RESERVE COPY

PATENT SPECIFICATION

Application Date: Dec. 21, 1939. No. 32671/39.

536,843

Complete Specification Accepted: May 29, 1941.

1680

COMPLETE SPECIFICATION

Process for the Production of Hydrocarbons by Conversion of Carbon Monoxide with Hydrogen

I, Harold Edwin Potts, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention, which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company, of 20, Wassenaarscheweg, The Hague, Holland, a Dutch Company), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a process for the production of hydrocarbons with more than one carbon atom in the molecule by conversion of carbon monoxide with hydrogen.

In this process the initial gases are passed over a catalyst at elevated temperatures and it has hitherto been the general practice to continue the treatment until the initial gases are converted as completely as possible into hydrocarbons. It was previously found after many experiments with different velocities of the initial gases that the best conversion of the initial gases is obtained when working with an amount of initial gas of about 100 cubic metres per cubic metre of catalyst per hour, when working at temperatures between 150 and 350° Centigrade and with catalysts containing cobalt, nickel or iron or mixtures of these metals, if desired, together with additional catalytic materials, such as thorium oxide and magnesium oxide, and carriers, such as diatomaceous earth, pumice stone and silica gel.

It has already been proposed in order to increase the yield of hydrocarbons with more than one carbon atom in the molecule that is the amount of these products per cubic metre of carbon monoxide and hydrogen, to work in two or more conversion stages in series and to completely or partially remove the hydrocarbons formed from the reaction products after each stage.

In the first stage or stages an incomplete conversion of the mixture of carbon monoxide and hydrogen into hydrocarbons is carried out, and only in the last stage the residuum of carbon monoxide and hydrogen is completely converted, if desired.

According to this proposal the specific throughput of the initial gases based on the total amount of catalyst, that is the throughput expressed as volume of initial gas per total volume of catalyst per hour, was, however, not different from the specific throughput used when working in a single stage.

According to the present invention when working in stages with complete or partial removal of the hydrocarbons formed in such stage, the throughput of the initial gas per cubic metre of catalyst is maintained substantially the same in each of the stages and is such that further increase in the throughput does not give a substantial increase in the amount of the hydrocarbons desired produced per volume of catalyst per hour.

When working under conditions giving the optimum output of hydrocarbons with more than one carbon atom in the molecule generally also the optimum output of liquid products is obtained.

When increasing the throughput of the initial gases in accordance with the present invention in all stages of the process to the multiple of the throughput which was hitherto usual, the yield of the desired products, calculated on the amount of gas introduced, decreases but the output of these products per hour based on the amount of catalyst, however, increases up to a certain limit. When still further increasing the gas throughput the output of the desired products again slightly decreases.

When working under conditions giving the optimum output small alterations in the throughput employed do not result in a substantial change in the output and therefore even with small variations in the supply of gas, such as may occur in practical operation, a constant of desired products is obtained. The gas throughput at which the optimum outputs based on the amount of catalyst is

[*Price* 1/-]

obtained, varies with the catalyst activity, the temperature, pressure and design of the apparatus. Generally, throughputs of 200 to 600 cubic metres per cubic metre of catalyst per hour give the desired results and preferably 3 or more stages are used.

When working in several stages with the above-mentioned throughputs, the amount of catalyst to be used in order to obtain certain output of desired products can be considerably decreased compared with the method of carrying out the conversion in a single stage or in several stages with the throughputs hitherto usual. The liquid hydrocarbons formed in the individual stages are suitably separated after each stage from the outgoing products by cooling. The gases coming from the first conversion vessel which have been freed from liquid constituents (for example, by cooling to about 30° Centigrade) may be passed, in accordance with the decrease in volume which has taken place, through a smaller reaction vessel, and the third vessel may again be smaller than the second one, and so on. Each of the vessels can be divided into any desired number of single spaces connected in parallel.

It is also possible to pass the hydrocarbons, which have been formed in one of the reaction vessels, partly together with the gases which have not been converted into the next reaction vessel.

The gases can also be recirculated, make up gases being added.

In general the time of contact of the reaction gases in a single reaction space is more than 6 seconds, even when recycling part of the gases.

In the individual reaction vessels the throughput can also be increased by an addition of fresh gas before the entry of the main gas stream into the vessel or at one or more points between the entry and exit of the main gas stream. In this case it is not necessary that the second and further reaction vessels be of smaller size but it is then possible to work with vessels of the same size.

The cooling of the reaction vessels, which is necessary in view of the exothermic reaction is preferably carried out by means of indirect heat exchange with a cooling agent which is in contact with the walls of the reaction vessels. The usual cooling media such as, for example, boiling water or oil under a suitable pressure can be employed. An additional cooling may be obtained by adding to the substances which are being converted a cold gas, for example, cold hydrogen or cold carbon monoxide or mixtures thereof or a cold inert gas.

The process may be carried out under normal or elevated pressure, for example, a pressure between 10 and 30 atmospheres, or also under higher pressures, such as 100 atmospheres or more. The reaction temperatures are between 150 and 350° Centigrade and preferably between 160 and 250° Centigrade. The process is not limited to any design of the conversion vessels. The usual catalysts may be employed, for example, those catalysts prepared by precipitation, sintering, melting or the like.

The following Examples further illustrate the nature of the present invention and in what manner the same can be carried out in practice but it should be understood that the invention is not limited to the said Examples.

EXAMPLE 1.

A gas consisting of 28 per cent. of carbon monoxide, 57 per cent. of hydrogen and 15 per cent. of accompanying gases is passed under 10 atmospheres and at 195° Centigrade over 1.17 cubic metres of catalyst consisting of 85 parts of cobalt and 15 parts of thorium oxide on 85 parts of diatomaceous earth in an amount of 110 cubic metres per cubic metre of catalyst per hour. The total volume of gas passed over is therefore 128.7 cub. metres per hour. A yield is obtained of 100 grams of liquid hydrocarbons per cubic metre of the mixture of carbon monoxide and hydrogen and thus 12.87 kg. of liquid products are obtained per hour. When the amount of initial gas is increased to 400 cubic metres of gas per cubic metre of catalyst per hour, then the yield amounts to 40 grams per cubic metre of the mixture of carbon monoxide and hydrogen and thus 18.72 kg. of liquid product are obtained per hour.

In the first case per 110 cubic metres of fresh gas and per cubic metre of catalyst 9.35 kilograms of liquid product are obtained, in the second case per 400 cubic metres of fresh gas and per cubic metre of catalyst 13.6 kilograms of liquid products are obtained. In the first case it is therefore necessary to use 45 per cent. more of the catalyst for obtaining the same output.

The gas remaining in the second case has, after being freed from the liquid products, a volume of 79 per cent. of that of the fresh gas. It is passed with a throughput of 400 cubic metres per cubic metre of catalyst per hour through a second reaction vessel, the catalyst space of which amounts to only 79 per cent. of the catalyst space of the first vessel. In this manner a further amount of 12.6 kilograms of liquid products are formed per cubic metre of catalyst.

The gas leaving the second vessel (with a volume of 64 per cent. of that of the fresh gas) is passed, after removal of the liquid constituents, with the same throughput per cubic metre of catalyst through a third reaction vessel, the catalyst space of which amounts to 64 per cent. of that of the first vessel. Hereby a further amount of 11.4 kilograms of liquid product is formed per cubic metre of catalyst.

The gas issuing from the third vessel (with a volume of 53 per cent. of that of the fresh gas) is passed, after removal of the liquid constituents, with the same throughput per cubic metre of catalyst through a fourth reaction vessel, the catalyst space of which amounts to 53 per cent. of that of the first vessel. Hereby a further amount of 10.1 kilograms of liquid products is formed per cubic metre of catalyst.

Altogether in the four vessels 36.22 kilograms of liquid products per hour are obtained per 2.96 cubic metres of catalyst or 12.2 kilograms per cubic metre of catalyst that is 30.5 per cent. more of liquid products than in the first case. To obtain the same quantity of hydrocarbons as in the first case the total catalyst space required in the second case can be 23 per cent. smaller than in the first case.

In both cases the heat generated in the conversion is removed by cooling of the reaction vessels.

Example 2.

A gas containing 28 per cent. of carbon monoxide and 57 per cent. of hydrogen is passed at a temperature of 195° Centigrade and at a throughput of 300 cubic metres per cubic metre of catalyst per hour through a space of 1.18 cubic metres filled with catalyst consisting of 46 per cent. of cobalt, 8 per cent. of magnesium oxide and 46 per cent. of diatomaceous earth, and subsequently, after separation of the liquid constituents formed, through a second vessel of 1 cubic metre filled with the same catalyst. The throughput in the second vessel is then only 261.5 cubic metres of gas per cubic metre of catalyst space compared with 300 cubic metres in the first vessel. The total yield is 10.6 kilograms of liquid products. This illustrates the process hitherto employed. By addition of fresh gas before the second reaction vessel in an amount of 15 per cent. of the gas freed from the liquid constituents coming from the first vessel however in this vessel also the optimum throughput of 300 cubic metres per cubic metre of catalyst space per hour is obtained and thereby an increase of the total yield with 0.6 kilogram is obtained.

In both cases the surplus heat evolved in the conversion is removed by cooling of the conversion vessels.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the production of hydrocarbons with more than one carbon atom in the molecule by conversion of carbon monoxide with hydrogen in stages in series with complete or partial removal of hydrocarbons formed from the reaction products after each stage, characterized in that the throughput of the initial gas per cubic metre of catalyst is maintained substantially the same in each of the stages and is such that further increase in the throughput does not give a substantial increase in the amount of the desired hydrocarbons produced per volume of catalyst per hour.

2. A process as claimed in claim 1, in which in each stage gas throughputs of 200 to 600 cubic metres per cubic metre of catalyst per hour are used.

3. In the process as claimed in either of claims 1 and 2, taking consecutive reaction vessels, the volume of which is decreased in accordance with the decrease in volume of the gases introduced in each stage.

4. A process as claimed in either of claims 1 or 2, working with reaction vessels of a similar size and adding fresh gas before the entry of the main gas stream into the reaction vessel or at one or more points between the entry and exit of the main gas stream.

5. A process as claimed in any of claims 1 to 4 in which make-up gases are added.

6. A process as claimed in any of claims 1 to 5 characterised in that the unconverted gases are recycled.

7. In the process as claimed in any of claims 1 to 6, working in 3 or more stages.

8. Processes for the production of hydrocarbons, substantially as disclosed in the foregoing Examples.

9. Products when obtained in accordance with any of the preceding claiming clauses.

Dated this 20th day of December, 1939.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1941.