PATENT SPECIFICATION

597,053

Convention Date (United States of America): May 26, 1944.

Application Date (in United Kingdom): May 28, 1945. No. 13339/45.

Complete Specification Accepted: Jan. 16, 1948.

1727

COMPLETE SPECIFICATION

Hydrogenation of Synthetic Hydrocarbon Oils

We, N. V. INTERNATIONALE HYDROGENEERINGSOCTROOIEN MAATSCHAPPIJ (INTERNATIONAL HYDROGENATION PATENTS COMPANY), a Dutch Company, of Willemstad, Curacao, Netherlands, West Indies, do hereby declare the nature of this invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

The present invention relates to the treatment of oil synthesized from carbon oxides and hydrogen, particularly to the low pressure hydrogenation of hydrocarbons produced by the so-called Fischer-Tropsch synthesis wherein carbon monoxide and hydrogen are caused to combine in the presence of a suitable catalyst to form normally liquid hydrocarbons.

It is of course a matter of record, broadly, to subject petroleum stocks to destructive hydrogenation. Thus, for example, processes are disclosed in the prior art in which heavy hydrocarbon oils are produced by destructive hydrogenation of coal, or obtained by hydrogenation of a petroleum hydrocarbon oil, to form desired products, such as hydrocarbons boiling in the gasoline range. Usually these processes of destructive hydrogenation are operated at high pressures, say pressures of 1000 lbs. per square inch or higher.

According to the invention, we hydrogenate crude Fischer-Tropsch synthesis products or other oil synthesized from carbon oxides and hydrogen under conditions of relatively high "throughputs" as hereinafter defined and high temperatures; i.e., at low contact or residence time of reactants in the reaction zone. According to this mode of operation, the isomerizing action of the catalyst, which is chosen with this feature in mind, is enhanced, and degradation of the feed to undesirable gaseous products is limited. Where the feed stock is highly paraffinic, as it is in the case of a product from a Fischer-Tropsch synthesis process, we are also able to operate at relatively low pressure as hereinafter defined.

It will be observed that the process involves a destructive hydrogenation process in which the boiling range of the crude Fischer synthesis product is substantially lowered. We may use any good hydrogenation catalyst, such as one chosen from the group, iron, nickel or cobalt, or we may use the oxide of a metal, such as sungsten, molybdenum and chromium, in conjunction with natural or synthetic cracking clays, such as acid-treated bentonitic clays, or cracking catalysts prepared synthetically and containing alumina and silica gel or magnesia gel.

The main object of the invention therefore is to provide an improved process for hydrogenating crude hydrocarbon Fischer-Tropsch synthesis oils to produce products such as gasoline, improved particularly as to the octane rating, or with increased yields or both, and we accomplish this result in an expeditious and cheap manner.

Another object of the invention is to hydrogenate a highly paraffinic stock under conditions which will give maximum yields of gasoline of relatively high octane number.

Other and further objects of the invention will appear from the following more detailed description and claims.

In the accompanying drawing, we have shown diagrammatically an apparatus in which a preferred modification of the invention may be carried into effect.

To illustrate the invention, but without placing any limitation thereon, we have chosen to illustrate the invention as applied to the hydrogenation of a crude Fischer synthesis product and in describing this operation we shall refer in detail to the drawing.

A crude Fischer synthesis product having the following properties: boiling range of 300—700°F., octane number of 300—400° cut, less than O, A.P.O. gravity of 50°, and an aniline point of 200°F., is withdrawn from storage drum (1) through line (3), thence pumped by pump (4) through a heating coil (6) disposed in a furnace (10), and thence discharged via line (12) into a reactor (14) containing a mass of catalyst (c) supported on a grid or screen (16) and provided

[*Price* 1/-]

with conventional means for removal of reaction heat. Simultaneously, hydrogen is withdrawn from storage (20) through line (22) by means of compressor (23) and after heating in a furnace (24) is likewise discharged through line (26) into the top of reactor (14). The operating conditions and the catalyst used in reactor (14) will be described in detail hereinafter. At this point it will simply be stated that the synthetic oil feed and the hydrogen pass through the reactor (14) and the former is hydrogenated during such passage to form gasoline fractions of greater octane number than in the original feed. The conversion products are withdrawn through line (30) and passed into a hydrogen separator (32) from which a hydrogen-containing gas is withdrawn overhead through line (34) and recycled to storage drum (20).

It is usually desirable to scrub hydrocarbons out of the recycle gas in line (34), and toward this end therefore, the gas is preferably forced through the scrubber which we have indicated by the reference character (S) wherein the gases are treated with a scrubbing oil, such as a light naphtha, for the purpose of dissolving out the said hydrocarbons, thereby enriching the hydrogen eventually discharged into storage (20). The product separated from the hydrogen is withdrawn from separator (32) through line (40) and thence passed into a fractionating column (42) wherein the product is fractionated to recover as a side stream through line (48) fractions boiling within the gasoline range which are cooled in exchanger (50) and finally collected in a receiving drum (52). Normally gaseous hydrocarbons are withdrawn from fractionater (42) through a line (60) while a heavy oil is withdrawn through line (62) and recycled to storage (1) for further treatment. A portion of this oil may be continuously withdrawn from the system through line (65).

It will be understood that the flow plan which is contained in the drawing and which we have described in detail immediately above, represents one suitable arrangement of apparatus in which the process may be carried out, and it will be understood that any other suitable apparatus may be employed in carrying out the invention.

As to operating conditions under which the invention is carried out in the reactor referred to above, these are defined as follows:—

Temperature - - - - -	680—800°F. depending on the feed stock.
Pressure - - - - - -	10—250 atmospheres.
Feed Rates - - - - - -	2—8 volumes of liquid charge per volume of catalyst per hour.
Catalyst - - - - - -	Any good hydrogenation catalyst may be used, such as hydrofluoric acid-treated clay of the montmorillonite type impregnated with tungsten sulfide.
Hydrogen - - - - - -	1000—8000 cu. ft. of hydrogen per barrel of oil feed.
Optimum Conditions - -	In the hydrogenation of a Fischer-Tropsch product temperatures of from about 700—750°F., pressures of 1500 lbs./square inch, and feed rates of from 4—8 volumes of liquid charge per volume of catalyst per hour give exceptional results.

We deem that one of the advantages of the invention, in the case of Fischer-Tropsch crude hydrogenation, is that, due to the fact that the Fischer-Tropsch product is of high hydrogen content, the consuption of hydrogen during hydrogenation is relatively small; under certain conditions it may be reduced to such a quantity that sufficient hydrogen is produced to maintain in the system the required hydrogen by recycling part of the release gases from the hydrogenation zone with or without oil scrubbing, to enrich the said gases in hydrogen content.

Ordinarily the feed stock to the hydrogenation reaction zone will include only portions of the Fischer-Tropsch product which boil higher than the gasoline being produced. Feeding of the material in the gasoline range usually results in somewhat higher gas losses. Little difficulty from coking is experienced in hydrogenating Fischer products. Consequently, either hydrogen partial pressure or total operating pressure may be considerably reduced from the 200 atmospheres conventionally used for hydrogenation of natural stocks. At lower pressures, higher temperatures may be required, or lower through-puts, or both, to obtain the desired octane improvement and degree of conversion to gasoline. The extent of pressure reduction possible is limited only by its effect on conversion and total liquid yield, and, if particularly high temperatures are required, by possible coking or other deposition on the catalyst.

To recapitulate, our present invention relates to improving paraffinic hydrocarbons, such as crude Fischer-Tropsch synthesis oils, produced by combining carbon monoxide and hydrogen in the presence of a catalyst according to known procedure, by subjecting these oils to destructive hydrogenation in the presence of a catalyst adaped to cause cracking and/or isomerization, as well as to promote hydrogenation. Furthermore, our process is characterized by the fact that we operate at high through-puts or high feed rates to a reaction zone, at relatively low pressures and at relatively high temperatures. We are thus enabled to produce from a Fischer synthesis oil, say an oil boiling in the gas oil range, a gasoline fraction in good yields, which has a greatly improved octane rating (5 to 20 numbers) over a gasoline produced from this source in comparable yield by any other method of which we are aware and believe the improvement is due to the fact that its content of isoparaffins and other octane improving constituents is great enhanced.

Numerous modifications of the invention will appear to those who are familiar with this art.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The method of forming from a hydro-carbon oil sinthesized from carbon oxides and hydrogen and boiling in the gas oil range a gasoline of improved octane rating which comprises subjecting the said gas oil to destructive hydrogenation conditions in the presence of a hydrogenation catalyst and added hydrogen in a reaction zone at feed rates of 2—8 volumes of liquid feed per volume of catalyst per hour.

2. The method set forth in claim 1 in which the feed stock is a crude Fischer-Tropsch synthesis product.

3. The method of improving a crude Fischer-Tropsch synthesis oil boiling in the gas oil range which comprises subjecting the said crude oil to a destructive hydrogenation reaction conducted in the presence of added hydrogen and a catalyst containing a hydrogenation catalyst and a cracking clay in a reaction zone, maintaining a temperature from 680—800°F. within said zone, and a pressure within the range of from about 5—25 atmospheres, by continuously feeding the said crude oil to said reaction zone at the rate of from 4—8 volumes of liquid oil per volume of catalyst per hour.

4. The method set forth in claim 3 in which the catalyst is tungsten sulfide supported on an acid-treated bentanitic clay.

5. The method set forth in claim 3 in which a temperature of from 750—850°F. is maintained in the reaction zone.

6. The method of improving a synthetic paraffinic oil of low octane number and boiling in the gas oil range which comprises subjecting the oil to a destructive hydrogenation conducted in the presence of added hydrogen and a catalyst body in a reaction zone, by feeding the said oil to the reaction zone at a rate of from 3 to 8 volumes of oil per volume of catalyst per hour while maintaining an effective destructive hydrogenation temperature in said reaction zone.

7. The method of claim 6 in which the temperature in the reaction zone is in the range of from about 680—800°F.

8. The method of claim 6 in which the catalyst body contains a hydrogenation catalyst and a cracking catalyst.

9. The method of claim 6 in which the catalyst consists of tungsten sulfide supported on an acid treated bentonitic cracking clay.

10. The method of claim 6 conducted at temperatures of from about 700—750°F., while under a pressure of about 1500 lbs. per square inch and at an oil feed rate of 4 volumes of oil per volume of catalyst per hour.

Dated this 28th day of May, 1945.
MARKS & CLERK.

Reference has been directed, in pursuance of Section 7, sub-section (4), of the Patents and Designs Acts 1907 to 1946, to Specification No. 552,731.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1948.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 1s. 0d. each (inland) 1s. 1d. (abroad) may be obtained.

[This Drawing is a reproduction of the Original on a reduced scale.]