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(54) PROCESS FOR THE SYNTHESIS OF HIGH BOILING VISCOUS HYDROCARBON MIXTURES

(54) PROCÉDE POUR LA SYNTHÈSE DE MÉLANGES D'HYDROCARBURES VISQUEUX DE HAUTE EBULLITION

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This invention relates to a process for the synthesis of high boiling viscous hydrocarbon mixtures.

10. The catalytic hydrogenation of carbon monoxide with the use of fine-grained moving catalysts having as their active components metals and/or metal oxides of the eighth group of the periodical system is known. The synthesis may be operated in accordance with either the so-called "fluidized process" in which the catalyst is maintained in a dense turbulent suspended phase or with the use of pulverulent suspended catalysts which are continuously conducted and pass through the reaction zone by the synthesis gas stream.

20. The quantity of catalyst used in the "fluidized" process is generally in the order of 400-2000 grams of catalyst per liter of fluidized catalyst layer. The grain size of the catalyst in the fluidized process is generally above 0.25 mm. When effecting the carbon monoxide hydrogenation with the use of pulverulent catalysts suspended in the synthesis gas, the quantity of catalyst is generally between 15 - 300 gms. of catalyst per liter of synthesis gas. The grain size of these suspended catalyst is generally somewhat smaller than in the fluidized process and may be, for example, from 0.04 - 0.25 mm.

The flow rate of the synthesis gas when effecting the hydrogenation with the fine grain moving catalyst is dependent on the grain size of the catalyst and may for example, be 50 - 15,000 cm/second and more. The synthesis temperatures are between 180° and 400° C. The ratio of carbon monoxide to hydrogen in the synthesis gases process may vary within wide limits and may range, for example, between 1 : 1 and 1 : 3. When using moving fine-grained catalyst, the synthesis gases are generally recycled using a recycle ratio of up to 10 and

more parts by volume of recycle gas per part by volume of fresh gas. The conversion of the carbon monoxide may, for example, be 70 - 80% with gas contractions of approximately 35 - 40% being reached.

10. The term "fine-grained moving catalyst" is intended to generically include catalyst in the fluidized process and the pulverulent suspended catalyst which are passed through the reaction zone by the synthesis gas stream. The active constituents of these catalysts in most cases consist of iron and/or iron oxides. Other metals and metal oxides of the eighth group of the periodical system such as, for example, cobalt or nickel are, however, also suitable for this purpose. The catalysts are preferably activated by non-reducible metal oxides as, for example, with alkali oxides, silicic acid, thorium oxide, manganese oxide, magnesium oxide, aluminium oxide, titanium oxide, and alkaline earth oxides. In addition, these catalysts may contain suitable carrier materials, as for example, kieselguhr, bleaching earths, aluminium oxide or magnesium oxide.

20. The fine-grain catalyst for effecting the hydrogenation with the moving catalyst masses may be prepared, for example, by the combustion of iron powder in an oxygen stream, by fusing the iron oxides thus formed, impregnating the same with potassium compounds, crushing the mass to a suitable grain size and treating the granular mass with reducing gases such as hydrogen. In accordance with another method the catalyst may be prepared by mixing the iron oxide with more than 2% of potassium carbonate, sintering the mixture at about 1000°C., dissolving out the potassium carbonate with water to residual content ~~is~~ as low as 1 - 2%, crushing the mass to a suitable grain size and reducing the granulated catalyst in the convention-

al manner. These catalysts may also be prepared from iron ores having a sufficiently high iron content by melting the same. In this case, the finished catalyst will also contain aluminium oxide, titanium oxide and silicic acid in addition to the iron. It is also possible to admix 1.2 - 1.4% of potassium oxide.

- If the carbon monoxide hydrogen containing gas mixtures are contacted with the fine grained moving catalysts of the eighth group of the periodical system and preferably with iron and/or iron oxide containing catalysts at superatmospheric pressures preferably at gas pressures ranging between 10 and 30 kilos/sq. cm. at temperatures sufficient to obtain conversions of more than 60 - 70%, then a smaller portion of the synthesis products is obtained as higher molecular weight, dark brown to black liquid or paste-like masses. These masses or liquids may either be separated from the condensed synthesis products as distillation residue or may be recovered in the working up and the regeneration of the catalyst as, for example, by extraction with solvents or steam. These products have a very nonuniform composition which is detrimental to a profitable utilization thereof. The carbon structures of these compounds are more or less partially aliphatic with branched chains, partially cyclic and mono- or polynuclear, and partially cyclic with side chains. In addition, these compounds are highly unsaturated and contain oxygen which is the reason for their dark color.
- 10.
- 20.

One object of this invention is the conversion dark liquid or paste-like compounds into high boiling viscous mixtures. This and still further objects will become apparent from the following description:

It has now been found that if the carbon monoxide hydrogenation is effected with fine grained moving catalysts

- substantially consisting of metals and/or metal oxide of the eighth group of the periodical system at super atmospheric pressures, and preferably at pressures of 10-30 kilograms per square centimeter at a temperature of about 180°-400°C. high boiling viscous hydrocarbons may be obtained from these higher molecular weight portions. The catalytic carbon monoxide hydrogenation under the synthesis conditions described above will produce synthesis products which in addition to aliphatic hydrocarbons contain mono- and poly-nuclear cyclic compounds. In accordance with the invention, portions boiling above 340°C. are separated from these products and treated with hydrogen in the presence of catalysts which contain metals of the eighth group of the periodical system. The hydrogen treatment is effected in a pressure of about 5-100 kilograms per square centimeter and preferably at a hydrogen partial pressure of 30 kilograms per square centimeter and at a temperature of about 100°-300°C. and preferably at approximately 250°C. This catalytic hydrogen treatment of these higher boiling portions will partially decyclize and completely or partly free the portions from their content of the oxygen containing groups and unsaturated bonds.
- 10.
- 20.

The production of the synthesis products containing these higher boiling portions may be effected in accordance with the so-called fluidized process using dense turbulent suspended catalyst phase. The synthesis may also be effected using pulverulent catalysts suspended in the synthesis gas with 15-300 grams of catalyst with a grain size below 0.25 millimeters being used per liter of synthesis gas.

The catalysts may be any of the known catalysts substantially consisting of metals or metal oxides of the

eighth group of the periodical system which are conventionally used for the fluidized process or for the process in which the catalysts in pulverulent form are suspended in the synthesis gas stream. These catalysts may be produced in the conventional manner.

10. The separated portions after the synthesis boiling above 340°C . may be hydrogenated by the same catalysts as are used for the carbon monoxide hydrogenation as described above. However, it is also possible to use other commercially known hydrogenation catalysts for this purpose. Particularly well suited for this purpose are, for example, nickel-magnesium oxide-kieselguhr catalysts. In addition other hydrogenation catalysts such as Raney nickel, molybdenum sulfide, tungsten sulfide, etc. catalysts are suitable for this hydrogenation of the products boiling above 340°C .

This hydrogenation of the higher boiling constituents will proceed smoothly and result in the formation of light colored products which may be easily separated by distillation or by extraction into individual fractions.

20. It is of particular advantage in accordance with the invention if the synthesis products which boil above 340°C . are diluted before the hydrogenation with low boiling hydrocarbons having at least 4 carbon atoms in the molecule. It is preferable to effect the dilution with hydrocarbon mixtures having molecular size between C-7 and C-9. The partial pressure of the hydrogen for this hydrogenation of the higher boiling portion should be preferably approximately 30 kilograms per square centimeter. Pure hydrogen or gas mixtures consisting of hydrogen and inert gases, as for example nitrogen, may be used as the hydrogenation gas. The hydrogenation conditions

are suitably so adjusted that the bi and poly cyclic compounds contained in the portions boiling above 340°C. are split up into alkylated mono- and/or poly cyclic hydrocarbons.

The hydrogenated products may be freed by distillation from the constituents which boil below 340°C. Before this distillation the products may be subjected to a cooling to a low temperature to separate the solidifying ceresin-like hydrocarbons. If the separation of the hydrogenated products is effected with solvents the conventionally known extraction agents such as, for example, aliphatic or aromatic hydrocarbons or chlorination products thereof and mixtures thereof or liquefied gases as, for example, liquid sulfur dioxide, may be used.

10.

The following examples are given by way of illustration and not of limitation.

Example I

A dark brown colored product boiling above 340°C. and prepared by the hydrogenation of carbon monoxide carried out at a gas pressure of approximately 17 kilos/sq. cm. and at a synthesis temperature of 325°C. with the use of a pulverulent catalyst suspended in the synthesis gas and with gas recycling had the following characteristics:

20.

Iodine number	39.0
Neutralization number	1.3
Saponification number	10.9
Hydroxyl number	2
Carbonyl number	0
Molecular weight	371
Ash	0.108%

1000 grams of this synthesis product were mixed with 50 gms. of a catalyst which consisted of 61 parts of nickel, approximately 8 parts of magnesium oxide and 31 parts of kieselguhr. The mixture was treated in an autoclave with stirrer for 4 hours at a temperature of 250°C. and a pressure of 50 kilos/sq. cm. with a gas mixture which contained 75 parts by volume of hydrogen and 25 parts by volume of nitrogen. After the hydrogenation was finished, the catalyst was separated from the hydrocarbon mixture by filtration.

10. The color of the liquid filtered off was light yellow. By fractionation, 11.8% of hydrocarbons which boiled up to 340°C. were separated thereof. The residue boiling above 340°C. amounted to 88.2%. This residue was mixed at 60°C. with dichloroethane in a mixing proportion of 1 : 4 and was then cooled to -25°C. By filtering the mixture at the low temperature, 23.5% of ceresin-like paraffinic hydrocarbons of low viscosity and an average pour point of approximately 50°C. and 76.5% of a lubricating oil having approximately a 6° freezing point were obtained.

Example II

20. A very dark brown colored product boiling above 343°C. and prepared by the hydrogenation of carbon monoxide with the use of pulverulent iron catalysts suspended in the synthesis gas had the following characteristics:

Iodine number	46.0
Neutralization number	1.0
Saponification number	26.5
Hydroxyl number	8
Carbonyl number	44
Molecular weight	467
Ash	0.144%

1000 grams of this synthesis product were mixed with 4000 cc. of a saturated C₇ fraction from the carbon monoxide hydrogenation. 100 gms. of a pulverulent catalyst consisting of 63 parts of nickel, 7 parts of magnesium oxide and 30 parts of kieselguhr were added to the mixture. The mixture was then treated for 4 hours at a total pressure of 60 kilos/ sq.cm. equal to a hydrogen pressure of approximately 30 kilos/sq. cm. and at a temperature of 250°C. with a gas mixture which contained 25 parts by volume of nitrogen and 75 parts by volume of hydrogen.

10. After the treatment with the gas mixture, the reaction mixture was cooled and separated from the catalyst by filtration. The catalyst was rewashed with the C₇ fraction used as the diluting agent.

The liquid product filtered off was nearly colorless and showed a blue-green fluorescence. It was cooled to -10°C. The solid hydrocarbon mixture separated thereby was separated at the same temperature from the liquid constituents by filtration. The solution filtered off was at first subjected to an atmospheric pressure distillation thereby separating the C₇ hydrocarbon added before the hydrogenation and then to a vacuum distillation thereby separating the constituents boiling between 100 and 340°C.

20.

After the separation of the C₇ hydrocarbon approximately 100 grams of a ceresin-like paraffin were obtained which had a pour point of 73°C. and a penetration number of 12. The distillate boiling between 100 and 340°C. had a density of 0.776 (20°C.), a refractive index of 1.4325 (n_D^{20}) and a molecular weight of 177. It consisted of approximately 40% naphthenic and 60% paraffinic hydrocarbons. It could be separated by distillation into 50 gms. of gasoline and 150 gms. of diesel oil.

The residue boiling above 340°C. comprised 700 gms. of
a very light yellow viscous oil having the following characteristics:

Iodine number	0
Neutralization number	0
Saponification number	0
Hydroxyl number	0
Carbonyl number	0
Density at 20°C	0.873
Refractive index n_D^{20}	1.4800
Viscosity at 50°C.	6.10° = 213 SSU.
Viscosity index	104
Flash point	212°C.
Conradson carbon test	0.27%
Molecular weight	470

The lubricating properties of this oil were good.

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

1. Process for the synthesis of high boiling viscous hydrocarbon mixtures which comprises contacting a carbon monoxide hydrogenation synthesis gas with a fine grained moving catalyst containing a member selected from the group consisting of metals and metal oxides of the eighth group of the periodical system at increased pressure at a temperature of about 180°-400°C., separating the portions boiling above about 340°C. from the synthesis products obtained containing aliphatic hydrocarbons and mono- and poly nuclear cyclic compounds, contacting the separated portions boiling above 340°C. with a hydrogen containing gas at a pressure of about 5-100 kilograms per square centimeter at a temperature of about 100-300°C. in the presence of a catalyst containing a metal of the eighth group of the periodical system whereby said portion boiling above 340°C. is at least partially decyclized and at least partially freed of the oxygen containing groups and unsaturated bonds, and recovering a high boiling viscous hydrocarbon mixture.
2. Process according to Claim 1 in which said synthesis gas is contacted at a pressure of about 10-30 kilograms per square centimeter.
3. Process according to Claim 1 in which said contacting of said portion boiling above 340°C. with said hydrogen containing gas is effected at a hydrogen partial pressure of about 30 kilograms per square centimeter at a temperature of about 250°C.
4. Process according to Claim 1 in which said fine grained moving catalysts is in the form of a fluidized bed.
5. Process according to Claim 1 in which said fine grained moving catalysts has a grain size below about 0.25 millimeters and

is suspended in the synthesis gas in amounts of about 15-300 grams of catalyst per liter of synthesis gas.

6. Process according to Claim 1 in which said portions boiling above about 340°C. are contacted with said hydrogen containing gases in the presences of said catalysts with which said carbons monoxide hydrogenation synthesis gas is contacted.
7. Process according to Claim 1 in which said portions boiling above about 340°C. are contacted with said hydrogen containing gas in the presence of a nickel containing catalyst.
8. Process according to Claim 7 in which said nickel containing catalyst is a nickel-magnesium oxide-kieselguhr catalyst.
9. Process according to Claim 1 in which said contacting of the portions boiling above about 340°C. with said hydrogen containing gas is effected in the presence of a hydrocarbon diluent.
10. Process according to Claim 9 in which said hydrocarbon diluent is a C₇-C₉ hydrocarbon.
11. Process according to Claim 1 in which said portions boiling above about 340°C. are contacted with said hydrogen containing gas for a period of time sufficient to at least partially split the bi- and polycyclic compounds contained therein to a member selected from the group consisting of alkylated mono- and poly cyclic hydrocarbons.
12. Process according to Claim 1 which includes separating said high boiling viscous hydrocarbon mixture recovered into ceresin paraffinic hydrocarbons of low viscosity and lubricating oils of higher viscosity.

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