

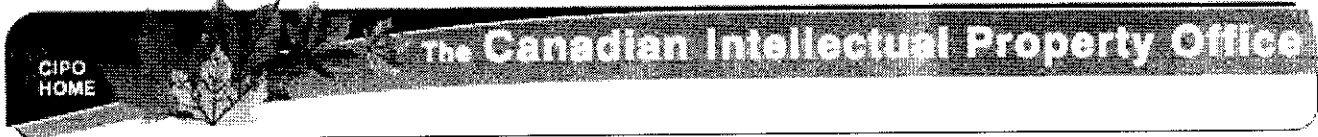


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(12) Patent:

(54) PROCESS FOR THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE, USING IRON CATALYSTS
(54) PROCÉDE POUR L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE EMPLOYANT DES CATALYSEURS DE FER

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The hydrogenation of carbon monoxide with iron catalysts is effected at atmospheric pressure and at a starting temperature within the approximate range $210^{\circ}\text{C}.$ - $220^{\circ}\text{C}.$ After a relatively quick traversing of the lower starting temperatures, a satisfactory carbon monoxide and hydrogen conversion of approximately 60 - 75% with a load of 100 cu.m. synthesis gas per cu. m. of catalyst volume 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 in the form of high molecular hydrocarbons, particularly paraffins, may be obtained 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 high molecular hydrocarbons and an increased length of life of the catalyst is obtained if the synthesis is effected at $170^{\circ}\text{C}.$ - $200^{\circ}\text{C}.,$ preferably at $190^{\circ}\text{C}.$ - $200^{\circ}\text{C}.$

These synthesis temperatures, employed according to the invention, in the synthesis under normal pressure hitherto usual with iron catalysts, are quickly traversed during the starting for the reason that they do not yield satisfactory conversions. The carbon monoxide and hydrogen conversion amounts in this temperature range to only 30% - 40%. The invention is based on the surpris-

observation that, in spite of the temperature being approximately 20° below the normal synthesis temperature, normal conversions can be obtained as soon as the catalyst was several times extracted, at these low temperatures.

5 It is known that iron catalysts, due to their high paraffin formation, have to be extracted relatively frequently. Such extractions are generally effected with hydrocarbon mixtures at the synthesis temperature prevailing at the time. An iron catalyst used in the synthesis at 170°C. - 200°C. according to
10 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% to 40%, a remarkably improved conversion is obtained after the first extraction, even though the synthesis temperature is not raised.
15 After 4 to 5 extractions of the catalyst, that is to say, after 500 - 700 hours of operations, the normal (CO + H₂) conversion of approximately 72% is attained. At the synthesis temperature of 190° - 200° the catalyst can be used for a long time, generally for about 2000 to 4000 operational hours, before its activity
20 is reduced. If the period of operation exceeds this, the reduced catalyst activity, 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. The extraction of paraffin material from iron catalysts to regenerate the same is
25 a conventional procedure and carried out with well known solvents for normally solid paraffin hydrocarbons, the preferred solvents usually being hydrocarbons or hydrocarbon mixtures such as for example so-called Diesel oil fractions having, for instance, a boiling point between 220-300°C. or hydrogenated Diesel oil
30 fractions having, for instance, a boiling point between 220 - 260°C. or any other paraffin solvent or solvent mixture within the known practice of the art for solvent extraction of paraffin

material for the regeneration of iron catalysts used in hydrocarbon synthesis of the Fischer-Tropsch type. Of particular advantage is the use of high boiling paraffins, naphthenic or aromatic hydrocarbons as solvent.

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To carry out the process of the invention, iron catalysts are advantageously used which have been impregnated with alkali salts of a non-volatile acid, for example, with potassium silicate or suitable potassium phosphates. The reduction of the catalysts has to be

effected at a high speed of flow with hydrogen at about 200°C. - 350°C., preferably at 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 effected at present with iron catalysts, in spite of a high total conversion. The yield in hydrocarbons boiling above 300°C. is considerably higher as compared with the yield using iron catalysts hitherto known.

Also the life of the catalysts is 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 hitherto. Furthermore, an increased temperature range is available for the gradual increasing of the synthesis temperature for the restoration of its original activity. The permissible end temperature in the synthesis under normal pressure at a normal charge of 100 litres gas per hour per litre of catalyst is approximately 230°C. - 235°C. If the catalyst is taken into operation at 210°C. in the manner hitherto known, then only an interval of 15°C. - 20°C. is available for the gradual increase in the synthesis temperature. With a synthesis temperature of 170°C. - 200°C. according to the invention, the total temperature interval available during the duration of life of the catalyst is raised to 35°C. - 40°C., which makes possible a correspondingly longer use of the catalyst.

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EXAMPLE.

An iron catalyst, which consisted of 100 parts iron, 5 parts copper and 10 parts calcium oxide, was

precipitated by means of soda from a solution of corresponding nitrates at a hydrogen ion concentration of $p_H = 7$. The precipitated mass was carefully washed and, after drying, impregnated with small quantities of alkali salt of a non-volatile acid (for example, potassium silicate). The reduction which followed was effected with hydrogen at 225°C . and at a high speed of flow within sixty minutes. The catalyst was then put into operation 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 $(\text{CO} + \text{H}_2)$ conversion of approximately 39%. During the course of the next forty-eight hours the conversion fell to 30% owing to the paraffin deposit.

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 $(\text{CO} + \text{H}_2)$ conversion increased to 48%. Owing to the paraffin deposit, this 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 mounted to 59%, 65%, 70% and 73% respectively, and fell after several days of operation due to the formation of paraffin.

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 necessary every seven days in the beginning, and later on

every 10 - 14 days, owing to the paraffin deposit. After each extraction the iron catalyst again showed practically its complete activity.

5 In spite of the high (CO + H₂) 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 started at the usual temperatures.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the catalytic hydrogenation of carbon monoxide at substantially atmospheric pressure by passage of a synthesis gas over and in contact with an iron catalyst, the process which comprises utilizing an iron catalyst which has been repeatedly extracted, and effecting the synthesis continuously at temperatures of approximately 170°C. - 200°C.
2. A process as defined in claim 1, wherein said temperatures are within the range 190°C. - 200°C.
3. A process as defined in claim 1, said catalyst being impregnated with an alkali salt of a non-volatile acid and reduced at a high speed of flow with hydrogen at approximately 200°C. - 350°C.
4. A process as defined in claim 3, said catalyst being reduced at 200°C. - 250°C.

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