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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Company of Homberg/Niederrhein, Germany, 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:—

The invention relates to a process for the hydrogenation of carbon monoxide.

It is an object of the invention to provide a process for the hydrogenation of carbon monoxide in a liquid medium in the presence of an iron catalyst, whereby the efficiency of the catalyst is increased. The increased activity of the catalyst so obtained gives an increased olefin yield while the formation of methane is repressed.

The advantage of effecting the hydrogenation of carbon monoxide in a liquid medium, in which the catalyst is suspended, over processes which are carried out with a fixed-bed catalyst, lies particularly in the fact that the catalyst, by virtue of the vigorous turbulence in the suspension, is substantially uniformly loaded and, in consequence, has substantially the same temperature throughout the suspension. Moreover, a particularly advantageous dissipation of heat is achieved. Hitherto a uniform loading and the maintenance of a certain or determined temperature constancy constituted a precondition for high catalyst efficiency.

Surprisingly, it has now been found, according to the invention, that in the hydrogenation of carbon monoxide carried out in a liquid medium in the presence of an iron catalyst, the efficiency of the iron catalyst is substantially increased while the olefin content of the synthesis product is considerably increased and the formation of methane is reduced, if the temperature in the catalyst suspension increases in the upward direction by 30°—150° C, preferably by 50°—100° C, whilst the temperature in the gas inlet zone is so low that synthesis does not take place in that zone.

It has been found that the zone in which the temperature is so low as not to permit synthesis to take place, should be adjusted in size or height in accordance with the activity of the catalyst. The more active the catalyst, the larger the zone should be. With highly active catalysts, this zone may even be extended up to half of the catalyst suspension.

The temperature difference or gradient may be attained by reducing the cooling area in the upward direction and/or by providing separate bundles of cooling tubes or the like and/or by insulating the cooling tubes by means of cushions of steam or synthesis gas. The carbon monoxide of the synthesis gas may be converted in one reactor to the extent of over 90%. It is, however, more advantageous to operate the synthesis in several stages, in all of which the temperature difference or gradient provided in accordance with the invention is employed, because then the methane formation will be even less and the CO conversion can be increased to 98%—99%.

Whilst it is known in the hydrogenation of carbon monoxide in the presence of fixed bed catalysts to increase the temperature in the direction of flow of the synthetic gas, the temperature differences used in normal hydrocarbon syntheses being up to 28° C and in methanisation processes up to 40° C, this did not permit any conclusions to be drawn with respect to the hydrogenation of carbon monoxide in a liquid medium, because, in contrast with fixed bed catalysts, the catalyst suspended in the liquid phase is in vigorous turbulent motion during the synthesis. With fixed bed catalysts, the object of increasing the temperature in the direction of flow of the synthesis gas, is to achieve a uniform conversion of the synthesis gas throughout the catalyst layer. In the liquid phase process, a uniform conversion by the catalyst is unobtainable under these conditions; the individual particles of the catalyst fluctuate steadily between a minimum and a maximum value. Moreover, with fixed bed catalysts, the indi-

vidual catalyst particle retains substantially the same temperature, even when the temperature is increased in the direction of flow of the synthesis gas, whereas, in the synthesis carried out in the liquid phase in accordance with the process of the invention, it has constantly to travel through the whole temperature gradient.

The results obtained by means of the invention are surprising. With fixed bed catalysts, the method of the invention would have the result that that part of the catalyst the temperature of which is so low that synthesis does not take place, would always be inactive.

In accordance with the process of the invention, the temperature difference required is much higher than is possible with fixed bed catalysts in gaseous phase operation, unless in such operation it is desired to produce methane or catalysts of different activities are used in a single reactor. However, in liquid phase operation, that is to say, that method of operation to which the invention relates, it is precisely the formation of methane which is reduced by the high temperature difference.

The process according to the invention is illustrated in the following comparative example, in which Run I is carried out in known manner and Run II is carried out in accordance with the invention.

The catalyst used in Runs I and II was prepared in the following manner:—

From an iron nitrate solution of 5% concentration containing 0.2% Cu based on Fe, the metals were precipitated with NH_4OH. After the precipitate had been filtered and washed, 0.5% of K_2CO_3, based on the Fe present, was added to the precipitate and the mixture was dried. The catalyst was then crushed and ground with slack wax (Gatsch). After the grinding operation, the catalyst suspension was diluted with sufficient slack wax so that 1 kilogram of suspension contained 100 grams of Fe.

RUN I.

Run I was carried out under known conditions. 4.5 kilograms of the catalyst suspension hereinbefore described were charged into a reactor which consisted of a tube 5 metres in length and having a diameter of 50 mm., the tube being provided over its entire length with a heating jacket.

After the catalyst suspension had been heated to 280° C whilst nitrogen was passed through, the reactor was switched over to synthesis gas ($H_2 : CO = 2 : 3$). The load first used was 1 normal litre of $CO + H_2$ per gram of Fe per hour and, in dependence upon the CO conversion, was gradually increased to 2.5 normal litres. After a CO conversion of 90% had been attained, the temperature could be reduced to 250° C. After 500 hours of operation, the catalyst suspension had again reached a temperature of 268° C, as shown in the Table hereinafter given. Determination of the yield gave the values given in the Table.

In a parallel test it was found that the catalyst, which with a constant temperature of 268° C achieved a CO conversion of above 90% at 230° C practically ceased to be effective to form any hydrocarbons, although the gas was passed through the whole of the catalyst layer. While approximately 2% of CO_2 was still formed, this was formed by the reaction of the carbon monoxide with water vapour which was present in the synthesis gas.

RUN II.

The conditions under which Run II was carried out were those in accordance with the invention, but were otherwise the same as those of Run I.

4.5 kilograms of the catalyst suspension hereinbefore described were charged into a reactor of the same size as that used in Run I. In order to produce in the catalyst suspension the temperature difference or gradient provided in accordance with the invention, the lowermost 90 cc. were not heated. The remaining part was heated with two separate heating jackets in such a manner that at the gas inlet position, the temperature in the catalyst suspension was from 60° C to 70° C lower than the temperature at the gas outlet position. The operation was started in the same manner as in Run I. After the catalyst suspension, whilst nitrogen was being passed through, had attained a temperature of 215° C at the gas inlet position and a temperature of 282° C at the gas outlet position, the reactor was switched over to synthesis gas ($H_2 : CO = 2 : 3$). The load first used was 1 normal litre of $CO + H_2$ per gram of Fe per hour. In dependence upon the degree of conversion, the load was increased to 2.5 normal litres per gram of Fe. After a CO conversion of 90% had been attained, the temperature was slowly reduced to 261° C at the gas outlet position and to 200° C at the gas inlet position.

After 500 hours of operation, the values given in the following Table were ascertained. It will be understood that the temperature of 232° C at a position 80 centimetres above the gas inlet, was so low that at this position synthesis did not yet take place. The figures in the Table also indicate that, by the process according to the invention, the yield was increased as a result of the lower methane formation, and that the olefin content of the total liquid products was increased.

In Run I, the output of the catalyst amounted to 400 grams of C_{3+} per gram of Fe (400 grams of products containing not less than 3 carbon atoms in the molecule per gram of Fe), and in Run II to 750 grams of C_{3+} per gram of Fe (750 grams of products containing not less than 3 carbon atoms in the molecule per gram of Fe). By the process according to the invention, the efficiency of the catalyst was thus almost doubled.

Run	Temperature in catalyst suspension				CO conversion %	Grams of $C_1 + C_2$ per normal cubic metre of $CO + H_2$	Grams of C_{3+} per normal cubic metre of $CO + H_2$	Olefine content of total liquid product %
	Total suspension °C.	At the gas inlet position °C.	80 cm. above gas inlet °C.	At gas outlet position °C.				
I	268	—	—	—	91.8	21.4	160.4	56.8
II	—	215	232	278	92.1	11.8	170.8	81.2

In Patent No. 752,465 there is described and claimed a method of carrying out the catalytic hydrogenation of carbon monoxide for the production of hydrocarbons containing more than one carbon atom in the molecule with the catalyst suspended in a liquid medium, in which the temperature of the catalyst suspension in the reactor rises to the extent of from 10° C to 100° C. in the direction of flow of the gas.

What we claim is:

1. A method of carrying out the synthesis of hydrocarbons by the hydrogenation of carbon monoxide wherein a synthesis gas containing carbon monoxide is passed upwardly through a liquid medium having an iron catalyst is suspension therein, which comprises maintaining a temperature increase of from 30° C to 150° C in the upward direction in the catalyst suspension, the temperature of the catalyst suspension in the synthesis gas inlet zone being such that no synthesis occurs in that zone.

2. A method according to claim 1, in which the temperature increase in the catalyst suspension is from 50° C to 100° C.

3. A method according to claim 1 or claim 2, in which the temperature in the whole of the lower half of the catalyst suspension is maintained at a level such that no synthesis occurs in the said lower half.

4. A process according to claim 1 or claim 2, in which the temperature in a part of the catalyst suspension disposed immediately above the gas inlet zone and below the mid-level of the catalyst suspension is such that no synthesis occurs in the said part.

5. A method according to any one of the preceding claims, in which the temperature increase in the catalyst suspension is obtained by reducing the area of cooling surfaces in the upward direction and/or by providing several separate cooling systems and/or by insulating the cooling tubes of one or more cooling systems by means of cushions or layers of synthesis gas or other vapour or gas, for example, steam.

6. A method according to any one of the preceding claims, in which the synthesis is operated in two or more stages.

7. A method for the synthesis of hydrocarbons, substantially as hereinbefore described with reference to Run II of the Example.

8. Hydrocarbons whenever produced by the method claimed in any one of the preceding claims.

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