PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the Catalytic Synthesis of Hydrocarbons

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America.)

I, CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention 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 improvements in the synthesis of hydrocarbons, and in particular, it relates to methods of improving the yield of hydrocarbons formed when carbon monoxide and hydrogen are reacted together in the presence of a suitable catalyst.

It was known prior to the present invention that liquid hydrocarbons could be synthesized from a mixture of carbon monoxide and hydrogen by contacting the same with a Fischer-Tropsch synthesis catalyst, usually a metal selected from Group VIII of the Periodic System. The most commonly used catalysts are probably cobalt, nickel and iron. At first, the synthesis was carried out in a reactor containing one or more fixed or stationary beds of catalyst, but more recently, at least in experimental units, the synthesis has been carried out employing the so-called fluid solids technique, in which the metallic catalyst in powdered form is suspended in the reactants in the reaction zone during the synthesis process. Whether the process is carried out employing a stationary bed of catalyst contained in a case, or whether the reaction is carried out employing a fluidized catalyst, the ratio of hydrogen to carbon monoxide in the fresh feed is an important consideration and prior investigators have realized this fact. If the hydrogen to carbon monoxide ratio is such that there are 2 mols of hydrogen per mol of carbon monoxide, in the prior practice the gasoline and gas oil fractions contained in the product have usually been paraffinic especially when cobalt catalysts are employed. On the other hand, if the molal ratio of hydrogen to carbon monoxide is about 1 to 1 then the gasoline and gas oil fractions formed in the product are more unsaturated. From the standpoint of manufacturing gasoline of good quality with cobalt catalysts, it is, therefore, desirable to employ, if possible, a 1 to 1 hydrogen to carbon monoxide ratio in the feed gas, for the olefinic character of the product resulting from this type of operation provides a product of good anti-detonation qualities which is more suitable for use as an automotive fuel than the more paraffinic product produced from a synthesis feed gas containing 2 mols of hydrogen per mol of carbon monoxide. On the other hand, if the low ratio of hydrogen to carbon monoxide be employed in the feed gas (say 1 to 1) with cobalt catalyst, the hydrogen is used up long before the carbon monoxide is consumed, and therefore, the gas issuing from the reaction zone will always contain a high percentage of unreacted carbon monoxide, which means that the carbon monoxide will have to be recycled to the reaction zone. Briefly stated, the present improvements provide means whereby there are obtained the advantages of using a 1 to 1 hydrogen to carbon monoxide ratio in the synthesis feed gas but at the same time additional means are provided whereby the consumption of carbon monoxide in its passage through the reaction zone is more complete than in the prior practice, and consequently the need for recycling unreacted carbon monoxide from the product gases or vapors to the reaction zone is substantially decreased. It will be appreciated by those familiar with chemical reactions performed on a commercial scale that it is always more desirable to carry out such a process on a once-through type of process rather than to be required to recycle a large quantity of unreacted material for the reason, among others, that, the capacity of the installation is greatly enhanced the closer one approaches the once-through operation.

A process has already been suggested for the synthesis of unsaturated hydrocarbons, from carbon monoxide and hydrogen utilizing a stationary bed of catalyst. In this process a ratio of less than 2 parts and preferably 0.9—1.5 parts by volume of hydrogen for each part by volume of carbon monoxide is maintained in the reaction zone by adding hydrogen at a plurality of places in such zone. However in such a process, the maintenance of a uniform ratio of carbon monoxide to hydrogen, by the addition of hydrogen is dependent on the rate of diffusion of the gases through the fixed catalyst bed.

My overseas correspondents have now studied data obtained from the experimental operation of hydrocarbon synthesis units employing a fluidized catalyst and have found that it is possible to employ in such a type of operation a substantially 1 to 1 hydrogen to carbon monoxide molal ratio in the original feed gas and at the same time secure the benefits of high carbon monoxide conversion during a single passage through a reaction zone by subsequent addition of hydrogen at spaced points progressively removed from the original entrance point of the synthesis gas mixture to the reaction zone. It has been found that by the use of the fluid solids technique, close control over the proportion of carbon monoxide to hydrogen through the reaction zone may be maintained.

Accordingly the present invention consists of a method of synthesizing hydrocarbons from hydrogen and carbon monoxide which comprises forcing a mixture of hydrogen and carbon monoxide proportioned in the ratio of from 0.7 to 1.3 mols of hydrogen per mol of carbon monoxide once through a dense fluidized mass of powdered synthesis catalyst in a single stage reaction zone maintained under Fischer synthesis conditions of temperature and pressure, permitting the reactants to remain in contact with the catalyst for a sufficient period of time to effect a carbon monoxide conversion approaching 100% of the amount fed to said reaction zone, adding substantially pure supplementary hydrogen at spaced points to the reaction zone in sufficient quantity to maintain the hydrogen to carbon monoxide ratio substantially within the range of from 0.7 to 1.3 mols of hydrogen per mol of carbon monoxide throughout the reaction zone, and recovering from said reaction zone a product containing normally liquid hydrocarbons.

In the accompanying drawing there is shown diagrammatically a fragment of a hydrocarbon synthesis apparatus serving to illustrate a preferred modification of this invention, omitting for the purpose of clarity nearly all accessory apparatus conventionally used in a process of the character described.

Referring in detail to the drawing, 1 represents a synthesis reacting vessel consisting essentially of a cylindrical shell having a convex crown and a conical base, and having disposed therein a grid or screen G through which gases are forced, the screen tending to promote good distribution. A mixture of carbon monoxide in the ratio of about 1 mol of hydrogen per mol of carbon monoxide enters the system through line 10, and is forced upwardly through said screen G into a fluidized mass of powdered catalyst, which catalyst may be composed of cobalt promoted with a relatively small amount of thoria and supported on a suitable spacing agent such as kieselguhr. The catalyst is maintained in the fluidized state by controlling the upward velocity of the gas within the range of from say, 0.25 to 3 feet per second, whereupon a dense turbulent suspension of catalyst in gas is formed. Depending upon the actual mass of catalyst in the reaction zone the dense suspension will have an upper level at some point L above which there is a dilute phase, or in other words, the reacting vessel in this type of operation is usually not completely filled with a dense phase for it is desirable to effect as nearly as possible separation of vapors from catalyst before the former is withdrawn from the reaction zone, all of which was known and appreciated prior to the present invention. The reactants remain resident in the reaction zone for a sufficient period of time to effect the desired conversion, the temperature and pressure being adjusted according to known methods, and eventually the vapors issue through line 13. It is also conventional to dispose in the upper part of reacting vessel 1 a plurality of solids-gas contacting devices, such as centrifugal separators, to separate catalyst fines and entrained coarse particles from the exiting gas. In order to secure substantially complete removal of catalyst from the vapors or gas the vapors may be forced through filters or through one or more electrical precipitators to remove, insofar as possible, the last traces of catalyst from the vapors, whereupon the latter are then delivered to conventional fractional distillation equipment (not shown) to recover the gasoline, gas oil and other products. Since the hydrocarbon synthesis reaction is exothermic, it is usually necessary to provide means for abstracting heat from the reacting vessel and numerous proposals have been made previously for accomplishing this result. Since, however, this phase of the operation is not involved in the present invention, there has also been eliminated a showing in the drawing of conventional cooling means employed in connection with the reacting vessel. And in this same connection, as previously indicated, there has been omitted a showing of pumps, flow meters, valves and other accessory apparatus and equipment in order to focus attention on the novel feature of the invention and to present the same in a simple and understandable manner. Up to this point the description of the process which has been given contains only features which were known and practiced prior to the present improvement.

With respect to the improvements, the same are directed to obtaining maximum conversion of carbon monoxide to desired products in spite of the fact that the original synthesis gas entering through line 10 contains substantially equal molal proportions of carbon monoxide and hydrogen. In order to show the insufficiencies in prior practice there is set forth below the results of two runs made under substantially the same conditions except for the fact that in one of the runs designated Run A, the ratio of carbon monoxide and hydrogen in the gas entering through line 10 is 1 to 1, whereas, in the run, designated Run B, the ratio of carbon monoxide to hydrogen in the feed gas entering through line 10 was about 2 mols of hydrogen per mol of carbon monoxide, and the additional fact that Run A was performed at a temperature some 35° above that employed in Run B. The results set forth in the tabulation below are arranged to indicate what occurred in different sections of the catalyst bed as the synthesis gas passed therethrough as well as to illustrate the overall result:

RUN A
430° F.—102 V/V/Hr.

% of Catalyst Bed	Inlet H_2/CO Ratio	% CO Conversion	Selectivity of CO Converted to Liquid Product, Mols per 100 Mols
0—20	0.9	30	55
20—27	0.6	—	—
27—51	0.4	—	—
51—100	0.2	—	—
0—100	0.9	56	67

RUN B
395° F.—101 V/V/Hr.

% of Catalyst Bed	Inlet H_2/CO Ratio	% CO Conversion	Selectivity of CO Converted to Liquid Product, Mols per 100 Mols
0—18	2.0	27	58
18—26	2.1	—	—
26—50	2.0	—	—
50—100	2.0	—	—
0—100	2.0	99	72

It will be noted from the foregoing runs that in the first 18—20% of the bed, that is to say, during passage of the reactants through the first fifth of the bed the conversion of carbon monoxide and the selectivity of carbon monoxide conversion to liquid product were substantially the same in both runs. It will further be noted, however, that in Run A where the feed gas contains equal mols of hydrogen and carbon monoxide the CO conversion dropped sharply beyond the first fifth of the catalyst bed whereas, in Run B where the ratio of hydrogen to carbon monoxide was 2 to 1 the conversion was maintained throughout the length of the reactor and of the total amount of carbon monoxide fed to the reacting vessel, 99% was converted as against merely 56% in Run A. In Run B, the ratio of hydrogen to carbon monoxide remained essentially constant at about 2 to 1 as synthesis gas passed through the reacting vessel whereas in the case of Run A, the ratio decreased from 0.9 to the inlet to 0.2 at a point about halfway through the reacting vessel. In Run B the overall or total selectivity was 72% as against 67% in the case of Run A. It may be observed that in the first 20% of the bed in Run A the conversion was higher than in an equal portion of the bed in Run B, but this may be expected from the higher temperature employed in Run A. However, the equal selectivity obtained in the case of Run A for the first fifth of the catalyst bed, to that obtained in Run B is unexpected in view of the high temperature in Run A and can only be attributed to the intrinsic desirability of 1 to 1 hydrogen to carbon monoxide ratio in the feed gas.

To maintain the desirable carbon monoxide conversion and selectivity to liquid products, according to the improvements it is proposed to add hydrogen in stages to separated points in the bed and, therefore, referring to the drawing, supplementary hydrogen from line 14 is injected into the bed at spaced points in the dense suspension through lines 15, 16 and 17. Sufficient hydrogen is added to maintain throughout the dense suspension substantially equimolal proportions of hydrogen to carbon monoxide and by this means the conversion of carbon monoxide and hydrogen and also the selectivity of carbon monoxide converted to desired liquid products is maintained at a high level.

In the foregoing description the use of a cobalt catalyst in reactor 1 is referred to, but in so doing it is not intended to impose any limitation on the invention and it is to be understood that instead of cobalt any other Fischer Tropsch synthesis catalyst such as iron or nickel may be used. It will be understood by those familiar with the art that as a matter of commercial operation a certain degree of tolerance may be allowed with respect to the ratio of carbon monoxide to hydrogen in the fresh feed and in the reaction zone and, therefore, good results are obtainable even though the ratio of hydrogen to carbon monoxide is not actually 1 to 1, for this ratio may vary from 0.7/1 to 1.3/1.

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. The method of synthesizing hydrocarbons from hydrogen and carbon monoxide which comprises forcing a mixture of hydrogen and carbon monoxide proportioned in the ratio of from 0.7 to 1.3 mols of hydrogen per mol of carbon monoxide once through a dense fluidized mass of powdered synthesis catalyst in a single stage reaction zone maintained under Fischer synthesis conditions of temperature and pressure, permitting the reactants to remain in contact with the catalyst for a sufficient period of time to effect a carbon monoxide conversion approaching 100% of the amount fed to said reaction zone, adding substantially pure supplementary hydrogen at spaced points to the reaction zone in sufficient quantity to maintain the hydrogen to carbon monoxide ratio substantially within the range of from 0.7 to 1.3 mols of hydrogen per mol of carbon monoxide throughout the reaction zone, and recovering from said reaction zone a product containing normally liquid hydrocarbons.

2. The method set forth in Claim 1 in which the ratio of hydrogen to carbon monoxide maintained throughout the reaction zone is 1 mol of hydrogen per mol of carbon monoxide.

3. The method set forth in Claim 1 in which the catalyst is metallic cobalt.

Dated this 6th day of September, 1946.
D. YOUNG & CO.,
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Chancery Lane, London, W.C.2,
Agents for the Applicants.

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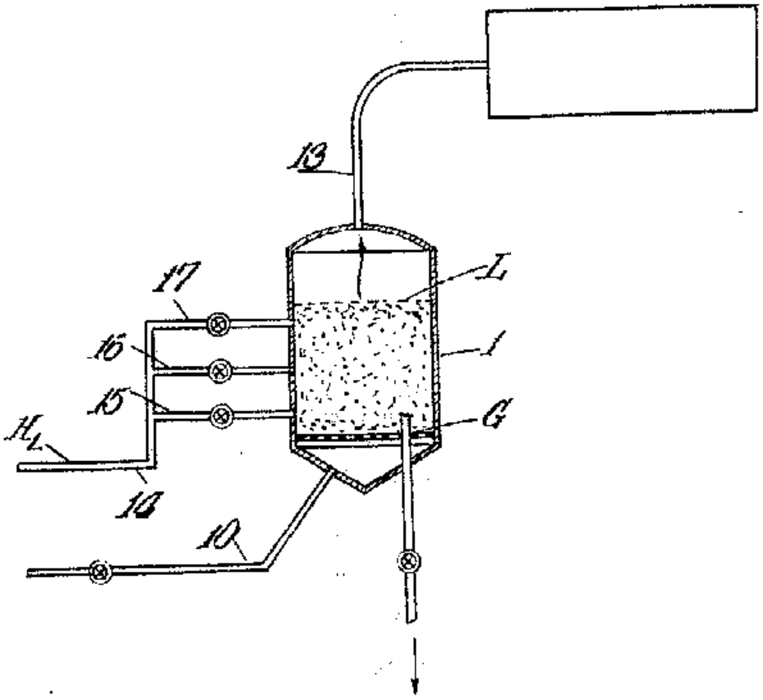
616,499 COMPLETE SPECIFICATION 1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale.]



H.M.S.O. (Ty.P.)