PATENT SPECIFICATION 685,962

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886

COMPLETE SPECIFICATION.

Improvements in the Production of Gaseous Mixtures of Hydrogen and Nitrogen.

We, THE POWER-GAS CORPORATION LIMITED, a British Company, of Parkfield Works, Stockton-on-Tees, County Durham, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to improvements in the production of gaseous mixtures of hydrogen and nitrogen and especially to the production of a hydrogen-containing gas low in methane with a controlled nitrogen content, for example, ammonia synthesis gas, from fuels containing appreciable quantities of volatile matter, such as bituminous coal, lignite, brown coal, peat, wood or vegetable refuse.

Ammonia synthesis gas is usually made from coke. The coke may be subjected to the water gas and producer gas reactions and the resulting water gas and producer gas mixed together. Alternatively the coke may be subjected to a water gas process suitably modified to yield a gas with a controlled nitrogen content. If similar processes are employed with fuels of high volatile content the resulting gas will contain appreciable quantities of methane and in any event the water gas process is not economically adaptable to many fuels of high volatile content.

It has previously been proposed to prepare producer gas from such fuels and split this producer gas into two streams. One of these streams is used as the reducing gas in the steam-iron hydrogen process, thus yielding hydrogen low in methane and containing carbon dioxide, carbon monoxide and nitrogen as impurities: the other stream is subjected to the water gas shift reaction to convert the bulk of the carbon monoxide to carbon dioxide and the steam to hydrogen according to the reaction $CO+H_2O=CO_2+H_2$ and after the removal of the bulk of the carbon dioxide the remaining gas is mixed with the hydrogen from the steam-iron process in such proportions as to yield the required hydrogen-nitrogen ratio, the gas being finally purified by known means. By this method whilst the hydrogen from the steam-iron process is low in methane, the hydrogen-nitrogen mixture from the second stream of producer gas made by the water gas shift reaction may contain appreciable quantities of methane. This either calls for special purification of the synthesis gas or entails a reduction in the efficiency of ammonia production due to the purging necessary for the removal of the methane from the circulating gases.

According to the present invention, therefore, a process for the production of a hydrogen-containing gas low in methane but containing nitrogen by the gasification with air, with or without steam and with or without oxygen addition, of solid fuels containing appreciable quantities of volatile matter is provided in which the gasification of the solid fuel is effected in two zones or stages, the gases produced in the zone or stage in which the fuel still retains a significant portion of volatile matter being then utilised to effect the reduction of iron oxide in a steam-iron process whereupon the reduced iron oxide is treated with steam to produce a gas rich in hydrogen and substantially free from methane or nitrogen, and the gases produced in the zone or stage in which the fuel has been substantially deprived of its content of volatile matter being obtained by the action of oxidising gas containing nitrogen and being then subjected to the water gas shift reaction and thereafter mixed, before or after removal of carbon dioxide, with the aforesaid gas rich in hydrogen in

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Price 4s 6d

such relative proportions as to give the desired nitrogen-hydrogen ratio.

The invention will be more clearly understood by reference to the accompanying drawings which illustrate two alternative methods of carrying it out.

In Figure 1 a producer 10 is provided with two outlets so that some of the "true" producer gas made from devolatilised fuel in the lower part of the producer passes up through the descending fuel, which is introduced at the top of the producer, providing the necessary heat for distillation, the resulting mixture of producer gas and distillation gas being taken off at the top of the generator, whilst a second stream of producer gas is drawn off at a lower level so that it is not contaminated with distillation gases to any appreciable extent. The mixed producer gas and distillation gas from the top outlet is used as the reducing gas in a steam-iron hydrogen plant 11, thus yielding hydrogen low in methane. The producer gas from the lower outlet will have a low methane content and this is subjected to the water gas shift reaction in the carbon monoxide conversion plant 12 and can be mixed, either before or after the removal of the bulk of the carbon dioxide, with the hydrogen from the steam-iron process to yield a mixture low in methane which can be purified by known means to yield a gas suitable for ammonia synthesis or other purposes requiring essentially a hydrogen-nitrogen mixture of controlled nitrogen content and low in methane.

In an alternative method of carrying out the present invention shown in Figure 2 producer gas is made from volatile-containing fuel which is introduced into the top of producer 13, and this producer is operated so that the fuel is not completely gasified, the residue removed from this producer, consisting of carbon and ash, being used in a second producer 14. The gas from the first producer 13 is used as reducing gas for the production of steam-iron hydrogen in a steam-iron hydrogen plant 15 whilst the gas from the second producer 14 will yield a producer gas low in methane and this can be subjected to the water gas shift reaction in the carbon monoxide conversion plant 16 and mixed with hydrogen as described above.

There may of course be one second stage producer operating in conjunction with more than one first stage producer.

If the fuel is suitable for water gas manufacture, then according to the present invention a mixed water gas and distillation gas can be produced for use as a reducing gas in the steam-iron hydrogen plant. A second gas containing appreciable quantities of nitrogen can be made from the devolatilised fuel in the lower part of the generator during the normal blow period of the water gas generator or during the run period by using a mixture of air and steam, and can be drawn off at a lower level.

Alternatively, the water gas generator may be operated to produce a mixture of water gas and distillation gas and sufficient carbon may be withdrawn from the ashes that this can be gasified in a second generator operating on the producer gas process to yield a gas with appreciable quantities of nitrogen and low in methane. This latter gas after being subjected to the water gas shift reaction can be mixed, either before or after the removal of the bulk of the carbon dioxide, with the hydrogen from the steam-iron hydrogen plant.

What we claim is :—

1. A process for the production of a hydrogen-containing gas low in methane but containing nitrogen by the gasification with air of solid fuels containing appreciable quantities of volatile matter in which the gasification is effected in two zones or stages, the gases produced in the zone or stage in which the fuel still retains a significant portion of volatile matter being then utilised to effect the reduction of iron oxide in a steam-iron process whereupon the reduced iron oxide is treated with steam to produce a gas rich in hydrogen and substantially free from methane or nitrogen, and the gases produced in the zone or stage in which the fuel has been substantially deprived of its content of volatile matter being obtained by the action of oxidising gas containing nitrogen and being then subjected to the water gas shift reaction and thereafter mixed with the aforesaid gas rich in hydrogen in such relative proportions as to give the desired nitrogen-hydrogen ratio.

2. A process as claimed in Claim 1, in which the gasification is effected in the presence of steam.

3. A process as claimed in Claim 1 or 2, in which additional oxygen is present during the gasification of the solid fuel.

4. A process as claimed in Claim 1, 2 or 3, in which the gas which has been subjected to the water gas shift reaction has the carbon dioxide removed before being mixed with the gas rich in hydrogen.

5. A process for the production of a hydrogen-containing gas low in methane but containing nitrogen by the gasification with steam of solid fuels containing appreciable quantities of volatile matter in which the gasification is effected in two zones or stages, the mixed water gas and distillation gas produced in the zone or stage in which the fuel still retains a significant portion of volatile matter being then utilised to effect the reduction of iron oxide in a steam-iron process whereupon the reduced iron oxide is treated with steam to produce a gas rich in hydrogen and substantially free from methane or nitrogen, and the gases produced in the zone

or stage in which the fuel has been substantially deprived of its content of volatile matter being obtained during the normal blow period of the water gas generator and being then subjected to the water gas shift reaction and thereafter mixed with the aforesaid gas rich in hydrogen in such relative proportions as to give the desired nitrogen-hydrogen ratio.

6. A process for the production of a hydrogen-containing gas low in methane but containing nitrogen by the gasification with steam of solid fuels containing appreciable quantities of volatile matter in which the gasification is effected in a water gas generator, the mixed water gas and distillation gas produced in this generator from fuel which still retains a significant portion of volatile matter being then utilised to effect the reduction of iron oxide in a steam-iron process whereupon the reduced iron oxide is treated with steam to produce a gas rich in hydrogen and substantially free from methane or nitrogen, and the devolatilised fuel obtained from the water gas generator being subjected to the producer gas process in a second generator to yield a gas with appreciable quantities of nitrogen and low in methane which after being subjected to the water gas shift reaction is mixed with the aforesaid gas rich in hydrogen in such relative proportions as to give the desired nitrogen-hydrogen ratio.

7. Process for the production of a hydrogen-containing gas low in methane, but containing nitrogen, substantially as herein described with reference to and as illustrated diagrammatically in the accompanying drawings.

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PROVISIONAL SPECIFICATION.

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This invention relates to improvements in the production of gaseous mixtures of hydrogen and nitrogen and especially to the production of a hydrogen-containing gas low in methane with a controlled nitrogen content, for example, ammonia synthesis gas, from fuels containing appreciable quantities of volatile matter, such as bituminous coal, lignite, brown coal, peat, wood or vegetable refuse.

Ammonia synthesis gas is usually made from coke. The coke may be subjected to the water gas and producer gas reactions and the resulting water gas and producer gas mixed together. Alternatively the coke may be subjected to a water gas process suitably modified to yield a gas with a controlled nitrogen content. If similar processes are employed with fuels of high volatile content the resulting gas will contain appreciable quantities of methane and in any event the water gas process is not economically adaptable to many fuels of high volatile content.

It has previously been proposed to prepare producer gas from such fuels and split this producer gas into two streams. One of these streams is used as the reducing gas in the steam-iron hydrogen process, thus yielding hydrogen low in methane and containing carbon dioxide, carbon monoxide and nitrogen as impurities : the other stream is subjected to the water gas shift reaction to convert the bulk of the carbon monoxide to carbon dioxide and the steam to hydrogen according to the reaction $CO+H_2O=CO_2+H_2$ and after the removal of the bulk of the carbon dioxide the remaining gas is mixed with the hydrogen from the steam-iron process in such proportions as to yield the required hydrogen-nitrogen ratio, the gas being finally purified by known means. By this method whilst the hydrogen from the steam-iron process is low in methane, the hydrogen-nitrogen mixture from the second stream of producer gas made by the water gas shift reaction may contain appreciable quantities of methane. This either calls for special purification of the synthesis gas or entails a reduction in the efficiency of ammonia production due to the purging necessary for the removal of the methane from the circulating gases.

According to the present invention, therefore, a process for the production of a hydrogen-containing gas low in methane but containing nitrogen by the gasification with air, with or without steam and with or without oxygen addition, of solid fuels containing appreciable quantities of volatile matter is provided in which the gasification of the solid fuel is effected in two zones or stages, the gases produced in the zone or stage in which

the fuel still retains a significant portion of volatile matter being then utilised to effect the reduction of iron oxide in a steam-iron process whereupon the reduced iron oxide is treated with steam to produce a gas rich in hydrogen, and substantially free from methane or nitrogen and the gases produced in the zone or stage in which the fuel has been substantially deprived of its content of volatile matter being obtained by the action of oxidising gas containing nitrogen and being then subjected to the water gas shift reaction and thereafter mixed, before or after removal of carbon dioxide, with the aforesaid gas rich in hydrogen in such relative proportions as to give the desired nitrogen-hydrogen ratio.

This may be accomplished by means of the present invention by providing a producer with two outlets so that some of the "true" producer gas made from devolatilised fuel in the lower part of the producer passes up through the descending fuel providing the necessary heat for distillation, the resulting mixture of producer gas and distillation gas being taken off at the top of the generator, whilst a second stream of producer gas is drawn off at a lower level so that it is not contaminated with distillation gases to any appreciable extent. The mixed producer gas and distillation gas from the top outlet is used as the reducing gas in a steam-iron hydrogen plant, thus yielding hydrogen low in methane. The producer gas from the lower outlet will have a low methane content and this is subjected to the water gas shift reaction and can be mixed, either before or after the removal of the bulk of the carbon dioxide, with the hydrogen from the steam-iron process to yield a mixture low in methane which can be purified by known means to yield a gas suitable for ammonia synthesis or other purposes requiring essentially a hydrogen-nitrogen mixture of controlled nitrogen content and low in methane.

In an alternative method of carrying out the present invention producer gas is made from volatile-containing fuel and the producer is operated so that the fuel is not completely gasified, the residue removed from the producer, consisting of carbon and ash, being used in a second producer. The gas from the first producer is used as reducing gas for the production of steam-iron hydrogen, whilst the gas from the second producer will yield a producer gas low in methane and this can be subjected to the water gas shift reaction and mixed with hydrogen as described above. There may of course be one second stage producer operating in conjunction with more than one first stage producer.

If the fuel is suitable for water gas manufacture, then according to the present invention a mixed water gas and distillation gas can be produced for use as a reducing gas in the steam-iron hydrogen plant. A second gas containing appreciable quantities of nitrogen can be made from the devolatilised fuel in the lower part of the generator during the normal blow period of the water gas generator or during the run period by using a mixture of air and steam, and can be drawn off at a lower level.

Alternatively, the water gas generator may be operated to produce a mixture of water gas and distillation gas and sufficient carbon may be withdrawn with the ashes that this can be gasified in a second generator operating on the producer gas process to yield a gas with appreciable quantities of nitrogen and low in methane. This latter gas after being subjected to the water gas shift reaction can be mixed, either before or after the removal of the bulk of the carbon dioxide, with the hydrogen from the steam-iron hydrogen plant.

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685,962 COMPLETE SPECIFICATION
1 SHEET This drawing is a reproduction of the Original on a reduced scale.

Fig. 1.

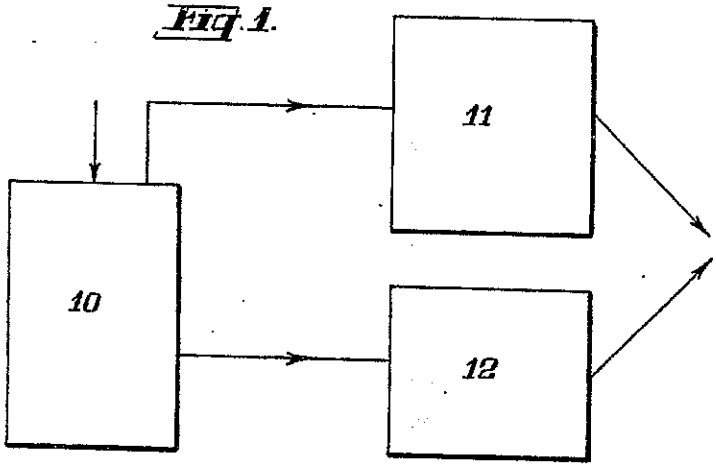

Fig. 2.