(12) UK Patent Application (19) GB (11) 2 021 635 A

(21) Application No 7917529
(22) Date of filing 21 May 1979
(23) Claims filed 21 May 1979
(30) Priority data
(31) 2822862
(32) 26 May 1978
(33) Fed. Rep. of Germany (DE)
(43) Application published
5 Dec 1979
(51) INT CL^2
C01B 2/14
(52) Domestic classification
C5E AL
(56) Documents cited
GB 803234
(58) Field of search
C5E

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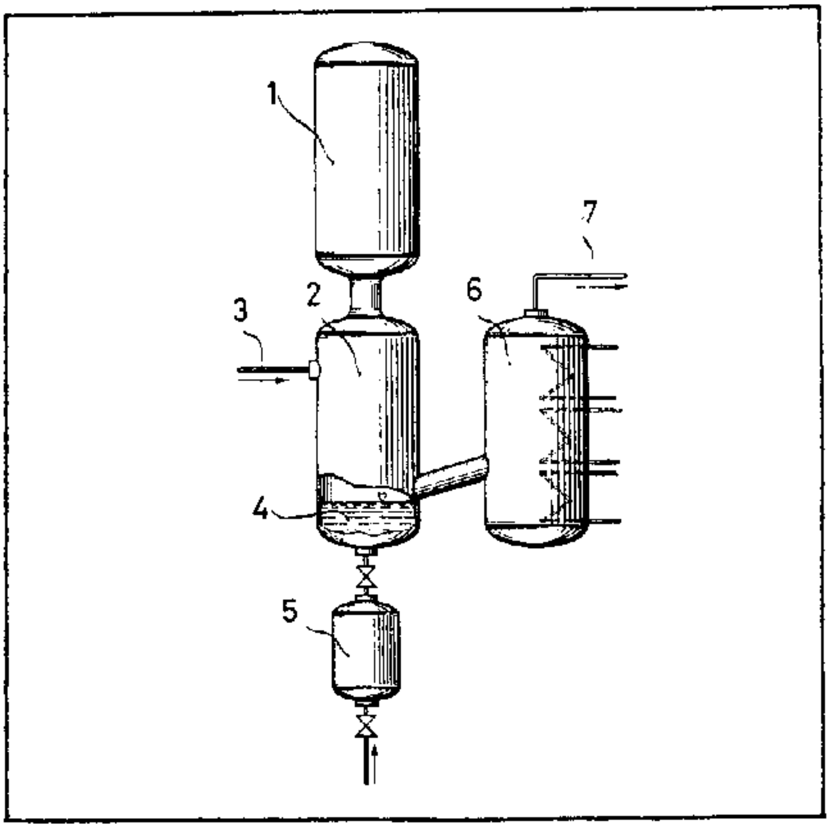
(54) Production of Gas Mixtures Containing Hydrogen and Carbon Monoxide via the Endothermic Partial Oxidation of Organic Compounds

(57) A gaseous mixture containing hydrogen and carbon monoxide is made by endothermic partial oxidation of one or more organic compounds with steam and/or carbon dioxide at a temperature of 900 to 1000°C and a pressure of up to 200 bar. The thermal energy required for the partial oxidation is obtained from the gasification of carbonaceous ash-forming fuels with oxygen in the presence of steam. The hydrogen and carbon monoxide are produced, in the partial oxidation, at a temperature above the melting point of the ash produced in the gasification.

Apparatus for carrying out the process of the invention comprises a gasification reactor (1), a separating chamber (2) connected to the gasification reactor and providing a water bath (4), a lock (5) for discharging ash from the water bath, and a convection boiler (6) connected to the separating chamber (2).



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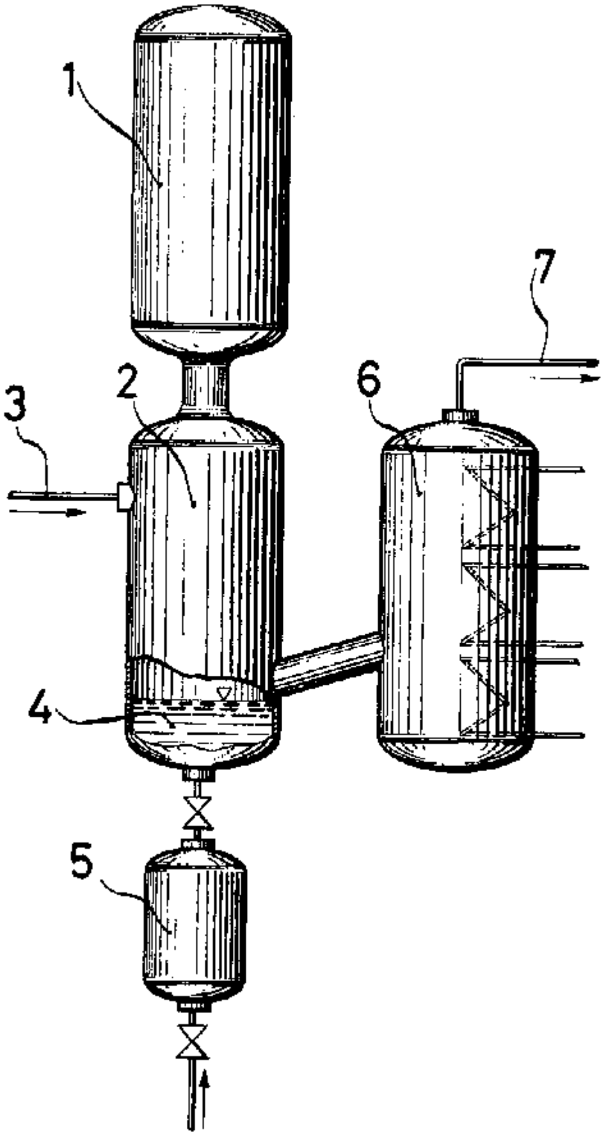

SPECIFICATION

Production of Gas Mixtures Containing Hydrogen and Carbon Monoxide via the Endothermic Partial Oxidation of Organic Compounds

Field of the Invention

The present invention relates to the production of gas mixtures containing hydrogen and carbon monoxide by endothermic partial oxidation (cracking) of organic compounds with steam and/or carbon dioxide at temperatures of ca. 900 to 1500°C and pressures up to 200 bar utilizing thermal energy recovered from the gasification of carbonaceous fuels to carbon monoxide and hydrogen.

Background of the Invention

Endothermic thermal or catalytic cracking of organic compounds, especially hydrocarbons, in the presence of water and/or carbon dioxide to produce carbon monoxide and hydrogen is an established reaction which is operated industrially using various processes. Such a process can be carried out in a tubular reactor, the necessary heat of reaction being supplied via heat transport through the walls of the tubes or in a medium of externally heated solid heat exchanger, material e.g. fine grained solid which is used in a fluidized bed.

The known processes necessitate involved technology and exhibit low thermal efficiency.

In the autothermic cracking of organic compounds, the necessary thermal energy is supplied by the process itself via partial combustion of the organic feedstock. This technique is also technically involved as well as requiring oxygen.

Brief Description of the Invention

An object of the invention is to facilitate the endothermic cracking of hydrocarbons under technically simpler conditions and in more economical manner thereby enabling the cracking of the carbon compounds with an optimal or near optimal consumption of energy and materials in the manufacture of synthesis gas from carbonaceous ash-forming fuels.

In accordance with the present invention, there is provided a process for producing a gas mixture containing hydrogen and carbon monoxide, comprising: endothermic partial oxidation of one or more organic compounds with steam and/or carbon dioxide at a temperature of 900 to 1000°C and a pressure of up to 200 bar; and gasifying one or more carbonaceous ash-forming fuels with oxygen in the presence of steam whereby a gaseous product and liquid ash is produced and to provide thermal energy for said endothermic partial oxidation; said carbon monoxide and hydrogen being produced at a temperature above the melting point of said ash.

By-products and waste products from chemical synthesis can be employed as the organic compounds.

In view of the depletion of oil reserves, the gasification of carbonaceous, ash-forming fuels to synthesis gas, which is a feedstock for many heavy chemicals, is a subject of growing interest.

The following carbonaceous, ash-forming fuels are particularly suitable as feedstock for the process according to the invention: hard coal, lignite, solid and liquid carbon-containing residues e.g. residues from coal hydrogenation and soot from oil gasification processes.

The gasification of carbonaceous feedstocks can take place according to various established processes.

These processes include coal gasification variants, especially those in which pulverized or dust-like coal is employed. The fluidized-bed processes comprise for example, the Winkler, the dust gasification processes according to Koppers-Totzek, Krupp-Koppers or Shell-Koppers, Texaco, Rummel-Otto, Ruhrgas fluidized-bed Babcock and Wilcox/Dupont or Lurgi-Ruhrgas process. Modern multi-step processes are also suitable. A comprehensive survey of the processes can be found in "Chemierohstoffe aus Kohle", editor J. Falbe, Thieme Verlag, Stuttgart (1977).

The gasification of pulverized or possibly dust-like fuels is particularly important at temperatures around 900 to roughly 1600°C, preferably 1100 to 1500°C and pressures up to 200 bar, preferably 5 to 100 bar. Coal is particularly suitable as the pulverized or dust-like solid fuel, as modern mechanized mining technology leads to the production of an increasing amount of dust-like coal. This type of coal can be readily metered and transported using a liquid medium. In addition, almost all types of coal dust, independent of baking tendency and ash content, can be converted into synthesis gas.

The Texaco process will now be described as a typical example of a coal gasification process utilizing finely divided coal. In this process, crushed coal is ground in a mill to a grain size below 0.1 mm and fed to a suspension vessel. On introducing fresh and recycle water, a stable, pumpable slurry results with a solid content between 55 and 60% coal. The coal slurry is then brought up to pressure by means of a pump and fed to the burner at the top of the gasifier.

The coal-water suspension is gasified in the presence of oxygen at temperatures above 1400°C. The reaction chamber is provided with a refractory lining. Cooling of the reactor casing is not required and only the burner is water-cooled.

The liquid ash resulting at high temperatures transported with the gas to a separating chamber where the ash falls into a water bath which is usually an integral part of this chamber. The ash is granulated to a fine slag and discharged via a lock system.

The hot raw gas is then fed to a heat recovery system where it is cooled to roughly 200°C. The heat released in this process is used for steam generation.

The raw gas is further cooled in a scrubber-cooler on injecting water and, in addition, the fine coal and ash particles are removed. The wash water is roughly clarified in a settler and recycled to the scrubber-cooler. The concentrated sludge then flows to the suspension tank via a pump.

As a consequence of the high gasification temperature, the resulting synthesis gas contains only small amounts of tars, thereby eliminating the necessity of using expensive purification steps. Raised pressure, high temperature and a finely divided coal feed lead to a high degree of conversion and relative to the volume of the gasification chamber, they effect a high gasification efficiency. In the majority of plants in which synthesis gas converted into products such as ammonia, Oxo compounds, methanol or products from the Fischer-Tropsch synthesis or the coal hydrogenation and which operate under pressure, a considerable part of the investment required for the compression can be saved on gasifying carbonaceous, ash-forming fuels under pressure. Compared to the established coal gasification processes in which lumpy coal is employed or which operate under normal pressure, the pressure gasification of finely divided coal permits a considerable saving in the manufacturing costs of synthesis gas.

A requirement for the technically smooth and economic operation of the pressure gasification using carbonaceous, ash-forming fuels of high thermal efficiency is a rapid cooling and separation of the mixture from the synthesis gas. The latter leaves the reactor at a temperature of 1100 to 1500°C and the light liquid ash droplets are deposited on lowering the temperature below the ash-melting point. In this way, the synthesis gas is freed from fine ash. The ash is separated in the usual manner for example by quenching, immersion, feeding the total gas stream through a water bath or cooling with cold recycle gas. A disadvantage of this purification process is the more or less great loss of the heat content of the resulting synthesis gas (entropy loss) and thus, the reduction in thermal efficiency of the total process.

The process of the invention avoids these drawbacks in that an endothermic reaction, namely the partial oxidation of organic compounds with steam and/or carbon dioxide, is used to cool the mixture of synthesis gas and liquid ash. This causes the ash to be deposited in the solid state.

In accordance with the invention on leaving the gasified the raw synthesis gas is immediately brought into contact with the organic compounds to be cracked with steam and/or carbon dioxide i.e. preferably in the above-mentioned separation chamber which is constructed as a mixing and separating chamber.

With the process of the invention, it is possible to conduct the gasification of solid or liquid fuels, preferably under pressure, with optimal heat recovery in the waste heat system whilst utilizing the highest possible temperature gradient. There is no blockage or baking in the units which are located after the gasifier, especially in the apparatus for recovering the waste heat. The endothermic reaction of the charge consisting of one or more organic compounds has a cooling effect on the synthesis gas and the light liquid ash. In this manner, a temperature below the ash melting point is reached leading to a deposition of solid ash particles. In addition, the process of the invention leads to the formation of an increased amount of synthesis gas as carbon monoxide and hydrogen result from the endothermic reaction between the organic compounds with water or carbon dioxide.

Hydrocarbons or oxygen-containing compounds are particularly suitable as organic compounds to be converted into carbon monoxide and hydrogen via the endothermic partial oxidation with steam or carbon dioxide. Some examples are methane, ethane, ethylene, propane, propylene, butane, butylenes, methanol, ethanol, propanol, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, acetone, methyl ethyl ketone, diethyl ketone, dipropyl ketones, dimethyl ether, methyl ethyl ether, diethyl ether, propyl formate, butyl formate, formic acid, acetic acid, propionic acid and phenols (aromatic hydroxy compounds). They are reacted either alone or as a mixture of any quantitative and qualitative content.

This summary shows that the endothermic cracking is particularly suitable for the by-products of those syntheses where synthesis gas is used as feedstock.

For example, in the Fischer-Tropsch synthesis lower hydrocarbons or oxygen-containing compounds are obtained as by-products. Ethers and other oxygen-compounds are formed during the methanol synthesis, while branched aldehydes and hydrocarbons result as by-products of the olefin hydroformylation.

Thus, the combination of the gasification with a chemical synthesis is of particular interest. If the non-required or undesired by-products are recycled on removal from the synthesis stage to the mixing and separating stage of the gasifier to produce hydrogen and synthesis gas, then the yields relative to the carbon feed and the thermal efficiency of the combined processes will be markedly increased.

The Fischer-Tropsch synthesis can be taken as an example. The plant consists of a synthesis gas production unit, the actual Fischer-Tropsch synthesis and the stage for processing the products. Control of the process as well as the total yield of valuable products and the thermal efficiency can be markedly improved when, in accordance with the process of the invention, the undesired low boiling by-products of the synthesis, e.g. methane as well as C_2^- and part of the C_3 hydrocarbons, are recycled with water and/or carbon dioxide to the mixing and separation zone of the gasifier where they are converted via an endothermic reaction to carbon monoxide and hydrogen. While the thermal efficiency of the combined coal gasification, synthesis and final processing steps (including the energy requirements of the conventional process) i.e. without recycling the Fischer-Tropsch by-products, amounts to roughly 44%, the thermal efficiency of the process of the invention increases to roughly 52% on recycling the by-products. There is a similar situation with oxygen-containing by-products of the Fischer-Tropsch synthesis, in particular with lower aldehydes and alcohols.

Utilizing the heat content of the synthesis gas leaving the gasifier, which can be at a temperature up to 1500°C, increases not only the yield of valuable products on cracking the worthless by-products to carbon monoxide and hydrogen but also considerably simplifies operation of the process. The endothermic cracking of the carbon-containing compounds can still proceed at a sufficient rate at only 900°C. The advantage of this *in situ* cooling with a simultaneous increase in yield can be so great that, for example, in the case of the Fischer-Tropsch synthesis, the carbon monoxide component of the residual gas is converted into methane which can be readily separated from nitrogen and, in accordance with the process of the invention, be then recycled to the gasification stage.

Similar positive results are achieved with all syntheses with carbon monoxide or a synthesis gas feedstock or in hydrogenation processes. The significance of the invention is therefore not limited to the combination of synthesis gas production with the Fischer-Tropsch-synthesis. It also encompasses in the same way the combination of synthesis gas production with methanol synthesis, Oxo synthesis or other processes which are based on a carbon monoxide or a carbon monoxide and hydrogen feed. The same applies to processes for the hydrogenation of coal under pressure where the hydrogen for the hydrogenation is produced by partial oxidation of fuels especially coal or solid-containing high boiling hydrocarbon fractions which are obtained from the coal hydrogenation. It is also advantageous to recycle the lower hydrocarbons or phenols from the hydrogenation process or from the make-up stages of the hydrogenation process to the thermal cracking.

It is particularly worth mentioning that, the process according to the invention, does not merely permit the utilization of the by-products from chemical synthesis but also the use of carbon dioxide, which always results from the autothermic gasification of fuels.

. The endothermic cracking of organic compounds can occur at temperatures as low as 900°C. Thus, the quantity of the organic compounds and therefore also the quantity of water and/or carbon dioxide is determined by the temperature of the synthesis gas leaving the reactor. For each gram-atom of carbon of the organic compound, at least 3 moles, usually 4 to 6 moles, of water and/or carbon dioxide are introduced.

Brief Description of the Drawing

The accompanying drawing shows diagrammatically an apparatus for carrying out a process according to the invention.

Description of Preferred Embodiment

The apparatus shown in the drawing is suitable for conducting the process according to the invention. This apparatus comprises a gasifier 1 connected to a mixing and separating chamber 2. Compounds to be endothermally cracked are fed to the mixing and separating chamber 2 through a pipe 3. In order to avoid deposition of soot at the feeding section, steam and/or carbon dioxide is introduced together with the compounds to be endothermally cracked. It is particularly advantageous to preheat the components to be endothermally cracked together with steam and/or carbon dioxide before they enter the mixing and separating zone. Due to the heat consumption in the mixing and separating chamber 2, light liquid slag droplets solidify and are deposited in a water bath 4. The ash in then removed through an ash lock 5. At this stage the hot synthesis gas, which is virtually free of ash particles, is fed to a conventional convection boiler 6 connected to the mixing and separating chamber 2. These measures ensure that no deposits occur in the convection boiler which would reduce the heat transfer or cause erosion.

The extent of the increase in thermal efficiency and yield of value products in connected plants, which according to the invention consist of gasification and synthesis units, depends on the prevailing conditions, in particular on reaction conditions, synthesis products and the efficiency of the heat and product recovery plants.

Preferred embodiments of the invention may be summarized as follows:

1. Process for the production of a gas mixture containing hydrogen and carbon monoxide via the endothermic partial oxidation of organic compounds with steam and/or carbon dioxide at ca. 900 1000°C and pressures up to 200 bar. The process is characterized by the fact that the thermal energy required for the partial oxidation is obtained from the sensible heat of the carbon monoxide/hydrogen mixture resulting from the gasification of carbonaceous ash-forming fuels with oxygen or oxygen-containing gas mixtures in the presence of steam. The resulting carbon monoxide and hydrogen are produced at temperatures above the ash melting points either at pressures up to 200 bar or at atmospheric pressure. By-products and waste products from chemical syntheses are suitable organic compounds.

2. Process according to Summary 1 characterized by the fact that finely divided coal is employed in the gasification as the carbonaceous ash-forming fuel.

3. Process according to Summaries 1 and 2 characterized by the fact that the gasification is conducted at 1100 to 1500°C and 5 to 100 bar.

4. Process according to Summaries 1 to 3,

characterized by the fact that the endothermic partial oxidation of the organic compounds ensues in mixing and separation zone situated after the gasification zone.

5. Process according to Summary 4, characterized by the fact that the compounds to be endothermally cracked are preheated together with steam and/or carbon dioxide before entering the mixing and separating zone.

6. Process according to Summaries 1 to 4, characterized by the fact that saturated or unsaturated hydrocarbons with 1 to 3 carbon atoms are employed as the organic compounds.

7. Process according to Summaries 1 to 4, characterized by the fact that the products of the Fischer-Tropsch, methanol or Oxo synthesis can be employed as the organic compounds.

8. Apparatus to conduct process according to Summaries 1 to 7, said apparatus consisting of a gasification reactor (1), a connected mixing and separating chamber (2), a water bath (4) for precipitation and a lock (5) for discharging the ash and a convection boiler (6).

Claims

1. A process for producing a gas mixture containing hydrogen and carbon monoxide, comprising: endothermic partial oxidation of one or more organic compounds with steam and/or carbon dioxide at a temperature of 900 to 1000°C and a pressure of up to 200 bar; and gasifying one or more carbonaceous ash-forming fuels with oxygen in the presence of steam whereby a gaseous product and liquid ash is produced and to provide thermal energy for said endothermic partial oxidation; said carbon monoxide and hydrogen being produced at a temperature above the melting point of said ash.

2. A process according to claim 1, wherein the carbonaceous ash-forming fuel is finely divided coal.

3. A process according to either preceding claim, wherein the gasification is conducted at a temperature of 1100 to 1500°C and a pressure of 5 to 100 bar.

4. A process according to any preceding claim, wherein the gasification is carried out in a gasification zone, the endothermic partial oxidation is carried out in a mixing and separating zone, and products of the gasification are fed from the gasification zone into the mixing and separating zone.

5. A process according to claim 4, wherein said one or more organic compounds are heated together with steam and/or carbon dioxide before entering the mixing and separating zone.

6. A process according to any preceding claim, wherein said one or more organic compounds comprise one or more saturated or unsaturated hydrocarbons having 1 to 3 carbon atoms in the molecule.

7. A process according to any preceding claim, wherein said one or more organic compounds comprise one or more products of the Fischer-Tropsch, methanol or Oxo synthesis.

8. A process according to claim 1, substantially as described herein.

9. An apparatus for carrying out a process according to claim 1, comprising: a gasification reactor; a separating chamber connected to the gasification reactor and providing a water bath; a lock for discharging ash from the water bath; and a convection boiler connected to the separating chamber.

10. An apparatus according to claim 9, substantially as described herein with reference to and as illustrated in the accompanying drawing.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.