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(54) PROCESS FOR CATALYTIC CARBON MONOXIDE HYDROGENATION

(54) PROCEDE POUR L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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Catalytic carbon monoxide hydrogenation, carried out at normal or at superatmospheric pressure, may be carried out for the preferred production of high molecular hydrocarbons as well as for the production of low molecular hydrocarbons; in both cases the formation of methane must be maintained at a minimum.

In general, and particularly with iron catalysts, the formation of high molecular weight hydrocarbons and stable paraffins is desired, since these synthetic products are very useful, and may be used to yield low molecular hydrocarbons by molecular fission. The formation of high molecular hydrocarbons depends, to a considerable extent, upon the alkali content of the catalysts since a high alkali content favours the development of such synthetic products and at the same time also to a large extent suppresses the methane formation.

By the use of catalysts of low alkali content, the formation of low molecular weight hydrocarbons may, for example, with suitable synthesis conditions, be appreciably increased. Synthetic products lying within the benzene boiling range are particularly desirable if the primary products of carbon monoxide hydrogenation are to be treated for the production of high anti-knock car or aircraft fuels as, for example, by catalytic after-treatment, if need be with the admixture of polymer benzene obtained by polymerization from gaseous synthetic products. If, with the usual catalysts, there is an increase in synthetic products boiling in the benzene range, there will nevertheless still be 15% - 20% of high molecular products formed. Furthermore, the relatively high methane formation is in this case also very disadvantageous.

This circumstance has led to the endeavour in almost all cases to ensure the highest possible yield of high molecular synthesis products, since it is only in this way that a small quantity of methane is formed.

5 It has been found, according to the invention, that surprising effects are obtained, preferably with iron catalysts, both in synthesis at normal pressure and also in synthesis at superatmospheric pressure, with gas pressures of approximately 10 - 30 kg per sq. cm.,
10 and also at higher synthesis pressures, if small amounts, preferably 0.5 - 5 vol.% of compounds having an alkaline reaction are added to the synthesis gas, the compounds being gaseous under the conditions of synthesis, and preferably being ammonia, methyl amine or their derivatives.
15 As synthesis gas water gas may, for example, be used, that is to say, gas mixtures containing 1 - 1.4 parts by volume of hydrogen, per one part by volume of carbon monoxide. The process may, however, also be carried out with synthesis gases of different composition containing,
20 for example, per 1 part by volume of carbon monoxide 0.5 - 2 parts by volume of hydrogen.

 As the cheapest additional agent having an alkaline reaction, gaseous ammonia is preferably used, particularly because, even in relatively small quantities
25 of, for example, 1%, it has a considerable influence on the composition of the resultant synthetic products, both at normal pressure and also at superatmospheric pressure. It is particularly fortunate that catalysts which have a high alkali content are suitable for the
30 treatment at normal pressure of synthesis gases which have been mixed with ammonia or gaseous compounds having

the same effect, in accordance with the present invention. Such catalysts, which, in synthesis at normal pressure favoured paraffin formation and extensively suppressed the methane formation in the presence of ammonia or similar compounds, yield hardly any high molecular hydrocarbons. In spite of this, however, no increased methane formation occurs.

The feed can be increased considerably above the normal extent, particularly when operating at increased pressure. The catalysts may be contacted hourly with 200-1000 litres, preferably, 300-500 litres, of synthesis gas per litre without there being any need to fear overloading. The synthesis may be carried out particularly advantageously if the gases are recycled.

In carrying out the process according to the invention, operation is preferably carried out at catalyst temperatures which rise slowly in the direction of the gas flow. In this way, on the one hand an overloading of the catalyst at the point of entry of the gas is avoided, and, on the other hand, a uniform utilization of the whole catalyst is obtained.

The olefine content of the liquid hydrocarbons obtained from the synthesis gases containing NH_3 is relatively high, particularly in the higher boiling ranges. The normally gaseous synthetic products also contain a large proportion of olefines, so that by polymerization of the olefines and by mixing the polymerizate with the primary hydrocarbons, high grade fuels may be obtained in a relatively simple manner.

It is particularly surprising that, in the method of operation according to the invention, a more or less extensive production of organic compounds containing nitrogen is also possible. The amount of these
5 nitrogen compounds, consisting in the main of primary amines, is dependent on the synthesis conditions and on the composition of the catalysts (the catalysts being of the category of catalysts known for catalytic carbon monoxide hydrogenation).

10 Together with the amino-compounds, other compounds containing nitrogen are also formed, for example, ammonium carbonate, ammonium carbamate, urea, and the like. Their production and utilization is, in connection with hydrocarbon synthesis, sometimes of considerable
15 economic importance.

EXAMPLE 1

Water gas, free of carbon dioxide and containing 1% of ammonia gas was passed over an iron catalyst consisting of 100 parts iron, 5 parts copper and small
20 quantities of alkali silicate. The synthesis was carried out at normal atmospheric pressure at a temperature of 220° C with a gas feed of 100 litres of synthesis gas per hour. A CO conversion of 85% - 95% was obtained, which corresponded to a (CO + H₂) conversion of 66% - 68%.
25 The methane formation was between 8% and 10%. The consumption ratio amounted to approximately 0.7 parts by volume of hydrogen to 1 part by volume of carbon monoxide.

Because of the very slight formation of high molecular hydrocarbons, it was possible to operate the
30 synthesis for long periods of time and with constant conversion without deterioration of the catalyst.

The processing of the synthesis products obtained showed that of the total yield only 5% to 6% boiled above 320° C. The high olefine content in all the fractions was remarkable. In the C₅ fraction, for example, an olefine content of 70% was found, whilst in the crude paraffin (320° C. - 460° C.) approximately 59% of olefines was present. In the benzine boiling range (40° C.- 220° C.) the synthetic products contained 5% of compounds containing oxygen, chiefly alcohols, and 9% of compounds containing nitrogen, preponderately primary amines. In the Diesel oil range (220° C. - 320° C.) there were present 4% of products containing oxygen, chiefly alcohols, and a further 6% of compounds containing nitrogen, mainly primary amines.

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EXAMPLE 2.

From a boiling solution of suitable nitrates a catalyst was precipitated with hot soda solution. The catalyst contained 5 parts copper (Cu) per 100 parts iron (Fe). The precipitated mass was impregnated with potassium phosphate (KH₂PO₄) in such manner that the final catalyst contained, per 100 parts of iron, 3 parts of K₂O in the form of KH₂PO₄. After drying, the catalyst was reduced with hydrogen at a speed of flow of 1.5 metres per second. For the synthesis, water gas was used mixed with 1.5 vol% of NH₃. The synthesis temperature was 213° C. The synthesis pressure was 20 kgs. per sq. cm. 100 litres of synthesis gas per litre of catalyst volume were passed through per hour.

The liquid synthetic products obtained contained 35% of compounds boiling above 320° C. In the C₁₁ hydrocarbon fraction were 57% olefines and in the C₁₈ hydrocarbon fraction there were present approximately 15% olefines.

EXAMPLE 3.

By precipitation with boiling soda solution there was manufactured, in the usual manner, a catalyst which consisted of 100 parts Fe, 5 parts Cu, 10 parts CaO and 10 parts kieselguhr. After washing out, the catalyst was impregnated with caustic soda solution in such manner that the final catalyst, in respect of its iron content, and reckoned as K_2O , had an alkali content of 8% K_2O . For the synthesis a water gas was used which contained 3% NH_3 , whilst the catalyst was contacted, per litre of volume, with 100 litres of synthesis gas per hour. The synthesis pressure amounted to 10 kg. per sq. cm. and the synthesis temperature to $198^{\circ}C$.

The synthetic products obtained consisted of approximately 15% of compounds whose boiling point was above $320^{\circ}C$. In the total liquid products obtained there were present 18% of organic compounds containing nitrogen, which products consisted predominantly of primary amines.

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

1. In a process for catalytic carbon monoxide hydrogenation by passage of a synthesis gas over a catalyst, the step which comprises adding to said synthesis gas a small quantity of at least one compound having an alkaline reaction and gaseous under the conditions of synthesis, said compound being selected from the group ammonia and its derivatives.
2. A process as defined in claim 1, wherein said compound is methyl amine.
3. A process as defined in claim 1, wherein said catalyst is an iron catalyst having a high alkali content.
4. A process as defined in claim 1, 2 or 3, said synthesis gas containing 0.5-2 parts by volume of hydrogen per 1 part by volume of carbon monoxide.
5. A process as defined in claim 1, 2 or 3, which includes the step of contacting said catalyst hourly per litre of their volume with 200 - 1000 litres of synthesis gas.
6. A process as defined in claim 1, 2 or 3, which includes the step of recycling the synthesis gas.
7. A process as defined in claim 1, 2 or 3, which includes the step of carrying out the operation at catalyst temperatures rising in the direction of the gas flow.
8. A process as defined in claim 1, 2 or 3, wherein the velocity of said gas is at least 1.5 metres per second.

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