PATENT SPECIFICATION

690,432

Date of Application and filing Complete Specification April 6, 1950.
No. 8683/50.
Application made in Germany on June 20, 1949.
Complete Specification Published April 22, 1953.

2919

Index at acceptance :—**Classes 1(i),** F3b(1 : 2x) ; **and 2(iii),** B1g, C3a11.

COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide in the Presence of an Iron Catalyst

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, 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 in the presence of an iron catalyst, whereby hydrocarbons and oxygen - containing organic compounds are produced.

The hydrogenation of carbon monoxide at atmospheric pressure with iron catalysts is generally effected at an initial temperature within the approximate range 210° C—220° C After a relatively quick traversing of the lower initial temperatures, a satisfactory carbon monoxide and hydrogen conversion of approximately 60—75% with a load of 100 volumes of synthesis gas per volume of catalyst per hour is obtained only within this temperature range. Having regard to the fact that iron catalysts effect a partial conversion of the gas constituents with the formation of carbon dioxide at normal atmospheric pressure, a pure carbon monoxide conversion of approximately 80%—96% is effected Approximately 15%—25% of the synthetic products may be obtained in the form of hydrocarbons of high molecular weight, particularly paraffin waxes, with weakly alkalized iron catalysts, the methane formation being generally between 10%—16%, of the total conversion.

It has been found that the methane formation is considerably reduced, and at the same time a considerably increased formation of hydrocarbons of high molecular weight and an increased length of life of the catalyst are obtained if the iron catalyst is extracted several times within the first 500 hours on-stream, the synthesis being thereafter continued at a temperature within the range 170° C.—200° C. preferably at a temperature within the range 190° C.—200° C. The number of extractions needed in the first 500 hours will vary from four to seven.

According to the invention, in a process for the synthesis of hydrocarbons and oxygen-containing organic compounds by the hydrogenation of carbon monoxide at atmospheric pressure in the presence of an iron catalyst, the catalyst is brought into operation in the synthesis at a temperature within the range 170° C.—200° C. and in such manner that in the course of the first 500 hours of operation the catalyst is extracted from four to seven times to remove high boiling synthesis products therefrom, the synthesis being thereafter continued at a temperature within the range 170° C.—200° C., preferably within the range 190°—200° C.

Hitherto, in the synthesis effected at normal pressure in the presence of an iron catalyst, the synthesis temperatures used in the process according to the invention have been quickly traversed when the iron catalyst is placed onstream, for the reason that satisfactory conversions have not been obtained at these temperatures. The carbon monoxide and hydrogen conversion in this temperature range normally amounts to only 30%—40%. The present invention is based on the surprising observation that, in spite of the temperature being approximately 20° below the synthesis temperature normally used with an iron catalyst, normal conversions can be obtained as soon as the catalyst has been extracted several times at these low temperatures.

It is known that iron catalysts, due to the high content of hydrocarbons of high molecular weight, particularly paraffin waxes, in the synthesis products, have to be extracted relatively frequently. Such extractions are generally effected with hydrocarbon mixtures at the synthesis temperature in use at the time. An iron catalyst used in the synthesis at 170° C.—

[*Price* 2/8]

200° C. according to the invention, has to be extracted on the average only after 70—150 hours of operation. Whilst up to the first extraction the conversion remains quite unsatisfactorily at 30%—40%, a remarkably improved conversion is obtained after the first extraction, even though the synthesis temperature is not raised. After 4 to 7 extractions of the catalyst, within the first 500 hours of operation, the normal $(CO+H_2)$ conversion of approximately 72% is attained. Thereafter, at the preferred synthesis temperature of 190°—200° C., the catalyst can be used for a long time, generally for about 2000 to 4000 operational hours, before its activity is reduced. If the period of operation exceeds this, the reduced activity of the catalyst, and with it the conversion, can always be brought back to the normal level by increasing the synthesis temperature in the manner usual at present.

To carry out the process of the invention, an iron catalyst is advantageously used which has been impregnated with an alkali-metal salt of a non-volatile acid, for example, with potassium silicate or a suitable potassium phosphate. The reduction of the catalyst has to be effected at a high speed of flow with hydrogen at temperatures within the range 200° C.—350° C., preferably at temperatures within the range 200° C.—250° C.

Owing to the low synthesis temperature, at which iron catalysts are used according to the invention, the methane formation remains considerably lower than in the hydrogenation of carbon monoxide as generally effected at present with iron catalysts, in spite a high total conversion. The yield in hydrocarbons boiling above 300° C. is considerably higher as compared with the yield when using iron catalysts in known manner.

The life of the catalyst is also considerably lengthened by the method of operation according to the invention. Due to the high conversions obtained at low temperatures, the thermal strain on the catalyst is considerably less than in processes hitherto used. Furthermore, an increased range of temperature is available over which the synthesis temperature may be gradually increased for restoring the catalyst to its original state of high activity. The permissible end temperature in the synthesis under normal pressure at a normal throughput of 100 volumes of synthesis gas per volume of catalyst per hour is approximately 230° C.—235° C. If the catalyst is taken into operation at a temperature of 210° C. in the manner as hitherto practised, then a temperature interval of only 15° C.—20° C. is available for the gradual increase of the synthesis temperature. With a synthesis temperature of 170° C.—200° C. according to the invention, the total temperature interval available during the life of the catalyst is raised to 35° C.—40° C., which makes possible a correspondingly longer use of the catalyst.

The invention is illustrated by the following example.

An iron catalyst, which contained 100 parts iron, 5 parts copper and 10 parts calcium oxide, was precipitated by means of sodium carbonate from a mixed solution of the corresponding nitrates at a hydrogen ion concentration of $pH=7$. The precipitated mass was separated by filtration and carefully washed and, after drying, was impregnated with small quantities of an alkali-metal salt of a non-volatile acid (for example, potassium silicate). The reduction which followed was carried through in sixty minutes with hydrogen at a temperature of 225° C. and at a high rate of flow. The catalyst was then put on stream in the synthesis at a temperature of 160° C., with a load of 100 normal litres of water gas per litre of catalyst per hour. Within 48 hours the synthesis temperature was raised to 195° C. This resulted in a $(CO+H_2)$ conversion of approximately 39%. During the course of the next forty-eight hours the conversion fell to 30% owing to the deposition of paraffin wax on the catalyst.

The catalyst was then extracted with four times its volume of a diesel oil fraction boiling in the range 220° C.—300° C.

Immediately after this extraction, the catalyst was again used in the synthesis with water gas when the $(CO+H_2)$ conversion increased to 48%. Owing to the deposition of paraffin waxes on the catalyst, the yield fell to 36% within the next 120 hours.

After further extractions, each with the quadruple quantity of the diesel oil used above, the conversion increased to 59%, 65%, 70% and 73% respectively, and fell after several days of operation due to the deposition of paraffin waxes on the catalyst. The second, third, fourth and fifth extractions of the catalyst were effected after 216 hours, 316 hours, 416 hours and 516 hours on-stream respectively.

After the fifth extraction, the catalyst could be operated with a conversion of approximately 72% at a constant operational temperature of 198° C. for several thousand hours, an extraction of the catalyst being thereafter necessary every seven days at first, and later on every 10—14 days, owing to the paraffin wax deposit. After each extraction, the iron catalyst again showed practically its complete activity.

In spite of the high ($CO+H_2$) conversion, the methane formation remained very small, and never exceeded 8%—10%. The yield of hydrocarbons boiling above 300° C. was considerably higher than with iron catalysts brought into operation at the usual temperatures.

What we claim is:—

1. A process for the synthesis of hydrocarbons and oxygen-containing organic compounds by the hydrogenation of carbon monoxide at atmospheric pressure in the presence of an iron catalyst, in which the catalyst is brought into operation in the synthesis at a temperature within the range 170°—200° C. and in such manner that in the course of the first 500 hours of operation the catalyst is extracted from four to seven times to remove high boiling synthesis products therefrom, the synthesis being thereafter continued at a temperature within the range 170° C.—200° C., preferably within the range 190° C. to 200° C.

2. A process according to claim 1, in which the iron catalyst, prior to use in the synthesis, is impregnated with an alkali-metal salt of a non-volatile acid, and is reduced with hydrogen at high rate of flow at a temperature within the range 200° C.—350° C., preferably within the range 200° C.—250° C.

3. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described.

4. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to the example.

5. Hydrocarbons and oxygen - containing organic compounds whenever produced by the process claimed in any one of the preceding claims.

EDWARD EVANS & CO.,
14—18, High Holborn, London, W.C.1,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1953.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.