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COMPLETE SPECIFICATION

A Process for the Hydrogenation of Carbon Monoxide

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, Homberg/Niederrhein, Germany, a German Company, 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 and particularly to a method, which is very effective, of carrying out the hydrogenation of carbon monoxide in the presence of a catalyst which is suspended in a liquid medium.

The advantage of carrying out the hydrogenation of carbon monoxide in a liquid medium over a process carried out with a fixed-bed catalyst in the gaseous phase, resides partly in the fact that, due to the high degree of turbulence in the suspension, the temperature of the catalyst is substantially the same throughout. When highly active catalysts are used, it is in some cases impossible completely to avoid the separation or deposition of carbon and the formation of methane and, with such feature or features, a shortening of the active life of the catalysts.

It has now been found that it is possible to extend the active life of the catalysts considerably; to increase the yield in reaction products by reducing the formation of methane, and to further the formation of hydrocarbons boiling in the gasoline range, by increasing the temperature of the catalyst suspension to the extent of from 10°C. to 100°C., and preferably from 20°C. to 50°C., from the gas inlet to the gas outlet. It has been found to be particularly advantageous to distribute the rise in temperature throughout the total height or depth of the catalyst suspension in such manner that the rise in temperature in the lower layer or layers exceeds that in the middle and upper layers.

In large-scale reactors this rise in temperature may be attained by reducing the areas of the cooling surfaces in the direction of gas flow or by providing the cooling system as a number of independent systems the temperatures of which may be adjusted or controlled individually. If necessary or desired, the size or area of the cooling surfaces of the independent systems may vary in such manner that the cooling area decreases in the upward direction, that is to say, in the direction of the gas flow.

The effect obtained by the method according to the invention is extremely surprising and could not be foreseen in any way, since with the predominant formation of gasoline hydrocarbons a relatively high formation of methane had hitherto also to be accepted; such is not the case in the process of the invention. According to the invention, by adjusting the rise in temperature in the catalyst suspension, it is readily possible to obtain 90%—95% of gasoline hydrocarbons without more than 6%—10% of methane, relative to the total yield, being formed. Moreover the catalyst efficiency increases from approximately 400 grams of hydrocarbons per gram of iron present in the catalyst to 600 grams—800 grams of hydrocarbons per gram Fe.

Whilst in the hydrogenation of carbon monoxide carried out in the gaseous phase in the presence of fixed-bed catalysts it is known to increase the temperature in the cooling system by approximately 5°—20°C., it has not been possible to draw conclusions therefrom in respect of the catalytic hydrogenation of carbon monoxide in a liquid medium, since in the liquid phase the catalyst is in vigorous, turbulent motion. Moreover it should be noted that when the synthesis is carried out in the gaseous phase, the rise in temperature in the cooling system is not to be equated with the temperature in the catalyst, which is known to decrease by 10°—15°C. in the direction of flow of the synthesis gas, so that the rise in temperature in the cooling system serves principally to equalize this temperature drop. However, the temperature in the catalyst is

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then only raised by 5°—8°C. in the downward direction, that is to say in the direction of flow of the synthesis gases. However, temperature differences of from 5°—8°C. do not produce any perceptible effect when the synthesis is carried out in the liquid phase.

The invention is illustrated in greater detail with reference to the following comparative example:—

A vertical tube having a length of 5 metres and an inner diameter of 50 mm. was provided with a heating jacket of 4.80 metres length. The tube was filled with 4.5 kilograms of a catalyst suspension which contained 450 grams Fe. The unsupported iron catalyst used was a distinct former of hydrocarbons boiling in the gasoline range and had the following composition:—

4500 grams of catalyst suspension contained 450 grams Fe, 0.7 grams Cu, 0.35 grams Ni, and 0.40 grams Mn in the form of metal-oxygen compounds, such as oxides, hydroxides, and/or carbonates, and 1.35 grams K_2CO_3.

1.2 normal cubic metres of synthesis gas, the H_2: CO ratio of which was approximately 2:3 and which was subjected to a pressure of 10 atmospheres gauge, were forced per hour through the catalyst suspension. As shown in the Table given hereinafter, a CO conversion of over 90% was obtained after 700 hours of operation and at a temperature of 278°C. measured in the suspension. The methane formation was relatively high. The catalyst efficiency was approximately 400 grams of hydrocarbons per gram Fe. 75% of the products had boiling points below 200°C.

In the second run, the tube of 5 metres length was provided with three separate heating jackets. The lowermost heating jacket had a length of 1.20 metres, the central heating jacket had a length of 1.50 metres, and the uppermost heating jacket had a length of 1.80 metres. Each jacket was heated separately. The tube was then charged with catalyst suspension of the same composition as that used in the first run and was then placed on stream with synthesis gas of the same composition, the only difference between the operating conditions of the first and second runs being that the temperature in the catalyst suspension at a position 10 centimetres above the synthesis gas inlet was, during the second run, 25°—40°C. lower than at a position 10 centimetres below the position at which the gas left the suspension. A CO conversion of over 90% was obtained after 700 hours at the temperatures shown in the Table (251°C. at 10 centimetres above the synthesis gas inlet and 287°C. at 10 centimetres below the gas outlet). The results given in the Table indicate that, due to the higher methane formation, the yield obtained in the first run—particularly having regard to the yield of C_3 and higher hydrocarbons—is less than the yield obtained in the second run, in which the temperature rise in the catalyst suspension was applied in accordance with the invention. The increase in the yield of C_3 and C_4 hydrocarbons obtained in the second run is particularly striking. Accordingly, the proportion of products having boiling points of below 200°C. and containing three or more carbon atoms in the molecule (C_3+), had risen to 87%. The catalyst efficiency was approximately 700 grams of hydrocarbons per gram Fe.

TABLE

						Analysis					
	Temp. °C	CO_2	C_3+C_4 olefins	C_2	CO	H_2	Saturated hydro-carbons	N_2	CO con-version %	g CH_4/ Ncbm $CO+H_2$	g C_3+/ Ncbm $CO+H_2$
Synthesis gas	—	2.4	—	—	57.0	36.3	0.1	4.2	—	—	—
End gas First Run	278°	58.0	3.2	0.7	10.0	12.6	7.1	8.2	91.5	25.9	154.2
End gas Second Run	bottom 251°										
	top 287°	58.7	6.0	0.6	9.2	12.3	4.5	8.7	92.5	12.7	167.2

C_3+ denotes hydrocarbons having three or more carbon atoms in the molecule

Ncbm signifies "Normal cubic metres"

What we claim is:—

1. 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.

2. A method according to claim 1, in which the temperature rise in the catalyst suspension is within the range 20°—50°C.

3. A method according to claim 1 or claim 2, in which the temperature rise, particularly in a large-scale synthesis reactor, is obtained by reduction in the cooling surfaces of the cooling system in the upward direction.

4. A method according to claim 1 or claim 2, in which the reactor is provided with a cooling system which consists of a number of independent part-systems, the temperature rise being obtained by individual adjustment of the temperatures in the individual part-systems.

5. A method according to any one of claims 1 to 4, in which the temperature rise in the catalyst suspension is obtained by means of a cooling system provided or constructed as a number of part-systems the cooling areas of which vary in size in such manner that the cooling area of the total cooling system decreases continuously or stepwise in the upward direction.

6. A method according to any one of claims 1 to 5 in which the rise in temperature in the lower part of the catalyst suspension is greater than the rise in temperature in the upper part.

7. A method according to any one of claims 1 to 6 in which the catalyst contains iron.

8. A method of carrying out the catalytic hydrogenation of carbon monoxide in the liquid phase for the production of hydrocarbons containing more than one carbon atom in the molecule, in which a temperature gradient is maintained in the catalyst suspension substantially as hereinbefore described.

9. A method of carrying out the catalytic hydrogenation of carbon monoxide in the liquid phase for the production of hydrocarbons containing more than one carbon atom in the molecule, substantially as hereinbefore described in the second run in the Example.

10. Hydrocarbons whenever obtained in the hydrogenation of carbon monoxide carried out by the method claimed in any one of the preceding claims.

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