PATENT SPECIFICATION

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(21) Application No. 15992/76 (22) Filed 20 April 1976
(31) Convention Application No. 2518982
(32) Filed 29 April 1975 in
(33) Federal Republic of Germany (DT)
(44) Complete Specification published 2 Nov. 1977
(51) INT CL^2 C07C 1/04 11/02
(52) Index at acceptance
C5E 7A1 7A2 7AY 8B2A1 8B2Y

(19) THE PATENT OFFICE LONDON

(54) PROCESS FOR THE PRODUCTION OF LOW MOLECULAR WEIGHT HYDROCARBONS

(71) We, RUHRCHEMIE AKTIENGESELLSCHAFT a German Company of 42 Oberhausen 13, Postfach 35, Germany, Federal Republic of 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 present invention relates to a process for producing a hydrocarbon mixture containing at least 50% by weight of one or more C_2 to C_4 hydrocarbons, and at least 50% by weight of one or more olefins (the percentages being based on the total content of hydrocarbons having at least 2 carbon atoms), the process comprising catalytic hydrogenation of carbon monoxide.

Depending upon the catalysts employed and the reaction conditions used, the catalytic hydrogenation of carbon oxides leads to mixtures of paraffins and olefins containing 1 to 40 carbon atoms and, in some cases, also to oxygen-containing compounds such as alcohols, aldehydes, ketones, esters or fatty acids. Minor proportions of aromatic hydrocarbons are also produced under selected synthesis conditions (see Ullmann, Encyclopädie der technischen Chemie, 1957, Vol. 9, pp. 701 et seq.).

Pronounced activity for the hydrogenation of carbon oxides is shown by the elements of group VIII of the Periodic Table, above all iron, cobalt and nickel.

Due to their high hydrogenation activity, nickel and cobalt catalysts predominantly give mixtures of saturated, unbranched hydrocarbons. On the other hand, iron-containing catalysts permit the production of hydrocarbon mixtures which contain high proportions of unsaturated aliphatic compounds and, additionally, oxygen-containing compounds especially aliphatic primary alcohols (Ullmann, loc.cit., pp. 697—698).

Mixtures containing at least 60% by weight of hydrocarbons containing more than about 20 carbon atoms, corresponding to a boiling range at atmospheric pressure above about 320°C., can be produced by known processes without any difficulty (see Ullmann, loc.cit., p. 722).

However, it has not been possible up to the present to direct the hydrogenation of carbon oxides towards reaction products which contain more than 50% of low molecular weight and preferably olefinic hydrocarbons having 2 to 4 carbon atoms, based on the total content of hydrocarbons having 2 and more carbon atoms.

Accordingly, it is an object of this invention to provide a process which permits the preferential production of low molecular weight olefinic hydrocarbons by catalytic reaction of carbon oxides with hydrogen.

In accordance with the present invention, there is provided a process for the production of a hydrocarbon mixture containing at least 50% by weight of one or more C_2 to C_4 hydrocarbons and at least 50% by weight of one or more olefins, the percentages being based on the total content of hydrocarbons having at least 2 carbon atoms, the process comprising catalytic hydrogenation of carbon monoxide in a fixed-bed reactor under superatmospheric total pressure and at elevated temperatures, wherein

the catalytic hydrogenation is carried out using one or more catalysts arranged in at least 2 and not more than 10 layers;

the catalytic hydrogenation is carried out in a reactor having a length of from 0.5 to 4.5 meters;

the pressure in the reactor is from 5 to 30 bars;

the temperature measured on the catalyst is from 250° to 370°C;

the space velocity of fresh gas through the reactor is adjusted to from 1,000 to 10,000 std. cu.m. per cu.m. of catalyst per hour; and

the rate of supply of recycle gas to the reactor is adjusted to from 5 times to 25 times the rate of supply of fresh gas to the reactor;

the total gas loading to the reactor is from 7,500 to 50,000 std. cu.m. per cu.m. of catalyst per hour and the catalyst is arranged in such a manner that:

the linear gas flow velocity through the reactor ranges between 1 and 10 m./second, based on normal conditions, and

the residence time of the gas in the reactor ranges between 0.05 and 1 second, based on normal conditions, and

the or each catalyst has an internal surface area of 5 to 150 sq.m. per gram of catalyst.

The catalysts may have the same or different grain sizes which are preferably 0.5 to 10 mm. and especially 1 to 6 mm. The particular grain size used is dependent upon various factors such as, for example, the activity of the catalyst, the diameter of the fixed bed reactor, the resistance to the flow and on the operating conditions. The shape of the catalysts is of minor importance. Moulded catalysts such as cylindrical pellets, spherical pellets, tablets polyhedra, hollow bodies as well as lumpy, crushed and comminuted catalysts may be used with equally good results.

Tubes having a minimum diameter (inside diameter) of 30 mm., tube bundles, vessels such as shaft furnaces of similar apparatus may be used as fixed-bed reactors. The reactors may be provided with devices for cooling or for removing the heat of reaction. For example, cooling media such as water, liquid salt melts or organic cooling liquids (based, for example, on biphenyl, o-dichlorobenzene or the isomers of benzyl benzene) may be used in case of tubes or tube bundles.

It has been found to be advantageous to remove the heat of reaction predominantly or almost completely by the total recycle gas mixture in connection, if necessary or desired, with a cooling medium. When operating in this manner, the temperature in the catalyst bed is not maintained constant but is increased in the direction of the gas stream in a carefully controlled manner. Thus, the temperature of the gas mixture entering at the top of the reactor at a temperature, of, for example, 280°C. may increase while the gas is flowing through the reactor by 50°C. to 330°C. by absorption of part of the reaction heat while the temperature of the catalyst increases by approximately the same amount and the overall gas mixture leaves the reactor at this temperature. This increase in temperature which is referred to as vertical temperature gradient should be at least 25°C. but not exceed 100°C., an increase in temperature by 30° to 50°C. being preferred.

Preferably, the reaction heat is removed by appropriately adjusting the gas recycle without the use of a cooling medium. It is necessary for technical and economical reasons to use 2 to 10 and preferably 2 to 5 stages, and it is recommended to cool the reaction mixture partially or completely between the stages and, if necessary or desired, to separate reaction products and reaction liquor after each stage.

Moreover, cold fresh gas may be fed downstream of each stage to partially cool the reaction mixture and to increase the proportion of carbon oxide and hydrogen in the gas mixture. It is also possible to operate with a reaction temperature which increases from stage to stage to permit better control of the conversion of carbon oxides and hydrogen, which decreases with the decreasing content of the starting materials in the reaction mixture. The increase in reaction temperature from stage to stage may be 5° to 20°C.

The length of the reactor used to carry out the reaction must not exceed 4.5 meters. Preferred are reactors having a length of less than 3 m. Reactors of 0.5 to 1.0 m. in length can be used without disadvantage to the reaction.

The synthesis pressure to be used is dependent upon the type of catalysts used and ranges between 5 and 30 bars. Pressures between 5 and 15 bars are advantageous. Lower pressures frequently result in a decrease in conversion of the starting materials.

The reaction temperatures to be maintained in the process according to the invention, and measured on the catalyst, range between 250° and 370°C. and advantageously between 270° and 340°C.

It is of great impartance to the process that a high fresh gas loading of the catalyst is maintained. While previously a loading of the fixed bed catalysts of 500 to 700 std. cu.m. of fresh gas per cu.m. of catalyst per hour was generally regarded as the upper limit in Fischer-Tropsch synthesis, higher fresh gas rates are used in the process according to the invention. It has been found to be desirable to supply at least 1,000 and not more than 10,000 std. cu.m. of fresh gas per cu.m. of catalyst per hour. Preferably 1,500 to 5,000 std. cu.m. of fresh gas are used per cu.m. of catalyst per hour.

The mode of operation according to the invention requires the use of gas recycling. Of particular importance is the ratio of the amount of recycle gas to the amount of fresh gas fed in. The recycled gas which may, if desired, be conducted through a plurality of stages as hot gas recycle must be adjusted to 5 to 25 times the amount of fresh gas. Preferred is a recycle gas rate of 7.5 to 15 times the fresh gas rate.

Moreover, the total gas loading of the catalyst, i.e. the sum of fresh gas and recycle gas, must range between 7,500 and 50,000 std. cu.m. per cu.m. of catalyst per hour, the preferred loading being 10,000 to 25,000 std. cu.m. of gas per cu.m. of catalyst per hour.

Directly related to the values mentioned above are the linear flow velocity of the gas mixture and the residence time, both of these variables being based on standard conditions. The linear gas flow velocity in the new process must range between 1 and 10 m./sec. and preferably 1.5 to 5.0 m./second. The residence time is 0.05 to 1 second and preferably between 0.5 and 0.05 seconds. The production of hydrocarbons of higher molecular weight is promoted by an increase in residence time.

Catalysts containing more than 50% by weight and especially more than 60% by weight of iron are advantageously used for the process according to the invention. Additionally, promoters such as copper and/or silver and alkali but also other additives such as alkaline earth metal compounds, zinc oxide, manganese oxide, cerium oxide, vanadium oxide, chromium oxide or similar compounds may be added. On the other hand, the use of support materials such as alumina, kieselguhr, or impregnating agents such as potassium or sodium water glass is less recommendable.

Boron, phosphorus, tungsten or molybdenum may be used as catalyst components in the form of their oxides, or as salts such as sodium borate or potassium tungstate. Catalysts based on iron, copper and/or silver and alkali (K_2O), e.g. in a ratio of $Fe:Cu/Ag:K_2O$ of, for example, 100:3 to 25:10 have been found to be particularly favourable.

The catalysts may be produced in a manner known *per se*, e.g. by precipitation, sintering, fusion or decomposition of salt mixtures. Moulding and reduction of the catalysts may also be effected in known manner. In some cases, sintered catalysts have been found to be advantageous.

The internal surface area of the catalysts used measured by the BET method is of importance for the process according to the invention. Catalysts having an internal surface area of more than 150 sq.m. per gram of catalyst are prone to produce higher molecular weight hydrocarbons. Therefore, the catalysts used in the present process must have an internal surface area of 5 to 150 sq.m. per gram of catalyst and preferably of 10 to 100 sq.m. per gram of catalyst. For catalysts which predominantly contain metals, especially iron, the data mentioned above for the internal surface area are based on the reduced state.

The pore size of the catalysts has a decisive influence on the proportion of low molecular weight hydrocarbons in the reaction product. The proportion of macropores having a diameter of more than 5×10^{-6} cm. in the total pore volume should be as low as possible because macropores promote the production of higher molecular weight hydrocarbons. On the other hand, pores having a diameter of less than 5×10^{-6} cm. should be preferentially present. It is advantageous if the catalysts to be used in accordance with the invention contain less than 50 per cent and especially less than 25 per cent of macropores, based on the total pore volume.

It may happen during the course of the operating period that part of the catalyst pores becomes plugged by deposition of small amounts of high molecular weight reaction products and, therefore, is no longer accessible to the synthesis gas. This obturation becomes perceptible by the decrease in conversion of carbon monoxide and hydrogen. The high molecular weight deposits may be removed by what is known as the extractive operation, i.e. extraction of the catalyst with hydrocarbon mixtures produced by the synthesis itself or with other hydrocarbon mixtures.

The ratio of carbon monoxide to hydrogen in the fresh gas may influence the production of low molecular weight hydrocarbons. While it is possible to use gases which are rich in carbon monoxide, gases rich in hydrogen are preferred in the process according to the invention. The ratio of carbon monoxide to hydrogen in the fresh gas preferably ranges above 1:1.2, e.g. between 1:1.5 and 1:1.2. Still higher proportions of hydrogen may be disadvantageous under certain circumstances.

The presence of inert gases such as methane, carbon dioxide or nitrogen generally does not interfere with the reaction. Since the proportion of these inert gases in the reaction mixture increases as the conversion of carbon monoxide and hydrogen increases, due to the gas contraction which occurs, it is desirable to keep the inert gas concentration in the fresh gas low.

The process according to the invention yields more than 50% by weight and preferably more than 60% by weight of hydrocarbons having more than 2 to 4 carbon atoms, based on all of the hydrocarbons with the exclusion of methane. The proportion of olefins is higher than 50%, also based on all hydrocarbons with the exclusion of methane.

The following Examples relate to the passage of carbon monoxide and hydrogen over a single catalyst layer and illustrate the reactions which occur at each catalyst layer in carrying out a process according to the invention.

Example 1

A catalyst obtained in the form of spherical pellets (about 2 to 2.5 mm. diameter) by sintering a homogeneous mixture of iron oxide (Alan Wood ore), copper oxide, zinc oxide and potassium carbonate in a ratio of $Fe:Cu:ZnO:K_2O=100:25:10:8$ for 2 hours at 1050°C. was reduced for several hours at 400°C. After termination of the treatment, the catalyst had a reduction value (proportion of free iron based on total iron) of 97%.

The catalyst was placed as a layer of 50 cm. depth into an electrically heated test reactor of 1 m. in length and 50 mm. inside diameter.

Fresh gas at a rate of 2,000 std. liters per liter of catalyst per hour (2,000 v/v/hr.) and recycle gas at a rate of 15,000 std. liters per liter of catalyst per hour (15,000 v/v/hr.) were passed over the catalyst under a pressure of 10 atmospheres. A $CO+H_2$ conversion of 36% was reached at a temperature of 260°C.

measured outside the catalyst and at a temperature of 292°C. measured inside the catalyst.

The reaction products had the following composition based on hydrocarbons having 2 and more carbon atoms:

C_2 to C_4	about 69.5% by weight; of these, 57% by weight were olefins;
C_5 to $\sim C_{11}$	about 30.4% by weight; of these, 60% by weight were olefins.

The proportion of methane was between 7 and 8% by weight.

The fresh feed gas had the following composition:

	% by volume
CO_2	3.6
C_nH_m	0
O_2	0
CO	30.7
H_2	53.0
CH_4	0.2
N_2	12.5
CO/H_2 ratio	1:1.72

Example 2

The sintered catalyst was produced as described in Example 1 except that only 5 parts by weight of Cu and 4 parts of K_2O were used with otherwise unchanged composition and unchanged production conditions.

At a fresh gas rate and recycle gas rate as in Example 1, the reaction temperature was 270°C. outside the catalyst and 313°C. inside the catalyst. The $CO+H_2$ conversion increased to about 40%.

The composition of the synthesis products (C_2 and higher hydrocarbons) according to the number of carbon atoms was as follows:

	% by weight
C_2 to C_4 about	98
$>C_4$ about	2

The olefin content of the C_2/C_4 fraction was 56% by weight. The proportion of C_2 hydrocarbons in the C_2/C_4 fraction was about 90%, the balance being about equal amounts of C_3/C_4 hydrocarbons.

Methane, in an amount of 10 to 12% by weight, was produced.

The synthesis gas used had the same composition as that of Example 1. With a $CO:H_2$ ratio of 1:1.3 in place of 1:1.72 in the synthesis gas, the proportion of olefins increased by about 4% to 5% by weight.

WHAT WE CLAIM IS:—

1. A process for the production of a hydrocarbon mixture containing at least 50% by weight of one or more C_2 to C_4 hydrocarbons and at least 50% by weight of one or more olefins, the percentages being based on the total content of hydrocarbons having at least 2 carbon atoms, the process comprising catalytic hydrogenation of carbon monoxide in a fixed-bed reactor under superatmospheric total pressure and at elevated temperatures, wherein

the catalytic hydrogenation is carried out using one or more catalyst arranged in at least 2 and not more than 10 layers;

the catalytic hydrogenation is carried out in a reactor having a length of from 0.5 to 4.5 meters;

the pressure in the reactor is from 5 to 30 bars;

the temperature measured on the catalyst is from 250° to 370°C.;

the space velocity of fresh gas through the reactor is adjusted to from 1,000 to 10,000 std. cu.m. per cu.m. of catalyst per hour; and

the rate of supply of recycle gas to the reactor is adjusted to from 5 times to 25 times the rate of supply of fresh gas to the reactor;

the total gas loading to the reactor is from 7,500 to 50,000 std. cu.m. per cu.m. of catalyst per hour and the catalyst is arranged in such a manner that;

the linear gas flow velocity through the reactor ranges between 1 and 10 m./second, based on normal conditions, and

the residence time of the gas in the reactor ranges between 0.05 and 1 second, based on normal conditions, and

the or each catalyst has an internal surface area of 5 to 150 sq.m. per gram of catalyst.

2. A process according to Claim 1, wherein the length of the reactor is from 0.5 to 3 meters.

3. A process according to either preceding claim, wherein the pressure in the reactor is from 5 to 15 bars.

4. A process according to any preceding claim, wherein the temperature measured on the catalyst is 270° to 340°C.

5. A process according to any preceding claim, wherein the space velocity of the fresh gas is adjusted to 1,500 to 5,000 std. cu.m. per cu.m. of catalyst per hour.

6. A process according to any preceding claim, wherein the rate of supply of recycle gas to the reactor is 7.5 to 15 times the rate of supply of fresh gas to the reactor.

7. A process according to any preceding claim, wherein the total gas loading to the reactor is 10,000 to 25,000 std. cu.m. per cu.m. of catalyst per hour.

8. A process according to any preceding claim, wherein the linear gas flow velocity through the reactor ranges betwten 1.5 and 5 meters per second, based on standard conditions.

9. A process according to any preceding

claim, wherein the residence time of the gas in the reactor ranges between 0.5 and 0.05 seconds, based on standard conditions.

10. A process according to any preceding claim, wherein the or each catalyst has an internal surface area of between 10 and 100 sq.m. per gram of catalyst.

11. A process according to any preceding claim, wherein the or each catalyst has an iron content of more than 60% by weight.

12. A process according to any preceding claim, wherein the or each catalyst contains less than 50% of macropores having a diameter of more than 5×10^{-6} cm.

13. A process according to claim 12, wherein the or each catalyst contains less than 25% of macropores having a diameter of more than 5×10^{-6} cm.

14. A process according to any preceding claim, wherein the one or more catalysts are arranged in 2 to 5 layers.

15. A process according to any preceding claim, wherein the catalyst has pores having a diameter of less than 5×10^{-6} cm.

16. Hydrocarbon mixtures whenever produced by the process claimed in any one of Claims 1 to 15.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.