

[54] **METHOD OF CONVERTING COAL TO PIPELINE QUALITY GAS**
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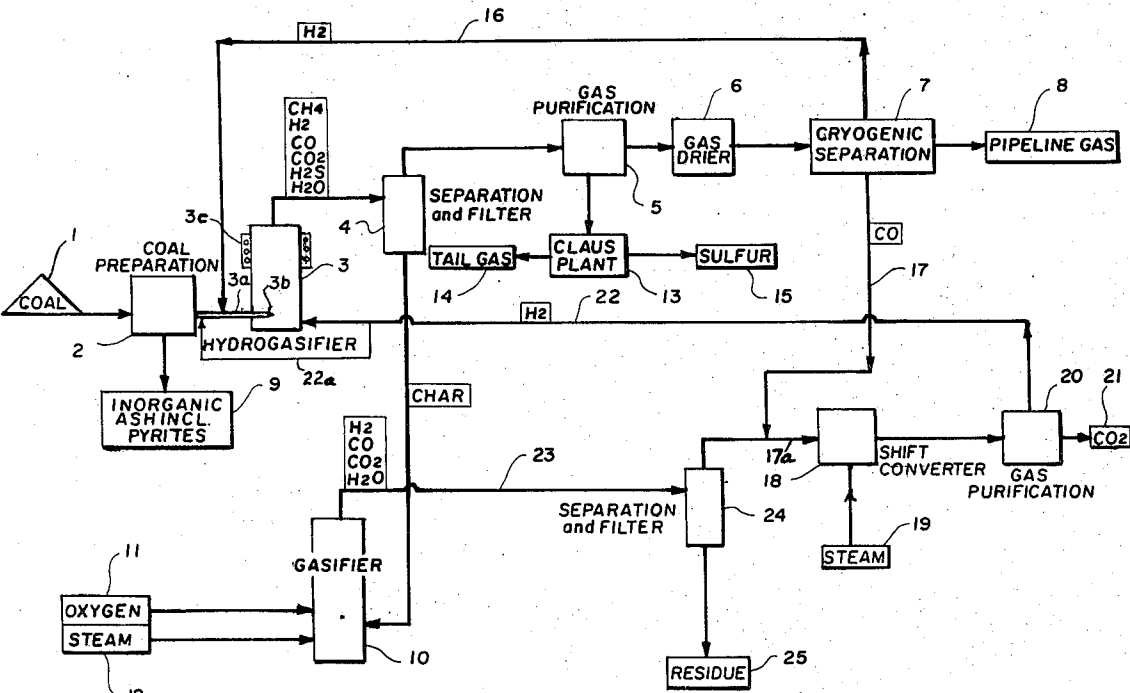
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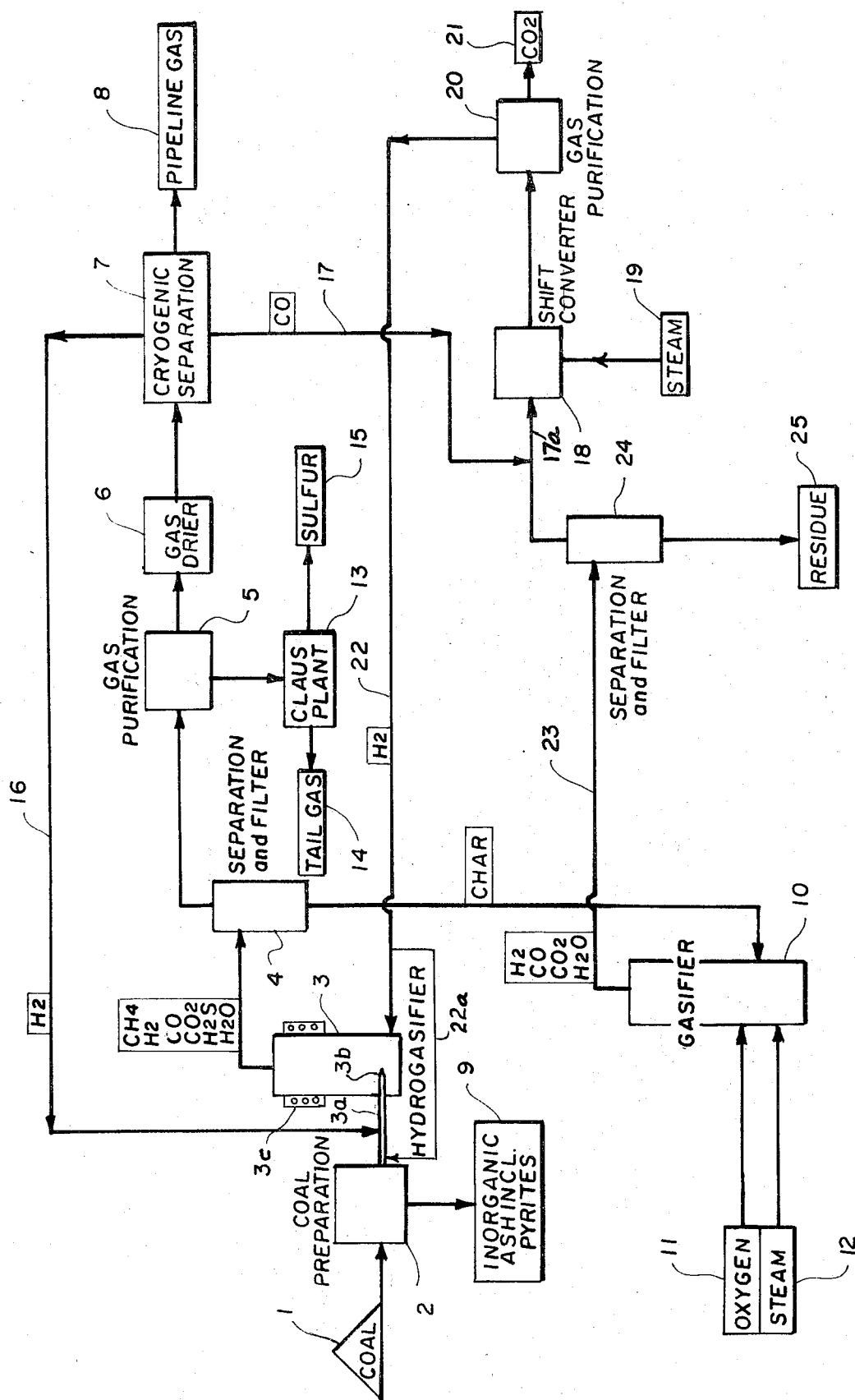
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[57] **ABSTRACT**
The method of converting coal to pipeline quality gas comprising introducing coal particles of a size of about 4 microns into a reactor, rapidly heating the interior, such as by an external heat source to cause thermal comminution and devolatilization, the products of fractionation being immediately reacted with hydrogen. A portion or all of the excess submicron coal particles are gasified in a separate gasifier to produce a synthesis gas.

14 Claims, 1 Drawing Figure





METHOD OF CONVERTING COAL TO PIPELINE QUALITY GAS

This invention relates to a method of conversion of coal to pipeline quality gas.

The shortage of domestically produced natural gas in the United States had made it economical to supplement traditional gas sources with relatively higher priced gas, such as imported LNG and substitute gas as produced from liquid hydrocarbons. In order to help meet the increasing demands for a clean burning gaseous fuel and to minimize our dependence on foreign countries for basic energy, it is desirable to develop an economical process for converting coal, which is in abundance in the United States, into pipeline quality gas.

The process proposed in accordance with the present invention is based on the direct methanation of ultrafine coal powder by reaction with relatively high purity hydrogen at high temperature and moderate pressure. The process is reliant on two primary phenomena for the high methane yield.

An outstanding disadvantage of traditional methods of coal comminution is that they generally involve the application of forces which subject the processed material to compressive stresses which result in brittle failure. The quantity of energy required to produce the fracture is proportional to the square of the material's strength. Further, it is noted that considerable experimental work has shown the tensile strength of coal to be one-thirtieth to one-seventieth of the compressive strength. Theoretically then it is apparent that it would be possible to produce breakage under tension with approximately one one-thousandth the energy input required to break particles of the same size under compression. To date, research has been unsuccessful in achieving an efficient or economical means of comminuting materials by means of tensile failure.

Because of the geology and the nature of its formation, coal is a very heterogeneous material which, within its structure, exhibits a microporous and capillary structure. Electron microscope studies of the ultrafine structure of coal have revealed structures in the general form of curved cylinders, round and polygonal platelets and spheroids. There are two general ranges of these forms, one in the order of hundreds of angstroms, the other, less than 100 angstroms. Research findings with the electron microscope, coupled with experimental work relative to internal surface area measurement, indicate that pores can range in size down to less than a few tenths of an A and that interconnecting channels between pores would probably be approximately 20 percent of the pore size. The shape of the pores in the coal tend to be flat rather than cylindrical or spherical. The internal capillary structure of coal is an important feature to be considered in conjunction with coal's low tensile strength when considering comminution. When coal particles are heated rapidly, almost explosive devolatilization occurs. There is evidence from work performed in Germany in the 1930's that under proper conditions, ultrafine coal particles can be carbonized to produce gaseous hydrocarbons and submicron (approximately one one-hundredth micron) char. The thermal comminution is very dependent on the size of the coal particles feeding the reactor. The first of the two phenomena on which the present invention relies is that with ultrafine coal feed (4mi-

crons and smaller), as the coal is heated rapidly, volatile matter is released exothermically with instantaneous pressure build up in the porous structure causing explosive comminution of the solid. The combination of the shape of the pores (flat), the low tensile strength, the thin wall of solid material, narrow gas escape channels and the exothermic devolatilization resulting in pressure build up contribute to the explosive failure. The design parameters for the carbonization reactor zone, the operating temperature and pressure in the reactor, the compositions of the heat source gas and/or transport gas, and the feed particle size and temperature all effect the composition and flow rates of the products as well as the degree of comminution achieved.

The second phenomenon on which the present invention relies is that rapid heating of pulverized coal in the presence of hydrogen results in the formation of methane in quantities which are in excess of those anticipated from the coal devolatilization and equilibrium in the reaction between carbon and hydrogen.

The first step is the instantaneous devolatilization of coal by a process which is activated by hydrogen but whose rate is not affected by hydrogen. As the volatile material is driven from the coal surface, the remaining char is unstable and highly reactive. The sites which give rise to the volatile evolution act as active sites with exposed carbon atoms that are susceptible to reaction with hydrogen. The second step in the mechanism involves a rapid stabilization reaction of the active sites either with hydrogen to form methane or within the particle itself by cross-linking polymerization to form an inactive char. The third step involves the slow reaction of hydrogen with the inactive char.

As would be anticipated based on the three-step mechanism for coal methanation, it has been proved experimentally that the extent of gasification and the methanation of the carbon increases with decrease in size of the coal particles feeding the reactor. As the particle size decreases, the surface area of active sites increases, thereby increasing the opportunity for the instantaneous reaction with hydrogen. The smallest particle size studied was approximately 63 microns.

It is noted that the three-step mechanism for methane formation with a highly reactive intermediate carbon-hydrogen material is the basis of the Bituminous Coal Research (BCR), Two Stage, Super Pressure, coal gasification process. This is a process under development by BCR with funding supplied by the U.S. Interior Department's Office of Coal Research and the American Gas Association. The coal feed to the gasification process which is sized to approximately 70 percent through 200 mesh (74 microns) is reacted, at elevated pressure and temperature, with steam and a synthesis gas containing primarily hydrogen, carbon dioxide, and a considerable quantity of carbon monoxide. Although considerable methane is formed in the gasification of 74 micron coal in a dilute hydrogen atmosphere, thermal comminution of the coal particles does not occur and more than 50 percent of the methane contained in the product gas is produced by catalytic methanation following gasification.

It should be noted that the extent of hydrogenation and mass conversion of the coal in a given contact time may vary depending on several factors which influence the rate of reaction. One of the factors is diffusion of the hydrogen and product gases through the pores of

the particles and another factor is reaction on the available external surface of the particles. With respect to these factors, 4 micron and one one-hundredth micron coal particles would be respectively 18.5 and 7,400 times as reactive as 74 micron coal particles. If the mass transport of reacting gases through a surface film of reactants and products limit the rate, the extent of hydrogenation varies approximately as the inverse of the particle diameter to the 1.5 power. In this case four micron and one one-hundredth micron coal particles would be 80 and 625,000 times more reactive than the 74 micron coal.

Other factors, such as formation of an ash film, may operate to mitigate the ratio of improvement indicated by the size comparisons above. However, for any given coal, the reactivity of the ultrafine and submicron coal particles will be several orders of magnitude more reactive than 74 micron coal particles.

From the above it is apparent that a maximum quantity of methane can be produced directly from coal when ultrafine coal is fed to a gasification reactor wherein the coal is rapidly heated and thermally comminuted in the presence of relatively pure hydrogen.

Simultaneous with coal devolatilization, the particles undergo tremendous size reduction with a corresponding increase in surface area of active centers and reaction of the active sites with the hydrogen to form methane. The heat requirements for the rapid heating of the feed material inside the reactor is provided by the methane forming reaction itself which is highly exothermic.

Other objects and advantages of the process will become apparent from the study of the following description taken with the accompanying drawing wherein:

The single FIGURE is a schematic illustration of a process of coal gasification by direct methanation, involving the principles of the present invention.

Referring to the single FIGURE of the drawing, coal 1, fed to the plant, is reduced in size by mechanical comminution at 2 to a size of 4 microns and smaller. Optional equipment 9 can be included in the coal preparation section for removal of inorganic minerals, including the pyritic sulfur. The beneficiation of the coal would minimize the effects of ash film on the gasification reactions and would improve the overall thermal efficiency of the downstream process. The ultrafine coal powder will be introduced through pipe 3a to the hydrogasifier, reactor 3 through a nozzle 3b which will be designed to prevent premature heating of the coal feed. Hydrogen rich gas at reduced temperature flowing through pipes 16 and/or 22 is used to pressurize the ultrafine coal powder and the mixture is introduced into the hydrogasifier 3 through pipe 3a. Within the reactor 3, the coal powder will be combined with the bulk of the hydrogen which will be introduced to the reactor through pipe 22. The methane forming reaction is exothermic and once initiated, the reactor is self sustaining as heat is produced in excess of that required for rapid heating of the material feeding reactor 3. The rapid heating of the ultrafine coal powder to between about 700° to about 1,000°C, such as by an electric induction coil 3c, will be accompanied by essentially simultaneous devolatilization, reduction in size of the coal powder to about one one-hundredth microns and methanation of the active centers so formed to produce methane directly from reaction with hydrogen. Excess

heat will be removed from reactor 3 by means of a heat rejection system 3c.

At the operating conditions of reactor 3, the oxygen present in the coal feed is converted to steam, carbon monoxide and carbon dioxide; the nitrogen is released from the coal primarily as free nitrogen; the coal sulfur reacts with hydrogen to form hydrogen sulfide; the coal hydrogen participates in the gas forming reactions and the carbon reacts to form methane and carbon oxides. The percentage of the carbon gasified will be dependent on the operating pressure of the reactor and the quantity of hydrogen introduced into said reactor 3. For the process depicted in the FIGURE, the hydrogen flow to the reactor and the reactor operating pressure would be controlled to permit withdrawal of unreacted carbon in a quantity equal to that required to produce the hydrogen requirements of the process.

The mixture which leaves the hydrogasifier 3 at an elevated temperature is separated at 4 into a methane rich gas stream and a stream composed of ash and submicron char (carbon) particles. The methane rich gas is treated at 5 by one of a number of gas purification processes commercially available for removal of carbon dioxide and hydrogen sulfide. The rejected acid gas is further processed in a Claus type plant 13 to convert the sulfur to its elemental form 15. If necessary for pollution control, the Claus plant tail gas 14 can be further processed for higher degrees of sulfur removal. The purified methane rich gas is dried by gas drier 6 and, if desired, in order to control the heating value of the product gas, and/or to reduce the toxicity of the gas, a cryogenic separation process 7 can be utilized to reject hydrogen through pipe 16 and carbon monoxide through pipe 17. The hydrogen cryogenically recovered from the pipeline gas stream will be recycled and used for pressurizing the coal feed. The carbon monoxide recovered cryogenically will be used in the process for producing hydrogen.

The submicron char leaving the hydrogasifier 3 will be used to produce the hydrogen required for the direct methanation. The char separated at 4 from the hydrogasifier effluent will be fed to the char gasifier reactor 10 where it will be endothermically reacted with steam 12 at an elevated temperature to form hydrogen and carbon monoxide. The required heat for this reaction is supplied by the exothermic reaction between a portion of the char with oxygen 11 to form carbon dioxide. At the operating temperature and pressure in the gasifier, a further reaction will result in the formation of carbon monoxide from carbon dioxide and carbon. Residue 25 consisting of ash and a relatively small quantity of carbon is removed from the char gasifier effluent gas at 24. The gas is mixed with carbon monoxide from the cryogenic separation system 7, if used, and the carbon monoxide is the resultant stream flowing through pipe 17a is reacted with steam 19 catalytically in the shift converter 18. The carbon monoxide reacts exothermically at 18 with steam to produce hydrogen and carbon dioxide. Subsequently the hydrogen rich gas is treated at 20 for acid gas removal and the relatively pure hydrogen is fed to the hydrogasifier through pipe 22 for direct methanation of the coal feed. Acid gases, primarily CO₂, are rejected at 21.

Advantages of the proposed process include the following:

1. The quantity of methane produced directly by the exothermic reactions of coal with hydrogen is maxi-

mized and consequently the oxygen requirements of the plant to achieve the necessary gasification of char is low in comparison with alternative processes. Inherently, the process provides for excellent coal utilization as the thermal efficiency of the entire plant, on a self sufficient basis, is in excess of 80 percent.

2. In the event it is necessary to control the carbon monoxide content of the final product gas a comparatively simple catalytic methanation system can be utilized since relatively little carbon monoxide is present in the hydrogasifier effluent.

3. Because of the highly reactive nature of the ultrafine coal and submicron char particles the operating pressure of the system can be lower than is required for alternative gasification processes.

4. The design conditions for the hydrogasifier, which will be a concurrent entrained bed reactor, will permit the use of essentially any type of coal without the requirement for coal pretreatment. (caking coals can be used directly)

5. A very high percentage of the sulfur contained in the ultrafine coal particles will be converted to hydrogen sulfide at the operating conditions of the hydrogasifier. The effluent gas from the hydrogasifier will be low in carbon dioxide content, in relation to the hydrogen sulfide content thereby facilitating gas purification with a high conversion of sulfur to its elemental form.

6. A minimal quantity of contaminants, such as tars, will be present in the hydrogasifier effluent stream.

Thus, the present invention provides a highly efficient and relatively inexpensive process for producing pipeline quality gas which is an excellent substitute for natural gas.

Variations which might be made in the process illustrated in the FIGURE and described above without changing its unique features include the following:

1. Incorporation of the steam-iron process utilizing air rather than oxygen for production of hydrogen from char.

2. In the event the heating value of the product gas from the hydrogasifier is acceptable, it may prove economical to eliminate the cryogenic separation 7.

3. The cryogenic separation 7 can be deleted and the carbon monoxide content of the product gas could be reduced to very low levels of toxicity by catalytically reacting the carbon monoxide with hydrogen to produce methane and water vapor. In this case, the gas drier 6 would be located downstream of the catalytic methanator.

4. As described in connection with FIG. 1, under proper conditions, feeding ultrafine coal particles into a reactor in which rapid heating occurs, there is a simultaneous production of gaseous hydrocarbon and submicron carbon particles. During this carbonization a considerable portion of the sulfur contained in the coal is converted to hydrogen sulfide which can be removed from the gas stream with relative ease. Therefore, if desired, the process can be simplified to produce a sulfur free gas and low sulfur submicron char particles. The heat required for the rapid heating of the coal to promote the devolatilization and comminution may be achieved by means other than exothermic reaction with hydrogen such as by an electric induction coil (not shown) or by the introduction of a high temperature gas into the reactor. The gas and char would be separated and subsequent to gas cleanup the char could

be blended into the gas in proportions to yield a clean burning fuel of high heating value. Additionally, a portion or all of the submicron char particles could be blended into oil to yield a readily transportable colloidal fuel.

5. Relatively pure, low sulfur submicron carbon particles could be withdrawn as a by-product of the basic process or of any of the modified processes suggested above.

While we have illustrated and described several embodiments of our invention, it will be understood that these are by way of illustration only and that various changes and modifications may be contemplated in our invention as covered by the following claims.

We claim:

1. The method of converting coal to gas comprising introducing coal particles of a size of about 4 microns and smaller into a reactor, rapidly heating said coal particles in said reactor, in the presence of pressurized hydrogen, to between about 700° to about 1,000°C to effect explosive devolatilization and comminution of said coal particles to form gaseous hydrocarbon and highly active char of a size of the order of one one-hundredth micron, and reacting said char directly with said hydrogen in said reactor to form a product gas containing methane.

2. The method recited in claim 1 wherein said direct reaction of char with hydrogen is exothermic.

3. The method recited in claim 1 together with the additional step of filtering and separating the product gas of said explosive devolatilization and comminution and methanation from said char, partially purifying said product gas by removing sulfur, CO₂ and excess water vapor from said product gas and thereafter conducting said product gas containing methane into a pipeline to provide a source of fuel.

4. The method recited in claim 1 wherein said product gas containing methane and char are passed upwardly and out of said reactor and thereafter are separated, the methane then being passed into a pipeline as a source of fuel.

5. The method recited in claim 3 wherein said product gas includes CO and H₂ and wherein before conduction into said pipeline, said CO and H₂ are cryogenically separated from said product gas.

6. The method recited in claim 3 wherein said separated char is introduced into a gasifier and wherein oxygen and steam are also introduced into said gasifier to form gaseous products including hydrogen and wherein said gaseous products are separated from the solid residue and the hydrogen content is enhanced by conversion of other gaseous products to hydrogen, the hydrogen then being introduced with said coal particles into said reactor.

7. The method recited in claim 1 wherein the interior space of said reactor is initially rapidly heated sufficiently to effect said explosive devolatilization and comminution.

8. The method recited in claim 1 wherein the interior space of said reactor is initially heated sufficiently to effect said explosive devolatilization and comminution by the introduction therein of a high temperature gas.

9. The method recited in claim 1 wherein inorganic materials including pyritic sulfur are removed from said coal particles before introduction of said coal particles into said reactor.

10. The method recited in claim 1 wherein said product gas and highly active char are passed upwardly and outwardly of said reactor at high temperatures, and include CH_4 , H_2 , CO_2 , H_2S and H_2O which are filtered and separated into a methane rich gas stream and a char stream, and wherein said methane rich gas is treated to remove CO_2 and H_2S , of which the H_2S is further processed by a Claus plant to convert sulfur to its elemental form.

11. The method recited in claim 10 wherein said methane rich gas stream is dried by a dryer and subjected to a cryogenic separation system to remove H_2 and CO for recycling.

12. The method recited in claim 10 wherein said char stream is introduced into a char gasifier and reacted with oxygen and steam at an elevated temperature to form an effluent gas containing H_2 and CO , and in which char gasifier a further reaction will result in the

formation of CO and CO_2 and carbon refuse, said H_2 being separated and ultimately introduced into said reactor at a controlled temperature.

13. The method recited in claim 11 wherein residue comprising inorganic ash and a relatively small amount of carbon is removed from the effluent gas from the char gasifier, which gas is mixed with CO from said cryogenic separation system and the CO in the resultant stream is reacted with steam catalytically in a shift converter wherein the CO is reacted with steam to produce H_2 and CO_2 , the H_2 being treated for acid gas removal and then fed into said reactor at controlled temperature for direct methanation of said coal particles fed therein.

14. The method recited in claim 1 wherein excess heat is removed from said reactor means of a heat rejection system.

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