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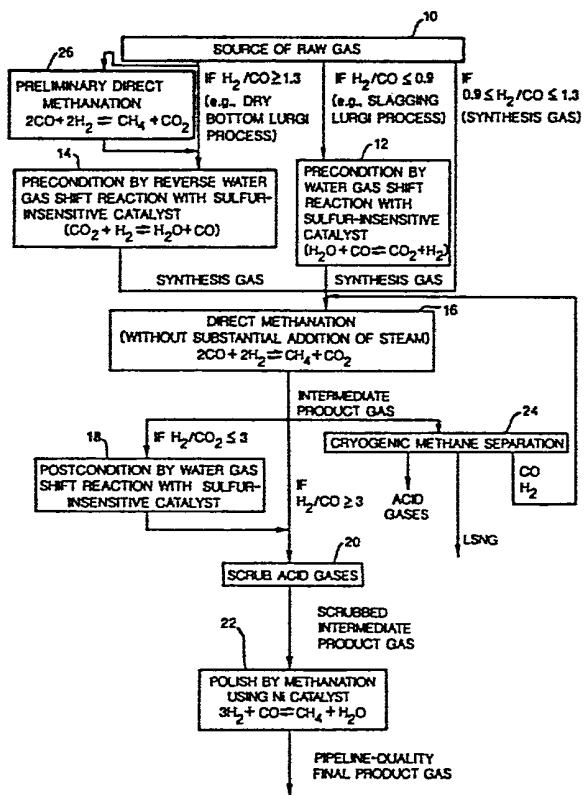
Production of pipeline gas from sulfur containing raw or synthesis gas.

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Described is a process for producing methane-rich, pipeline-quality gas from raw gas produced by gasifying carbonaceous materials. Following any needed adjustment of its H<sub>2</sub>/CO ratio, which can be by a preconditioning water gas shift reaction or its reverse, the raw gas is fed to a direct methanation reaction ( $2H_2 + 2CO \rightleftharpoons CH_4 + CO_2$ ) which does not require substantial addition of steam. If needed, the intermediate product gas from the direct methanation reaction can be passed over a water gas shift catalyst to control its H<sub>2</sub>/CO ratio so that after removal of acid gases its methane content can be raised further over a nickel catalyst. This enables production of a very high heating value pipeline gas with only one acid gas removal step in the entire process sequence. In the alternative, the intermediate product gas can be subjected to cryogenic methane separation, with the separated H<sub>2</sub> and CO fed back to the direct methanation and the separated methane used as SLNG. A preliminary direct methanation step can be carried out prior to any needed preconditioning step.

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PRODUCTION OF PIPELINE GAS  
FROM SULFUR CONTAINING RAW OR SYNTHESIS GAS

FIELD OF INVENTION

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This invention relates to the conversion of coal and carbonaceous materials to natural gas substitutes, and particularly to processes in which raw gas or synthesis gas produced by primary gasification is converted into methane-rich, pipeline-quality gas.

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DESCRIPTION OF PRIOR ART

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A number of processes are known for the production of methane-rich gas by the gasification and subsequent methanation of coal or other carbonaceous materials.

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Some examples of gasification processes for coal are known as the dry bottom Lurgi, slagging Lurgi and HYGAS processes. The H<sub>2</sub>/CO ratio in the synthesis gas produced by these processes varies from about 0.4 to 2.2. The Lurgi process has been selected by a number of firms for construction of the first commercial gasification units in the United States because it has been operated for a long time on a commercial scale. It is based on the steam-oxygen gasification under pressure of sized coal particles in a mechanically stirred fuel bed. The effluent gases from the gasifier are quenched to remove tars and oils, and the resulting gases are then passed through a carbon monoxide shift converter where part of the carbon monoxide reacts with steam to produce hydrogen and carbon dioxide by the so-called water gas shift reaction. The next stage consists of the removal of acid gases and residual sulfur compounds followed by passage through iron oxide boxes. The slagging Lurgi process is similar to the commercial Lurgi process described above except that the gasifier is modified to accept caking coals and operates at a higher temperature. Coal is crushed, screened to remove fines and then fed to the gasifier through coal locks. The bottom half of the gasifier is different from the conventional Lurgi gasifier.

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According to a British Gas Corporation development, steam and oxygen

are injected through tuyeres into the high temperature reaction zone. Ash is removed in the form of liquid slag through a tap and dropped into a quench vessel where it is removed as a glasslike frit. Operating conditions of the gasifier are 400-600 psi and about 2300°F. Shift  
5 conversion and purification steps similar to those of the conventional Lurgi process are employed in further processing. The HYGAS process of the Illinois Institute of Gas Technology in Chicago is based on the hydrogenation of a fluidized bed of specially prepared coal. The latter is introduced as a slurry into the top layer of three superposed  
10 fluidized beds. Hot hydrogen enters the bottom bed and fluidizes all three beds, evaporating at the same time the oil from the slurry that was injected into the top. The fluid bed gasifier is maintained at a pressure of 75-90 atm and this is conducive to the formation of methane during the gasification process. The ungasified portion of the coal is  
15 obtained in the form of a reasonably reactive char which is withdrawn from the bottom of the bed and transferred to a hydrogen generator. The latter is normally operated by injecting a steam/oxygen mixture into the fluidized char, but can in the absence of oxygen operate on steam alone, provided the bed is electrically heated. A third possible method  
20 of hydrogen production, based on the steam-iron reaction and a subsequent reduction of the iron by means of char, has also been proposed. This process also involves the employment of a raw gas purifier.

Usually one finds that in the above and similar gasification  
25 processes, apart from methane, two low calorific value gases are produced simultaneously. Oxygenation and steam reforming both produce carbon monoxide, the calorific value of which is about 300 Btu/cu ft, and hydrogen, which also has a heating value of around 300 Btu/cu ft. In order to convert these low calorific gases into methane, the carbon  
30 monoxide can be reacted with hydrogen. In the usual methanation process using nickel catalyst, a H<sub>2</sub>/CO ratio of about 3 is used. This means that either extra hydrogen must be introduced or that there will remain an excess of surplus carbon monoxide. Carbon dioxide can also react with hydrogen to produce methane, but since production of hydrogen usually  
35 involves the conversion of carbon monoxide to carbon dioxide by the

shift reaction, this reaction is not usually advantageous. Carbon dioxide typically is removed by absorption in alkaline absorbents and this constitutes one of the major costs in obtaining high heating value gases. In all processes described above, if the aim is to produce synthetic natural gas, the carbon monoxide is hydrogenated.

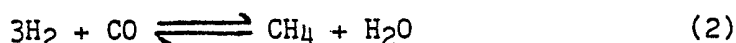
Methanation, as an industrial process, has been known for many years since it is an essential gas purification step in the synthesis of ammonia from hydrogen and nitrogen. Nickel has generally been the active component in the production of synthetic natural gas (SNG) from synthesis gas produced by primary gasification processes such as those described above.

Although nickel is a very active catalyst it possesses a number of disadvantages. It is deactivated irreversibly by the presence of very small proportions of sulfur compounds in the feed gas. Another problem in the employment of nickel methanation catalysts is the loss in activity due to carbon deposition. Carbon formation is favored at the high methane concentrations required for production of methane, in part due to the reaction:

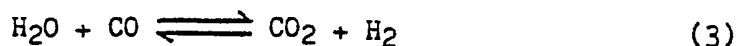


This reaction, if it occurs, again irreversibly poisons the nickel catalyst. Generally it is necessary to employ feed gas with high ratios of H<sub>2</sub>/CO, equal to at least about 3 (on a molar or volumetric basis), to avoid this possibility. Generally, operating conditions involve temperatures below 400°C and pressures up to 1000 psi.

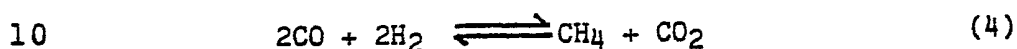
Under these conditions the predominant reaction for methane formation over nickel catalysts is:



The hydrogen for the high H<sub>2</sub>/CO ratio needed for reaction (2) can be supplied by the water shift reaction:



One way to avoid the necessity of using a separate water gas shift reaction step (reaction (3)) is to conduct the methanation in the presence of a large excess of steam (Roberts, F.F.S., Hibden, D., Brooks, C.T., Sudburg, J.D., Paper IGU/Bz-79, 14th World Gas Conference, Toronto, International Gas Union, Paris, 1979). If such large  
5 excess of steam is supplied, it is then possible to apparently promote direct formation of methane (by a combination of reactions (2) and (3) in the known prior art):



Reaction (4) does not involve water at all. To avoid water formation with nickel catalysts it is therefore necessary for a large concentration of steam to be maintained so that water formed by reaction  
15 (2) is consumed by reaction (3). This introduction of steam also serves to suppress carbon formation with these catalysts.

There has also been considerable effort devoted to the attempt to reduce sulfur sensitivity of nickel catalysts and/or substitute other catalysts which would be less affected by sulfur. One proposal is  
20 discussed in U.S. Patent 3,928,000 (Child, et al.). The proposal involves gasifying a high-sulfur carbonaceous fuel by partial oxidation to obtain a process gas stream which is cooled, cleaned and subjected to catalytic methanation. In the methanation step synthesis gases are to be reacted without any preliminary water gas shift, though water is to  
25 be employed in the primary partial oxidation step, thereby affording some increase in the H<sub>2</sub>/CO ratio. The methanation catalyst is a typical Co/Mo/Al hydrodesulfurization catalyst, available commercially. The feed to the methanation reactor (Example I of the Child et al. patent) is said to have a H<sub>2</sub>/CO ratio equal to 1.76, which is still substantially higher than would correspond to the H<sub>2</sub>/CO = 1/1 ratio for the  
30 direct methanation reaction, Equation (4). Operation at 98 atmospheres (1440 psi) is said to result in a product stream which is scrubbed to remove the gases CO<sub>2</sub>, H<sub>2</sub>S, COS and H<sub>2</sub>O. This product is said to contain 3.8 vol. % of CO. It is next to be processed (Example II of the Child  
35 et al. patent) by addition of 11.4 vol. % of steam and passing over a

fixed bed conventional water-gas shift catalyst consisting of a mixture of copper and zinc oxides. This is said to reduce the CO content to 1.88 vol. % with simultaneous production of hydrogen, so that the hydrogen content of the exit gases from the shift converter was 5.63 vol. %, corresponding to a H<sub>2</sub>/CO ratio of 3/1. After removal of H<sub>2</sub>O and CO<sub>2</sub> the process gas was to be introduced into a conventional adiabatic catalytic methanation zone using a nickel containing catalyst. CO<sub>2</sub> was said to be again removed from the product through this methanation reaction to obtain the final product SNG.

Thus, the processing sequence proposed by Child et al. uses three acid gas removal steps. Acid gas removal is one of the most expensive operations, costing far more than the catalytic processing steps themselves. Also, the use of additional steam both in the original gasification and the subsequent water gas shift adds considerable cost to the process.

Another attempt to produce pipeline quality gas economically by so-called combined shift and methanation had been proposed earlier, in U.S. Patent No. 3,904,386 (Grabowski, et al.). In this case the synthesis gas feed is said to be derived from a coal gasifier. The cooled synthesis gas is to be introduced into a combined shift and methanation system where the mixture comes in contact with a catalyst at a temperature between 500°F and 1050°F and a pressure between 500 psig and 2000 psig. The catalyst employed is said to be based on molybdenum and alumina, although addition of cobalt and other promoters are mentioned, so that the catalyst employed seems to be similar to that specified in the Child et al. patent. Finally, as in the Child et al. patent, the sulfur-free gas is to be treated to produce a gas of SNG pipeline quality through conventional fixed bed methanation using a nickel catalyst.

In the Grabowski et al. proposal, a much lower ratio of H<sub>2</sub>/CO in feed gas to the combined shift and methanation reaction is to be employed than in the Child et al. patent, namely H<sub>2</sub>/CO = 0.66 (from Table II of U.S. Patent No. 3,904,386). Thus, there is not enough hydrogen present in this case for direct methanation, as in reaction (4). In order to supply sufficient hydrogen, 0.5 vol. of steam must be

fed to the combined shift-methanation reactor for each volume of dry gas. In order to avoid deactivating the catalyst by this large addition of steam, it is necessary to recycle a portion of dry product gas from the shift-methanation reactor back to the feed. This feature is  
5 believed to be an essential part of the process and, of course, adds substantially to the cost of that process.

SUMMARY OF THE INVENTION

10 The invention is in the field of conversion of carbonaceous materials or products thereof into natural gas substitutes, and is useful for a final product gas which is rich in methane and has a sufficiently low content of carbon monoxide and hydrogen sulfide to be useful as pipeline quality gas either directly or when blended with  
15 other gases.

In an exemplary and nonlimiting example of a process embodying the invention, the synthesis gas for direct methanation contains hydrogen and carbon monoxide in the ratio of about 0.3-1.7, and preferably in the ratio of about 0.9-1.3, and also sulfur containing gas and up to about  
20 30 vol. % carbon dioxide on water-free basis, and preferably but not necessarily some methane. Hydrogen and carbon monoxide in the synthesis gas react in the presence of a direct methanation catalyst to produce methane and carbon dioxide, to thereby convert the synthesis gas to a methane-rich intermediate product gas which contains residual  
25 amounts of hydrogen and carbon monoxide, as well as carbon dioxide and sulfur containing gas. This intermediate product gas is scrubbed to remove acid gases, such as carbon dioxide and hydrogen sulfide, and the scrubbed gas is polished by methanation over a catalyst such as nickel, in which the residual hydrogen and carbon monoxide react to produce  
30 methane and water and thereby convert the scrubbed gas into a final product gas which is methane-rich, in that it contains at least 75 vol. % methane, and is suitable for direct pipeline use or for blending into pipeline gas because its carbon monoxide content is no more than about 0.1 vol. % and its sulfur content is no more than about 5 ppm.

35 If synthesis gas having the desired H<sub>2</sub>/CO ratio (about 0.9-1.3) is



not available, it can be produced by preconditioning raw gas from processes such as certain types of coal gasification. If the raw gas has too high a ratio of hydrogen to carbon monoxide, e.g. a ratio greater than about 1.3, it can be converted to synthesis gas having the preferred range of about 0.9-1.3 by a reverse water gas shift reaction in the presence of a sulfur-insensitive catalyst, in which hydrogen and carbon dioxide in the raw gas react to produce carbon monoxide and water until the hydrogen to carbon monoxide ratio drops to the preferred range and preferably to about one. Conversely, if the raw gas hydrogen to carbon monoxide ratio is less than the preferred range of about 0.9-1.3, it can be subjected to a water gas shift reaction over a sulfur-insensitive catalyst with the addition of steam, in which carbon monoxide and water react to produce hydrogen and carbon dioxide, to thereby raise the H<sub>2</sub>/CO ratio to the preferred range, and preferably to about one.

If the intermediate product gas from the direct methanation reaction has residual hydrogen to carbon monoxide ratio of less than about 3, i.e., has insufficient hydrogen content for efficient polishing methanation over a catalyst such as Ni, its ratio can be raised prior to the acid gas scrubbing step by subjecting it to a post-conditioning step involving a water gas shift reaction over a sulfur-insensitive catalyst, in which residual carbon monoxide reacts with steam to produce hydrogen and carbon dioxide until the H<sub>2</sub>/CO ratio increases to at least about 3.

The scrubbed gas is polished by a final methanation reaction, e.g., reaction (2) over a Ni catalyst, to produce the methane-rich final product gas which can be used as a pipeline gas either directly or in a blend.

In the alternative, the above steps following direct methanation can be replaced by cryogenic separation which involves feeding CO<sub>2</sub> and H<sub>2</sub> separated from the intermediate product gas back to the direct methanation step and supplying separated methane in the form of, e.g., liquid (synthetic) natural gas.

As another alternative, a preliminary direct methanation of the raw gas can be added, for partial methanation prior to any needed

preconditioning step preceding the main direct methanation step.

This invention makes use of the discovery that oxysulfide catalysts based on the transition elements W, Mo, and V have much higher activity for direct methanation reaction (4) than nickel catalysts while being relatively less active for the water gas shift reaction. Direct methanation is the predominant reaction over these catalysts even in the presence of substantial concentrations of water and carbon dioxide. A process sequence employing the reaction takes advantage of this discovery.

If a gas contains approximately equal proportions of  $H_2$  and  $CO$ , the occurrence of the direct methanation reaction, Equation (4), is favored. Actually a slight excess of  $H_2$  is preferable because the reaction shown by Equation (2) occurs to minor extent. For gases such as those produced by the HYGAS process after the usual quench it is possible and economical to pass the raw gas containing the acid gases  $H_2S$  and  $CO_2$  directly through a reactor system containing catalysts such as those described in our Patents Nos. 4,151,191 and 4,320,030. The direct methanation reaction converts to methane up to 95% of the  $CO$  in the feed gas from the HYGAS quench. It is then only necessary to adjust the  $H_2/CO$  ratio of the intermediate product so that a final clean-up (polishing) operation can be conducted to reduce the  $CO$  content to the drastic pipeline gas specification of less than 0.1% vol. A convenient way to accomplish this is to drop the temperatures of the effluent from the methanation step and pass it over a sulfur-insensitive water gas shift catalyst. Several such catalysts are available including the formulation given in our Patent 4,151,191. No or little addition of water is necessary with active catalysts which can bring the reaction close to equilibrium at  $300^\circ C$ . The gas then should have a  $H_2/CO$  ratio of greater than 3/1. Following this the  $CO_2$  produced both in the last step and the previous methanation is removed along with sulfur containing gases by scrubbing with an alkaline solvent. The effluent gas is methanated in a clean-up operation using a conventional nickel catalyst to produce a high Btu synthetic natural gas. This gas is produced by addition of very minor proportions of process steam and involves only one acid gas removal step.

If the raw gas contains a higher ratio of  $H_2/CO$ , such as for example that produced by the dry bottom Lurgi gasifier which has a  $H_2/CO$  ratio equal to about 2, it can be preconditioned (prior to the direct methanation step) by  $CO_2$  methanation. For preconditioning, the raw gas is passed over a sulfur-insensitive water gas shift catalyst at an elevated temperature ( $600^\circ$ ) at which the water gas shift equilibrium constant is small. The  $H_2/CO$  ratio is thus reduced to a lower value and the resulting synthesis gas ( $H_2/CO \approx 0.9-1.3$ ) can be processed as previously described.

An alternative scheme is to immediately use the raw gas in the direct methanation reaction. The conversion of CO is high but excess hydrogen is produced. In the subsequent acid gas removal step, some  $CO_2$  is left in the product gases. These gases are passed to a nickel catalyst step in which not only CO but also  $CO_2$  methanation ( $4H_2 + CO_2 \rightleftharpoons CH_4 + 2H_2O$ ) is conducted so as to use up the excess hydrogen. In both cases only one acid gas removal step is required.

If the  $H_2/CO$  ratio is low (e.g., below about 0.9), such as in the raw gas produced by the slagging Lurgi gasifier, which has a  $H_2/CO$  equal to about 0.4, after the usual quench the gas is passed at a low temperature (about  $300^\circ C$ ) over a water gas shift catalyst in order to raise the hydrogen/carbon monoxide ratio. It is then subsequently processed as previously described.

#### THE DRAWING

The sole Figure is a flowchart of processes embodying aspects of the invention.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

The term "raw gas" used in this specification refers to a mixture which includes carbon monoxide, hydrogen and preferably some methane gases. Examples of raw gases are the effluents of the primary gasification steps in processes such as the dry bottom Lurgi, slagging Lurgi, HYGAS, or other similar processes. The raw gas can contain from

about 0.4 to 2.2 volumes of hydrogen for volume of carbon monoxide, and up to about 3 vol. % of H<sub>2</sub>S. It can also contain CO<sub>2</sub> and/or water, along with smaller quantities of nitrogen, aromatic hydrocarbons and phenols derived from the carbon source. The term "synthesis gas" is used herein to mean a raw gas in which the H<sub>2</sub>/CO ratio is, or has been adjusted to, a figure in the range of about 0.3-1.7, and preferably about 0.9-1.3. The term "intermediate product gas" refers herein to the product of the direct methanation step.

Referring to the flow diagram, source 10 of raw gas can be a conventional gasifier process such as HYGAS, slagging Lurgi, dry bottom Lurgi, etc., which includes the conventional "quencher" step, at a quenching temperature dictated by the desired quality of the raw gas and H<sub>2</sub> to CO ratio of the stream, and a conventional water and oil scrubbing operation to remove tars, oils, phenol<sup>ammonia</sup> and other coal by-products.

Depending on the H<sub>2</sub> to CO ratio of the raw gas, a preconditioning step can be used to adjust this ratio to around 0.9 to 1.3 for more effectively employing direct methanation of CO and H<sub>2</sub> to produce CH<sub>4</sub> and CO<sub>2</sub> without employing steam.

If the H<sub>2</sub> to CO ratio in the raw gas stream from step 10 is lower than about 0.9, as in the case of the slagging Lurgi coal gasification process, a gas water shift reaction (3) is used at step 12 to shift some of the CO in the raw gas to H<sub>2</sub> to bring the ratio up to within about 0.9-1.3, and preferably to around 1.0. If the H<sub>2</sub> to CO ratio is greater than about 1.3, as in the case of dry bottom Lurgi coal gasification process, at step 14 CO<sub>2</sub> in the raw gas is reacted with hydrogen to form CO and water by the reverse of the water gas shift reaction (3) to bring the ratio down to within about 0.9-1.3, and preferably to about 1. These reactions occur readily over commercially available water gas shift catalysts that are insensitive to sulfur compounds. A commercially available unit for either of these preconditioning steps 12 and 14 can be operated at a range of space velocities from 1,000 to 15,000 V/V/HR(STP) and comparable temperatures and pressures in a manner known in the art. The output of the preconditioning step (12 or 14) is "synthesis gas," as the term is used in this specification. Of course, if the raw gas has an H<sub>2</sub>/CO ratio in the range specified for synthesis

1  
2  
2

gas, no preconditioning is needed, although some scrubbing to remove tars, oils, ammonia liquid and other coal by-products can still be carried out if desired.

5 The synthesis gas enters at step 16 a reactor system that promotes a direct methanation reaction in which the bulk of the methanation occurs. The direct methanator reactor system can take various forms. It can use a series of plug flow reactors arranged and engineered in a configuration for effective heat removal, or a combination of fluidized and fixed bed reactors. The direct methanation process can be conducted  
10 at temperatures in the range of about 450°F to 1200°F and at pressures in the range of 150 to 2,000 psig and at space velocities in the range of 1,000 to 25,000 V/V/HR (STP). Since the final product gas is typically delivered to the pipeline at 1,000 psig, it can be advantageous to operate the direct methanation reactor at step 16 at high  
15 pressures in order to deliver the final product gas at pipeline specification without additional compression. The specific operation of the reactor depends on the activity of the catalysts employed.

The synthesis gas fed to the direct methanation system at step 16 can contain up to about 30 vol. % of CO<sub>2</sub> on a water free basis, depending  
20 on the basic gasification (and any preconditioning) system which supplies it. For conversion of the synthesis gas to methane, the gas entering the direct methanation reactor at step 16 does not need a H<sub>2</sub> to CO ratio greater than about 1, which is the requirement for direct methanation. Higher ratios of H<sub>2</sub>/CO in the feed to step 16 typically  
25 result in an increase in the H<sub>2</sub> to CO ratio in the product of that step. It has been found possible in accordance with this invention to operate with H<sub>2</sub>/CO ratios below 1 to 1, down to 0.8 to 1, and in some cases even as low as 0.3 to 1, without carbon formation. However, generally best results are obtained by supplying step 16 with synthesis gas having  
30 H<sub>2</sub>/CO ratios between about 0.9 and 1.3, depending on catalyst activity, temperature, and pressure of operation and space velocity.

The catalyst employed in the direct methanation system at step 16 is preferably a sulfided catalyst, based on one or more elements of the group consisting of tungsten, molybdenum and vanadium and being  
35 supported and/or promoted by one or more selected from the group Al, Si,

B, Ce, Ti, Zr. A particularly effective catalyst is described in our co-pending patent application S.N. 431,192, entitled High Activity Transition Metal Catalysts and Methods for Making Them, and filed on September 30, 1982.

5           The intermediate product gases leaving the direct methanator contain some small amount of H<sub>2</sub> and CO, the ratio depending on the ratio of the H<sub>2</sub> and CO in the feed to step 16. A postconditioning reactor can be used, if needed, to adjust the H<sub>2</sub> to CO ratio to a level suitable for a polishing methanation reaction at step 22. The reaction at step 22  
10       can be, for example, over a nickel catalyst, which is most effective at ratios of H<sub>2</sub> to CO somewhat in excess of 3 to 1. The specific ratio depends on the desired heating value of the product gas. If the highest heating value is to be obtained, a ratio slightly greater than 3 is desired.

15           If postconditioning is needed or desired, to bring up the H<sub>2</sub>/CO ratio, a postconditioning reactor is used at step 18 in which some of the CO in the intermediate product gas is shifted, by a conventional water gas shift reaction preferably over a sulfur-insensitive catalyst, to produce additional hydrogen, and preferably at low temperatures. If  
20       needed for this reaction, water can be added at this point. Such H<sub>2</sub>O addition is a function of the degree of conversion that is necessary and the activity of the catalyst employed.

          Whether a postconditioning reactor is employed or not, the gases next are passed to a solvent treater system used at step 20 to remove  
25       acid gases. Step 20 involves the use of conventional processes for sulfur compounds such as H<sub>2</sub>S and CO<sub>2</sub> removal. Such known processes can involve refrigeration and physical or chemical absorption with solvents such as methyl alcohol, n-methyl pyrrolidone, monoethanol amine, diethanolamine, triethanol amine, or hot potassium carbonate. After  
30       absorption the solvent is regenerated by stripping the acid gases.

          In addition to selective solvent step for the removal of sulfur compounds such as H<sub>2</sub>S and CO<sub>2</sub>, it can be advantageous to pass the gases through zinc oxide boxes for final removal of H<sub>2</sub>S down to approximately 0.2 ppm (parts per million by volume) using known processes. Indeed,  
35       this can be desirable to avoid catalyst poisoning should a nickel

catalyst be employed in the final polishing step 22. However, if sulfur tolerant catalysts are used in the final polishing step 22, such zinc oxide guard is not needed.

5 Following conventional scrubbing of acid gases at step 20, the scrubbed intermediate product gas stream entering the final polishing step 22 typically contains from about 75 vol. % of methane up to about 96 vol. % of methane. It can contain up to about 5 vol. % of CO and up to 20 vol. % H<sub>2</sub>. The specific ratios and amounts depend on the H<sub>2</sub>/CO ratio of the raw gas and the degree of any pre- and postconditioning  
10 that may be required. The composition of the gas entering the polishing reactor at step 22 should be such as to ensure that a single pass adiabatic operation is feasible without excessive temperature rise. The CO<sub>2</sub> content will normally be less than 1 vol. %.

15 Following the polishing conversion at step 22 (e.g., by a known methanation reaction over Ni catalyst) the final product gas is now of pipeline quality. It typically contains about 90 vol. % CH<sub>4</sub>, less than 10 vol. % H<sub>2</sub>, small amounts of CO<sub>2</sub> and other gases which can be introduced in the original raw or synthesis gas (such as N<sub>2</sub>), and small proportions of other hydrocarbons present in the synthesis gas and also  
20 produced during methanation. The sulfur content is typically less than about 0.1 ppm, and the CO content is typically less than about 0.1 vol. %.

As an alternative to steps 18, 20 and 22, the intermediate product gas produced in the direct methanation step 16 can be subjected to  
25 cryogenic methane separation at step 24. The separated products of the cryogenic methane separation step 24 are carbon monoxide and hydrogen (which can be recirculated back into the direct methanation step 16), pipeline-quality final product gas in the form of liquid synthetic natural gas, and acid gases. The advantages of using cryogenic methane  
30 separation in the invented process include avoidance of the need for use of zinc oxide boxes for hydrogen sulfide reduction below 1 ppm, as can be required in connection with nickel methanation as in step 22, elimination of the need for methanation as in step 22 and the fact that the methane from step 24 can be used directly for LSNG and in any event  
35 it need not be heated again for polishing methanation.

As another alternative, a preliminary direct methanation, similar to that in step 16, can be carried out at step 26, prior to the preconditioning step 14, to effect partial methanation of the raw gas from a process such as dry bottom Lurgi gasification.

5

#### EXAMPLES

The following Examples should assist for a better understanding of the invention, but it should be clear that the invention is not limited to these examples but encompasses all others which are within the scope of the appended claims.

10

#### Example 1

This example demonstrates the application of the direct methanation chemistry to process a raw gas that is produced from a HYGAS-type gasifier. See Table 1.

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A simulated HYGAS raw gas similar to that reported in a Final Report for the Department of Energy #FE-1772-11 prepared by Dravo Corp. for the Institute of Gas Technology gasifying a Bituminous Pittsburgh #8 coal was used in the laboratory to demonstrate the production of pipeline-quality final product gas. The quenched raw gas (1), which is a synthesis gas in this example because its  $H_2/CO$  ratio is within about 0.9-1.3, enters the direct methanation process of step 16, where about 92% CO conversion and 57.6% CO selectivity to  $CH_4$  is achieved. The effluent (2) from the direct methanation step 16 enters at step 18 a conventional postconditioning shift reactor carrying out step 18, where about 43% of the CO is shifted with additional water to form  $H_2$ . The acid gases from the product (4) of the postconditioning step 18 are then removed at step 20 in a conventional scrubbing operation to the desired specifications to produce feed (5) to be further methanated in a conventional reaction over a nickel catalyst at step 22. The product of step 22 after being dried is rich in  $CH_4$ , has a high caloric value, and meets the specifications of pipeline-quality gas.

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Table 1  
Direct Methanation of a HYGAS Synthesis Gas

Stream No.	(1)	(2)	(3)	(4)	(5)	(6)
Stream Name	Quenched	Direct Methanation	Feed to Post	Prod. from Post	Feed to	Pipeline*
Component	Raw Gas	Product From	Conditioning	Conditioning	Polish	Gas
	To Step 16	Step 16	Step 18	(Feed to Step 20)	Step 22	(Product from Step 22)
H <sub>2</sub> lb. moles/hr	12,616	1,434	1,434	1,725	1,725	614
CO	8,827	675	675	384	384	13
CO <sub>2</sub>	9,950	13,504	13,504	13,795	138	138
CH <sub>4</sub>	7,876	12,492	12,492	12,492	12,492	12,863
C <sub>2</sub> H <sub>6</sub>	276	276	276	276	276	276
H <sub>2</sub> O	-	1,043	1,882	1,591	-	-
CO <sub>2</sub> + H <sub>2</sub> S	477	477	477	477	-	-

\*Caloric Value, 987 BTU/SC.FT. (600, 1 atm, H<sub>2</sub>W)

Example 2

This example demonstrates the application of the direct methanation chemistry to process a raw gas that is produced from a slagging Lurgi gasifier. See Table 2.

5 A simulated slagging Lurgi raw gas similar to one reported by CONOCO in their report to the Department of Energy, FE-2540-10 (Vol. 1) was used to demonstrate the production of pipeline gas. Since the H<sub>2</sub> to CO ratio is low, at about 0.4, some preconditioning of this gas (as in step 12) is desired to bring the H<sub>2</sub> to CO ratio to about 1.0. This  
10 requires about 16 volume % water in the gas to the precondition reactor. Thus, the raw gas is quenched to a temperature to retain sufficient water in the gas as required for shifting the CO to produce H<sub>2</sub> in the preconditioning reactor. Having achieved the desired composition of the quenched gas (1), about 26% of the CO is converted to H<sub>2</sub> by shifting  
15 with water in the preconditioning reactor at step 12. The resulting synthesis gas (2) then enters the direct methanation process at step 16, where about 90% CO conversion and 50% CO selectivity to CH<sub>4</sub> is achieved. The effluent (4) from the direct methanation section enters a post-conditioning shift reactor at step 18, where about 63% of CO is shifted  
20 with additional water to form H<sub>2</sub>. The acid gases are then removed at step 20 from the product (6) of step 18 to the desired specification to enable the gas (7) to be further processed at step 22 in a conventional nickel polishing methanation reactor. The final product gas from step 22 after being dried is rich in CH<sub>4</sub> and has a high caloric value and is  
25 of pipeline quality.

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Table 2  
Direct Methanation of a Slagging Lurgi Synthesis Gas

Stream No.	1	2	3	4	5	6	7	8
Stream Name	Feed to	Product from	Feed to	Product from	Feed to	Product from	Feed to	Product from
Component	Pre-condi- tioning	Pre-Conditi- oning	Direct Methanation	Direct Metha- nation	Post Con- ditioning	Post Condition- ing	Polishing Reactor	Pipeline *
	Reactor	Reactor						
CO lb. moles/hr	56411.7	41556.9	41556.9	4159.1	4159.1	1289.3	1289.3	25.8
CO <sub>2</sub>	6208.0	21062.7	21062.7	39761.5	39761.5	42831.3	213.2	213.2
H <sub>2</sub>	29764.5	39619.3	39619.3	2221.4	2221.4	5091.2	5091.2	1300.7
CH <sub>4</sub>	5870.6	5870.6	5870.6	24569.4	24569.4	24569.4	24569.4	25832.8
C <sub>2</sub> +	482.0	482.0	482.0	482.0	482.0	482.0	482.0	482.0
H <sub>2</sub> S+CO <sub>S</sub>	1976.1	1976.1	1976.1	1976.1	1976.1	1976.1	684.4	684.4
N <sub>2</sub>	684.4	684.4	684.4	684.4	684.4	684.4	684.4	684.4
H <sub>2</sub> O	15406.5	552.0	552.0	552.0	7494.6	4624.9		

\* Caloric Value about 962 BTU/SCF (HHV, 60°F, 1 atm)

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Example 3

This example demonstrates the application of the direct methanation chemistry to process a raw gas that is produced from a dry bottom Lurgi gasifier option #1 (CO<sub>2</sub> Methanation). See Table 3.

5 A simulated dry bottom Lurgi raw gas was used to demonstrate the production of pipeline gas. The raw gas composition was taken from the El Paso study conducted by Stearns-Roger Co. in which a New Mexico sub-bituminous coal was gasified in a dry bottom Lurgi gasifier. The raw synthesis gas is first quenched to remove the oils, tars and most of  
10 the water and produce quenched raw gas (1). The gas then enters, as feed (2), the direct methanation processing unit at step 16, where about 87% CO conversion and around 50% CO selectivity to CH<sub>4</sub> is achieved and gas (3) is produced. The acid gas removal system removes at step 20 from gas (3) substantially all of the sulfur compounds, but only about 90% of the  
15 CO<sub>2</sub>, to produce feed (4) to step 22. This feed (4) enters a conventional nickel type methanation reactor at step 22, where substantially all of the CO and the CO<sub>2</sub> are methanated, consuming the majority of the excess H<sub>2</sub>. The final product gas from step 22 after being dried is rich in CH<sub>4</sub> and has a high caloric value.

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Table 3  
 Direct Methanation of a Dry Bottom Lurgi Synthesis Gas  
 Option #1 (CO<sub>2</sub>-Methanation)

Stream #	1	2	3	4	5
Stream Name Component	Quenched Raw Gas	Feed to Direct Methanation	Product from Direct Methanation	Feed to 2nd Methanator	Pipeline* Gas
H <sub>2</sub> lb. moles/hr	38860	38860	22523	22523	1972
CO	18675	18675	2338	2338	29
CH <sub>4</sub>	10814	10814	18983	18983	24698
CO <sub>2</sub>	25939	25939	34107	3416	34
C <sub>2</sub> +	943	943	943	943	943
H <sub>2</sub> S+COS	375	375	375		
H <sub>2</sub> O	568	568	568		

\* Caloric Value 989.7 BTU/SCF (60°F, 1 atm, HHV)

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Example 4

This example demonstrates the application of the direct methanation chemistry to process a raw gas that is produced from a dry bottom Lurgi gasifier option #2 (Feed Preconditioning). See Table 4.

5 A simulated dry bottom Lurgi raw gas was used. The raw gas composition was taken from the El Paso study conducted by Stearns-Roger Co. in which a New Mexico sub-bituminous coal was gasified in a dry bottom Lurgi gasifier. The raw gas is first quenched to remove the oil and tars and most of the water and produce quenched raw gas (1) which  
10 becomes feed (2) to a preliminary direct methanation step 24 which operates similarly to step 16 to effect partial methanation of the raw gas. The product (3) from step 24 is feed (4) to preconditioning step 14, whose product (5) is feed (6) to direct methanation step 16, which effects a high degree of conversion. The product (7) of step 16 already  
15 has a high enough  $H_2/CO$  ratio, so there is no need for post-conditioning at step 18. Instead, product (7) from the direct methanation step 16 is directly supplied to scrubbing step 20, to remove acid gases to a degree allowing effective conventional Ni polishing methanation, and the product of step 20 is feed (8) to polishing step 20, whose product (9)  
20 is methane-rich, pipeline-quality gas of high caloric value.

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**Table 4**  
**Direct Methanation of a Dry Bottom Lurgi Synthesis Gas**  
**Option #2 (Feed Pre-Conditioning)**

Stream #	1	2	3	4	5	6	7	8	9
Stream Name Component	Quenched Raw Gas	Feed to 1st Dir. Methanat. Unit	Product from 1st Dir. Methanation Unit	Feed to Pre-Conditioning Reactor	Product from Conditioning Reactor	Feed to 2nd Direct Methanation unit	Product from 2nd Direct Methan. Unit	Feed to Polish. Reactor	Pipeline Gas
H <sub>2</sub> lb. moles/hr	39047	39047	29872	29872	21005	26005	6235	6235	551
CO	18764	18764	12200	12200	16067	16067	1924	1924	29
CH <sub>4</sub>	10895	10895	14830	14830	14830	14830	23308	23308	25203
CO <sub>2</sub>	26063	26063	28693	28693	24826	24826	30491	309	309
C <sub>2</sub> +	947	947	947	947	947	947	947	947	947
H <sub>2</sub> O	570	570	1875	1875	5742	5742	8556		
H <sub>2</sub> S+COS	377	377	377	377	377	377	377		

\* Caloric Value 1013.6 BTU/SCU (HHV, 60°F, 1 atm)

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What we claim is:

1           1. A process of converting synthesis gas containing (i) hydrogen  
2 and carbon monoxide in the ratio of about 0.9-1.3 and (ii) sulfur  
3 containing gas to methane-rich, pipeline-quality final product gas  
4 comprising:

5                 reacting synthesis gas hydrogen and carbon monoxide in the  
6 presence of a first catalyst and in the presence of said sulfur  
7 containing gas in a direct methanation reaction without substan-  
8 tial addition of steam to produce intermediate product gas rich in  
9 methane and containing residual hydrogen and carbon monoxide as  
10 well as acid gases;

11                 scrubbing acid gases from the intermediate product gas; and

12                 reacting residual hydrogen and carbon monoxide in the  
13 scrubbed gas in the presence of a second catalyst to increase the  
14 methane content of the scrubbed gas and to reduce its carbon  
15 monoxide content to no more than about 0.1 vol. % and thereby  
16 convert it to methane-rich, pipeline-quality final product gas.

1           2. A process as in claim 1 including gasifying raw material to  
2 produce said synthesis gas.

1           3. A process as in claim 2 in which said gasifying step produces  
2 raw gas containing hydrogen and carbon monoxide in a ratio outside the  
3 range of about 0.9-1.3, and including preconditioning the raw gas by  
4 adjusting the hydrogen to carbon monoxide ratio therein to produce said  
5 synthesis gas.

1           4. A process as in claim 3 in which the raw gas contains hydrogen  
2 and carbon monoxide in a ratio greater than about 1.3, as well as carbon  
3 dioxide, and the preconditioning step comprises reacting the raw gas  
4 hydrogen and carbon dioxide in the presence of sulfur insensitive  
5 catalyst, in a reverse water gas shift reaction, to reduce the hydrogen  
6 content and increase the carbon monoxide content sufficiently to convert  
7 the raw gas to said synthesis gas.



1           5. A process as in claim 3 in which the raw gas contains hydrogen  
2 and carbon monoxide in a ratio of less than about 0.9, as well as water,  
3 and in which the preconditioning step comprises reacting the raw gas  
4 carbon monoxide and water in the presence of a sulfur insensitive  
5 catalyst, in a water gas shift reaction, to reduce the carbon monoxide  
6 content and increase the hydrogen content sufficiently to convert raw  
7 gas to said synthesis gas.

1           6. A process as in claim 3 including reacting raw gas hydrogen  
2 and carbon monoxide in the presence of a sulfur-insensitive catalyst in  
3 a preliminary direct methanation reaction without substantial addition  
4 of water to effect partial methanation of the raw gas and feeding the  
5 resulting gas to said preconditioning step.

1           7. A process as in claim 1 in which said intermediate product gas  
2 contains residual hydrogen and carbon monoxide in the ratio of less than  
3 about 3, as well as water, and including the postconditioning step of  
4 reacting the product gas water and carbon monoxide in the presence of a  
5 sulfur-insensitive catalyst, in a water gas shift reaction, to raise the  
6 hydrogen to carbon monoxide ratio therein to at least about 3 prior to  
7 feeding the product gas to the acid gas scrubbing step.

1           8. A process as in claim 2 in which said intermediate product gas  
2 contains residual hydrogen and carbon monoxide in the ratio of less than  
3 about 3, as well as water, and including the postconditioning step of  
4 reacting the product gas water and carbon monoxide in the presence of a  
5 sulfur-insensitive catalyst, in a water gas shift reaction, to raise the  
6 hydrogen to carbon monoxide ratio therein to at least about 3 prior to  
7 feeding the product gas to the acid gas scrubbing step.

1           9. A process as in claim 3 in which said intermediate product gas  
2 contains residual hydrogen and carbon monoxide in the ratio of less than  
3 about 3, as well as water, and including the postconditioning step of  
4 reacting the product gas water and carbon monoxide in the presence of a  
5 sulfur-insensitive catalyst, in a water gas shift reaction, to raise the

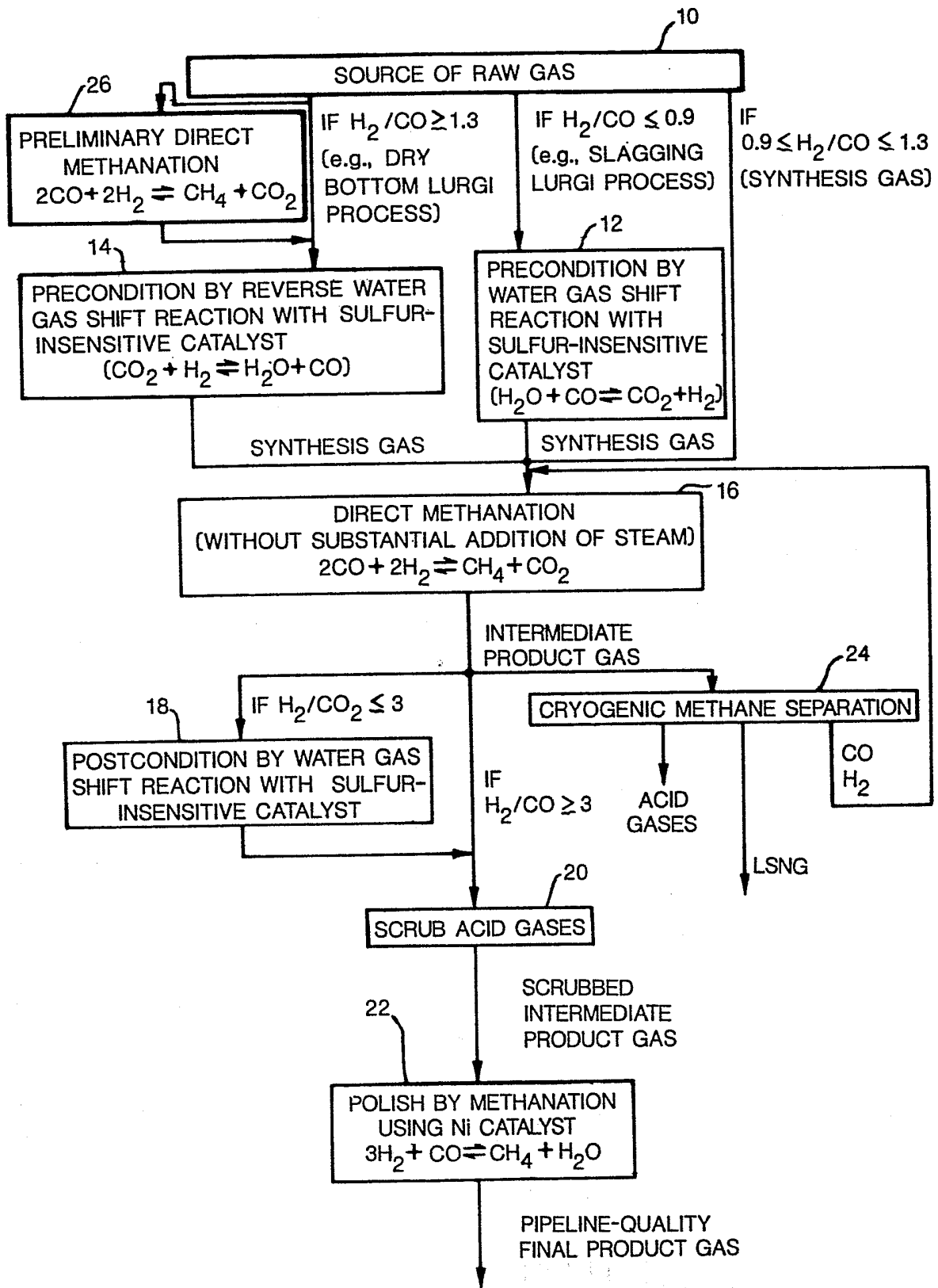
6 hydrogen to carbon monoxide ratio therein to at least about 3 prior to  
7 feeding the product gas to the acid gas scrubbing step.

1 10. A process of converting synthesis gas containing hydrogen and  
2 carbon monoxide into methane-rich pipeline-quality final product gas  
3 comprising:

4 reacting synthesis gas hydrogen and carbon monoxide in the  
5 presence of a sulfur-insensitive catalyst and in the presence of  
6 said sulfur-containing gas in a direct methanation reaction  
7 without substantial addition of steam to produce intermediate  
8 product gas rich in methane and containing residual hydrogen and  
9 carbon monoxide as well as acid gases; and

10 subjecting the intermediate product gas to cryogenic methane  
11 separation producing separated carbon monoxide and hydrogen fed  
12 back to the direct methanation step, separated acid gases and  
13 separated methane-rich, pipeline-quality final product gas.

1 11. A process as in claim 10 in which said separated final product  
2 gas is substantially liquified.





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
A, D	US-A-3 928 000 (CHILD et al.)		C 07 C 1/04
A	DE-A-2 747 517 (THYSSENGAS, DIDIER ENGINEERING)		
A	DE-A-2 907 943 (BERGWERKSVERBAND)		
A, D	US-A-3 904 386 (GRABOSKI et al.)		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )
			C 07 C 1/00
Place of search THE HAGUE		Date of completion of the search 25-05-1984	Examiner VAN GEYT J. J. A.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			