideration of both overal gasification kinetics, and product gas distributions must be made in evaluating catalyst performance.

The estimated total costs and recommended program period are also the same as those described for Program II.

IV) Catalysis of Secondary Reactions in Coal Gasification Systems

Although physical mixtures of coals or coal-chars and catalysts have been used in previous experimental studies, it is difficult to interpret the results of these studies in terms of separating chemical catalytic effects from effects due to the nature of gas/solids contacting, and also to distinguish between catalytic effects on primary gasification reactions, and catalytic effects on secondary reactions. It is, therefore, recommended to study catalytic effects relevant to secondary reactions by simulating gas phase conditions pertinent to gasification systems, but in the absence of coal char. It is further recommended that this study be conducted using a back-mixed reactor which is an ideal application for a strictly catalytic gas/solids reaction system. Variables to be studied include catalyst type, catalyst support, catalyst concentration, temperature, pressure, and gas composition.

As in previously recommended studies, more active catalysts should be further investigated to determine stability, particularly in the presence of hydrogen sulfide and ammonia, and methods of catalyst reactivation should be evaluated.

The recommended test program should take about one year at an operating cost of about $75,000 to generally screen about 10 catalysts, and study more extensively 2-3 of the potentially best catalysts. Construction of the experimental apparatus, if necessary, would take an additional 4-6 months at a cost of about $50,000.

V) Catalysis of Oxygen Pretreatment of Agglomerating Coals

The objective of this program is to study the effects of different catalyst types, and conditions of catalyst combinations with the coal, with respect to affecting acceptable reduction of the agglomerating tendencies of bituminous coals, with a minimum loss of volatile matter and carbon during oxygen pretreatment. This requirement would generally correspond to achievement of effective pretreatment at lower temperatures than are commonly used in the absence of a catalyst.

It is recommended that this study be conducted using an integral fluid bed system, since the use of oxygen would tend to preclude the use of a differential reaction system. Feed gases would generally consist of a mixture of steam, oxygen, and nitrogen. The catalyst should be precipitated, and variables to be studied include catalyst type, catalyst concentration, conditions of catalyst addition to the coal, temperature, pressure, feed gas composition, reaction time and space velocity. For simplicity the study should be conducted using a fixed charge of feed coal, with a continuous gas flow through the fluid bed. More effective catalysts should be more extensively investigated to determine stability and recoverability, using procedures described in the research programs recommended above.

The recommended test program should take about one year at an operating cost of about $75,000 to screen about 10 catalysts, and study more thoroughly 2-3 of the potentially best catalysts. Construction of the experimental apparatus, if necessary, would take an additional 3-5 months at a cost of about $50,000.

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References Cited

1. Gardner, N., Samuels, E., and Wilks, K., "Catalyzed Hydrogasification of Coal Chars," Paper presented at the 165th National Meeting of the American Chemical Society, Division of Fuel Chemistry, Dallas, April 8-12, 1973.

2. Haynes, W. P., Gasior, S. J., and Forney, A. J., "Catalysis of Coal Gasification at Elevated Pressure," Paper presented at the 165th National Meeting of the American Chemical Society, Division of Fuel Chemistry, Dallas, April 8-12, 1973.

3. Hill, E. R., Anderson, L. L., Wiser, W. H., Qader, S. A., Wood, R. E., and Bodily, D. M., "Conversion of Coals into Liquids," U.S. Office of Coal Research R& D Report No. 18, Final Report, Washington, D.C.: U.S. Government Printing Office, 1970.

4. Pyrcioch, E. J., Feldkirchner, H. L., Tsaros, C. L., Johnson, J. L., Bair, W. G., Lee, B. S., Schora, F. C., Huebler, J. and Linden, H. R., "Production of Pipeline Gas by Hydrogasification of Coal," IGT Res. Bull. No. 39. Chicago, November 1972.

5. Johnson, J. L., "Kinetics of Bituminous Coal Char Gasification with Gases Containing Steam and Hydrogen," Paper presented at the 165th National Meeting of the American Chemical Society, Division of Fuel Chemistry, Dallas, April 8-12, 1973.

6. Schroeder, W. C., "Hydrogenation of Coal," U.S. Patent 3,030,297, April 1962.

7. Willson, W. E., Sealock, L. G., Hoodmaker, F. C., Hoffman, R. W., Cox, J. L., and Stinson, D. L., "Alkali Carbonate and Nickel Catalysis of Coal Steam Gasification," Paper presented at the 165th National Meeting of the American Chemical Society, Division of Fuel Chemistry, Dallas, April 8-12, 1973.