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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide with the Simultaneous Production of Town Gas

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The invention relates to a process for the hydrogenation of carbon monoxide with the simultaneous production of a gas, such as town gas, of high calorific value.

The advantages of the gasification under pressure of solid fuels, such as coal with pure oxygen and with the addition of steam are known. This pressure gasification yields a gas which is almost free from nitrogen and which is very rich in hydrogen. It was this richness in hydrogen which prevented pressure gasification from being directly applied to the production of synthesis gas for the Fischer-Tropsch synthesis. Some of the advantages of pressure gasification have, however, been employed for the production of synthesis gas for the Fischer-Tropsch synthesis by adding carbon dioxide to the gasifying medium and by using gas recycling. In this process a part of the carbon dioxide is decomposed into carbon monoxide thereby changing the ratio of carbon monoxide to hydrogen in the product from the pressure gasification from 1:2 to 1:1.4—1:1.2. These conditions of operating the pressure gasification are, however, not the optimum; moreover, they yield a gas having a high content of carbon dioxide, which content must be lowered or removed before the gas is used in the synthesis.

It has now been found that the pressure gasification may be advantageously carried out in the conventional manner, that is to say, without the addition of carbon dioxide to the gasifying medium, to the production of synthesis gas for the Fischer-Tropsch synthesis process whilst a tail gas of high calorific value suitable for use as town gas or long-distance gas, is recovered from the synthesis.

According to the invention, a process for the hydrogenation of carbon monoxide with the simultaneous production of a gas of high calorific value suitable for use as town gas or long-distance gas comprises subjecting a carbon-containing solid fuel, such as coal, to pressure gasification with oxygen and steam without the addition of carbon dioxide, purifying the carbon monoxide and hydrogen containing gas so obtained by freeing it from sulphur compounds and by reducing its content of carbon dioxide, reducing the carbon monoxide content of the synthesis tail gas, without removing the carbon dioxide, by converting a part of the tail gas in a water-gas shift reaction, and mixing the converted part of the tail gas with the unconverted part of the tail gas to yield a gas of high calorific value.

The tail gas of the synthesis is somewhat rich in carbon monoxide and the carbon monoxide content of the tail gas is reduced, preferably to below 10% or to below 8%. This is achieved by converting the carbon monoxide in a part of the tail gas with steam, that is to say subjecting the carbon monoxide to the water gas shift reaction, and mixing the converted part with the unconverted part of the tail gas. It has been found convenient for fine adjustment of the heating value of the synthesis tail gas, to divert a small part of the synthesis gas directly to the conversion step without passing it through the synthesis reactor.

In carrying out the process of the invention, the conventional solid fuels suitable for pressure gasification, such as brown coal or non-caking coal, are used as the starting materials. These fuels are gasified under pressure with oxygen and steam, but without the addition of carbon dioxide. The pressure to be used is determined, on the one hand, by the solid fuel and, on the other hand, by the composition desired of the town gas to be obtained as the finished product and consequently of the synthesis gas. In general, pressures of 10—40 atmospheres and preferably of 20—30 atmospheres are used. As is known, the ratio of hydrogen to carbon monoxide in the gas from the pressure gasification increases as the pressure of the gasification increases. When using the preferred pressure conditions a gas is obtained the $H_2:CO$ ratio of which is 2.5 to 3:1 according to the solid fuel used.

In this presure gasification, a gas is obtained the nitrogen content of which is low but the carbon dioxide content of which is too high for the synthesis. This gas is largely freed from carbon dioxide and is freed to synthesis purity from organic and inorganic sulphur compounds, cyanogen compounds, gum and other admixtures harmful to the synthesis catalyst. For this purpose, the known purifying methods may be used. It is advantageous so to select the conditions of the purification that a gas is obtained which contains less than 2% of carbon dioxide and preferably 0.5—1% of carbon dioxide. Particularly good results are obtained by purification with low molecular weight alcohols, especially methanol, ethanol or mixtures thereof, at low temperatures of −30° C. to −50° C., it being conveninent to effect this purification under the same pressure as that used in the pressure gasification.

After this purification, a gas is obtained which, for example, contains 61.0% H_2, 23.5% CO, 14.0% CH_4, 0.5% CO_2 and 1.0% N_2. The ratio of $H_2:CO$ in this gas is 2.6:1. This gas is too rich in hydrogen to allow a complete working up of the carbon monoxide and hydrogen, in the carbon monoxide hydrogenation, in the ratio mentioned above. Therefore, it would not be fully utilizable as pure synthesis gas. On the other hand, this gas has a heating value which, for town gas and even more for long-distance gas, is too low. Both of these disadvantages may be avoided in accordance with the invention by combining the Fischer-Tropsch synthesis with the production of town gas or long-distance gas with the conversion of a part of the synthesis tail gas. Care should be taken in the synthesis to obtain a sufficiently high consumption of carbon monoxide relative to hydrogen in order that the content of carbon monoxide in the synthesis tail gas may be as low as possible. On the other hand, the consumption of carbon monoxide in the synthesis should not be too high, otherwise the increased formation of carbon dioxide in the synthesis would necessitate scrubbing the tail gas for the removal of all or part of the carbon dioxide.

Of the various methods of operating the synthesis a one-stage synthesis over an iron catalyst has been found to be particularly advantageous. Particularly suitable catalysts are those which, in addition to iron, contain silicic acid (SiO_2) and alkali and, to the usual extent, copper or other activating metals. The silicic acid and the alkali are conveniently incorporated in the catalyst as potassium silicate using 20 to 25 parts of SiO_2 for every 100 parts of iron. For the removal of the excess alkali which may thereby be introduced, the catalyst is treated during its preparation with such a quantity of nitric acid that a $K_2O:SiO_2$ ratio of about 1:4 to 1:5 remains in the catalyst mass. In general, no supporting or carrier materials or only small amounts of such materials are contained in the preferred catalysts. In certain circumstances, however, it is advantageous to incorporate only so much potassium silicate as to give the catalyst the alkali content which is desired and to incorporate the remainder of the SiO_2 content as SiO_2 of another type such as in the form of an activated bleaching earth or clay, such as a Filler's earth, rather than as alkaline-metal silicate. This will eliminate the necessity for the nitric acid wash. The best results are obtained with catalysts such as are described and claimed in Specification No. 679,785 and in Application No. 8322/52 (Specification No. 702,246).

It is convenient to effect the synthesis under the same pressure as that used in the pressure gasification and with a high loading of the catalyst, that is to say, with a high throughput of the synthesis gases, for example, with a load of 400—1000 volumes of synthesis gas per volume of catalyst per hour.

The tail gas is conveniently recycled using a recycle ratio of 1:0.5 to 1:3.5 (fresh synthesis gas:recycle gas).

The synthesis conditions set forth above and particularly the high catalyst load necessitate the synthesis being carried out in reaction tubes of large volume. Thus, reaction tubes of more than 5 metres in length, preferably of 10—12 metres length, and of more than 20 mm. diameter, preferably of 30—80 mm. diameter, are used according to the invention.

The exit gas from the synthesis reactor, in which exit gas normally liquid synthesis products are still contained, is cooled by heat exchange with the synthesis gas and is then passed through a condenser in which the normally liquid synthesis products, such as hydrocarbons, are condensed and which are combined with the liquid products withdrawn from the synthesis reactor. The off-gas from the condenser is subjected to an oil scrubbing to wash out gaseous hydrocarbons. This results in a tail gas which contains, for example, 53.4% H_2, 10.1% CO, 28.7% CH_4, 5.3% CO_2, 0.6% C_2 hydrocarbons and 1.9% N_2. Accordingly, the $H_2:CO$ ratio in this gas is higher than 5:1.

The carbon monoxide content of this tail gas is reduced by converting part of the carbon monoxide. For example, approximately one fourth of this gas may be subjected to the conversion (water gas shift reaction) resulting in a conversion product which contains 56.8% H_2, 2.0% CO, 26.6% CH_4, 12.3% CO_2, 0.6% C_2 hydrocarbons and 1.7% N_2. By mixing the converted part of the tail gas with the remaining, unconverted, part of the tail gas, a gas is obtained which contains 54.3% H_2, 7.9% CO, 28.2% CH_4, 7.2% CO_2, 0.6% C_2 hydrocarbons and 1.8% N_2. The heating value of this gas is 523 B.Th.U./standard cubic foot.

In general, it has frequently been found desirable to subject from $^1/_5$ to $^1/_3$ of the total tail gas to the conversion.

The conversion with steam of the carbon monoxide contained in a part of the tail gas, is advantageously effected in two stages in the presence of an iron catalyst, or in the presence of a nickel or cobalt catalyst, with the production of carbon dioxide and hydrogen. When an iron catalyst is used, it is generally advantageous to effect the conversion under elevated pressure. If the converted gas is to be transmitted over long distances, the pressure used in the conversion may advantageously be equal to or greater than the pressure at which the gas is to be transmitted. When the converted gas is to be used as town gas, the conversion is advantageously carried out under pressure at which the town gas network is operated, for example, 500 to 1000 mm. of water.

What we claim is:—

1. A process for the hydrogenation of carbon monoxide with the simultaneous production of a gas of high calorific value suitable for use as town gas or long-distance gas, which comprises subjecting a carbon-containing solid fuel, such as coal, to pressure gasification with oxygen and steam without the addition of carbon dioxide, purifying the carbon monoxide and hydrogen containing gas so obtained by freeing it from sulphur compounds and by reducing its content of carbon dioxide, subjecting the purified gas to the Fischer-Tropsch synthesis reaction, reducing the carbon monoxide content of the synthesis tail gas without removing the carbon dioxide by converting a part of the tail gas in a water-gas shift reaction, and mixing the converted part of the tail gas with the unconverted part of the tail gas to yield a gas of high calorific value.

2. A process according to claim 1, in which a part of the purified synthesis gas is passed directly to the conversion stage, to adjust the heating value of the tail gas.

3. A process according to claim 1 or claim 2, in which the gasification is effected under a pressure of 10—40 atmospheres.

4. A process according to claim 3, in which the pressure is in the range 20—30 atmospheres.

5. A process according to any of claims 1 to 4, in which the gas from the pressure gasification is purified by treatment with an alcohol of low molecular weight at a low temperature, whereby inorganic and organic sulphur compounds, cyanogen compounds, carbon dioxide and other harmful impurities are removed to such an extent as to avoid poisoning of the Fischer-Tropsch catalyst.

6. A process according to claim 5, in which the purification is carried out under the pressure used in the step of pressure gasification.

7. A process according to any of claims 1 to 6, in which the purified synthesis gas contains less than 2%, preferably 0.5—1%, of carbon dioxide.

8. A process according to any of claims 1 to 7, in which the synthesis is carried out under such conditions that the H_2:CO ratio of the tail gas is greater than that of the synthesis gas.

9. A process according to any of claims 1 to 8, in which the Fischer-Tropsch synthesis is carried out in the presence of an alkali-containing iron catalyst containing 20—25 parts of SiO_2 per 100 parts of iron, the ratio of alkali-metal oxide (calculated as K_2O) to SiO_2 having a value of from 1:4 to 1:5, the catalyst being unsupported or containing only small amounts of a supporting material.

10. A process according to any of claims 1 to 8, in which the Fischer-Tropsch synthesis is carried out in the presence of a catalyst described and claimed in Specification No. 679,785 or in Application No. 8322/52 (Specification No. 702,246).

11. A process according to claim 9 or claim 10, in which the catalyst contains copper and/or other activating metals in the usual amounts.

12. A process according to any one of claims 1 to 11, in which the Fischer-Tropsch synthesis is carried out with a gas throughput of more than 100 volumes of gas per volume of catalyst per hour.

13. A process according to claims 12, in which the gas throughout lies in the range 400—1000 v/v/hr.

14. A process according to any of claims 1 to 13, in which the synthesis is effected at the same pressure as that used in the gasification stage.

15. A process according to any of claims 1 to 14, in which the synthesis is operated with a recycle ratio of from 1:0.5 to 1:3.5.

16. A process according to any of claims 1 to 15, in which the synthesis is effected in reaction tubes having a length greater than 5 metres and a diameter greater than 20 mm.

17. A process according to claim 16, in which the tubes are from 10 to 12 metres in length and from 30 to 80 mm. in diameter.

18. A process according to any of claims 1 to 17, in which exit gas from the synthesis, after being passed in indirect heat exchange with the synthesis gas, is cooled for the removal of liquefiable hydrocarbons and subjected to an oil wash or scrubbing for the removal of gaseous hydrocarbons to yield the tail gas, the tail gas being then divided into two streams, the smaller of which, preferably constituting from $^1/_5$ to $^1/_3$ of the total tail gas, is subjected to the water gas shift reaction and is mixed with the untreated part of the tail gas.

19. A process according to any of claims 1 to 18, in which the carbon monoxide of the tail gas is reduced to a value below 10% by the conversion.

20. A process for the hydrogenation of carbon monoxide with the production of a gas suitable for use as town gas, substantially as hereinbefore described.

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