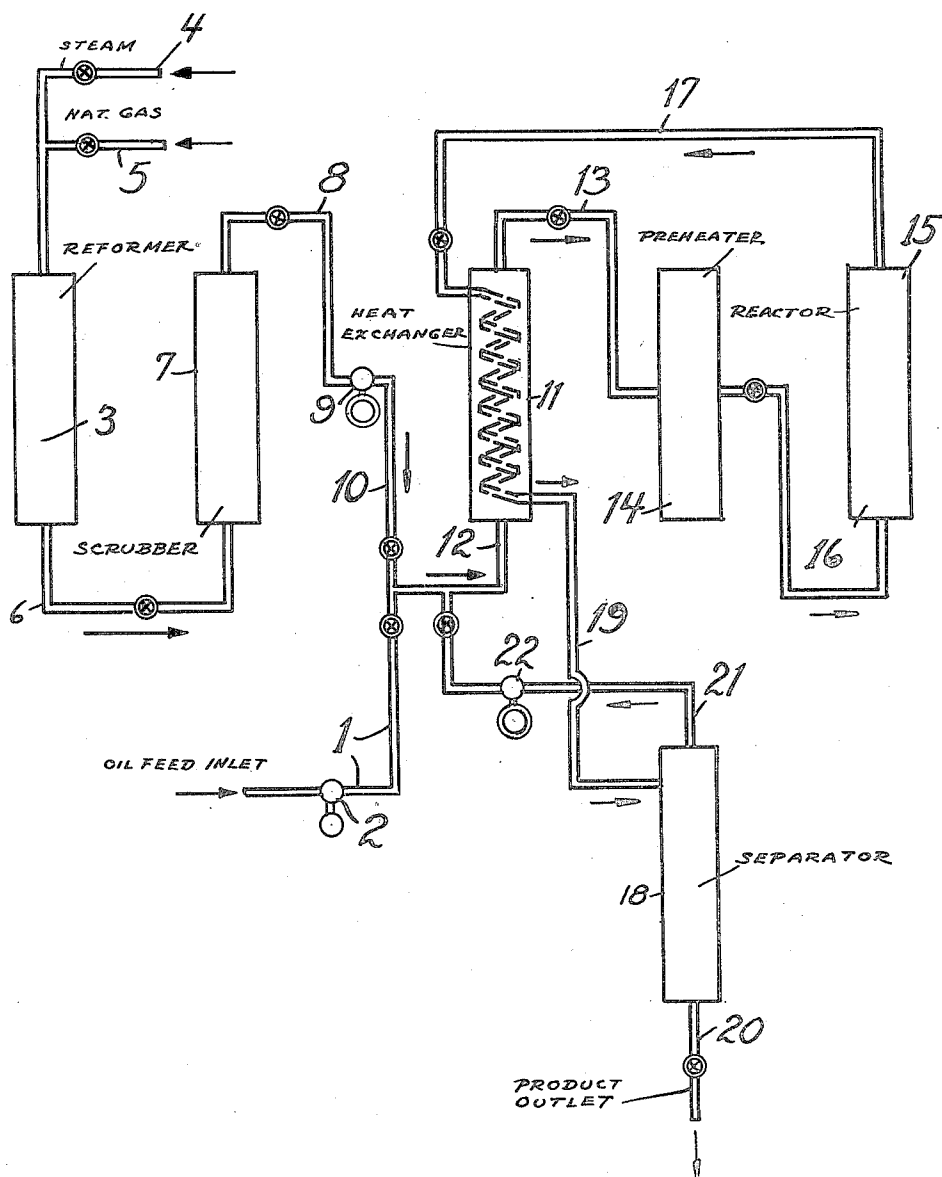


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REFINING MINERAL OIL

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REFINING MINERAL OIL

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5 Claims. (Cl. 196—53)

The present invention is concerned with the refining of mineral oils. The invention is more particularly concerned with the treatment of relatively high boiling petroleum oil fractions for the production of products boiling in the motor fuel boiling range and especially relates to an improved operation in which relatively high boiling oils are destructively hydrogenated under conditions in which the hydrocarbon constituents evolved and hydrogen present react with oxides of carbon to produce hydrocarbons boiling in the aviation and motor fuel boiling ranges. In accordance with the present process, relatively high boiling petroleum oil fractions such as oil fractions boiling in the kerosene and gas oil boiling ranges are treated with a mixture of oxides of carbon in the presence of an iron group catalyst under conditions suitable for both destructive hydrogenation and the Fischer Synthesis reaction.

It is known in the art to manufacture valuable hydrocarbon products boiling in the motor fuel boiling range by the hydrogenation of oxides of carbon. Although these reactions are generally conducted utilizing nickel and cobalt catalysts at temperatures in the range from about 330° F. to about 410° F., higher temperatures up to about 750° F. are employed when iron type catalysts are utilized. In these reactions, it is essential in order to secure a satisfactory yield of the desired quality product that the temperature of the reaction does not vary substantially from the predetermined operating temperature. For example, in reactions employing nickel and cobalt catalysts, carried out at temperatures in the range from about 330° F. to about 410° F., it is desirable that the temperature of the reaction does not vary over a temperature range in excess of about 10° F., and preferably over a temperature range in excess of about 5° F.

In these reactions the catalyst is selected from the class of substances which are known as suitable substances for aiding the hydrogenation of oxides of carbon. Suitable catalysts which may be supported on various carriers are, for example, cerium, chromium, cobalt, manganese, palladium, titanium, zinc, iron, nickel, and oxides or other compounds of these metals. Mixtures of these catalysts are also employed and the same impregnated with suitable agents adapted to increase their efficiency or strength. The oils and the catalysts are contacted by various methods, such as an operation in which the catalysts are supported in beds, or an operation in which a powdered catalyst is employed.

It is also known in the art to treat relatively high boiling petroleum oils under so-called destructive hydrogenation conditions for the production of relatively low boiling oils as, for example, oils boiling in the motor fuel and aviation fuel boiling ranges. In operations of this character, the feed oils and the catalysts are contacted at temperatures in the range from about 500° F. to about 1000° F., and at pressures in the range from about 100 pounds to about 3,000 pounds per square inch, and higher. Various catalysts are satisfactory for utilization in destructive hydrogenation operations, such as metals or compounds of tungsten, molybdenum, iron, cobalt, nickel, vanadium, copper, chromium, magnesium, and zinc. These metals or their compounds may be employed alone or supported on a suitable carrier. It has been found that metallic iron, cobalt, or nickel supported on a suitable carrier, such as an acid treated clay, silica-magnesia, or silica-alumina gel are effective for the destructive hydrogenation of hydrocarbon oils which are relatively free of sulfur.

I have now discovered a process by which feed oils may be destructively hydrogenated under conditions to form lower boiling constituents and under conditions simultaneously to hydrogenate oxides of carbon. In accordance with my invention, these reactions are carried out in a single reaction zone in the presence of an iron group catalyst at a temperature in the range from about 500° F. to about 800° F., and at a pressure in the range from about 100 pounds to about 3,000 pounds per square inch, or higher. The process of my invention may be readily understood by reference to the attached drawing illustrating an embodiment of the same.

Referring specifically to the drawing it is assumed that the feed oil comprises a petroleum oil boiling in the kerosene oil boiling range. The feed oil is introduced into the system by means of feed line 1 and pump 2. The feed is combined with oxides of carbon which are prepared in reforming zone 3 by a reaction involving steam, which is introduced by means of line 4, and natural gas which is introduced by means of line 5. The steam and natural gas in reforming zone 3 contact a catalyst which comprises nickel on kaolin at a temperature in the range from about 1400° F. to about 1500° F. The reaction products comprising oxides of carbon and hydrogen are withdrawn from zone 3 by means of line 6 and passed into scrubbing zone 7 wherein the reaction products may be treated to remove undesirable constituents. The oxides of carbon and

hydrogen are removed from scrubbing zone 7 by means of line 8, compressed by means of compressor 9 and introduced into the feed oil by means of line 10. The mixture is passed into heat exchanging zone 11 by means of line 12, withdrawn by means of line 13, passed through preheating zone 14, and introduced into reaction zone 15 by means of line 16. Temperature and pressure conditions in zone 15 are adjusted to secure the simultaneous destructive hydrogenation of the feed oil, the hydrogenation of the oxides of carbon, and the reaction between hydrocarbons and the oxides of carbon. The temperature is in the general range from about 500° F. to about 800° F. while the catalyst comprises nickel supported on a hydrogen fluoride treated bentonite clay which has been subjected to sulfuric acid treatment before hydrogen fluoride treatment. The reaction products are withdrawn from reaction zone 15 by means of line 17, passed through heat exchanging zone 11, and introduced into separation zone 18 by means of line 19. The reaction product is removed from separation zone 18 by means of line 20, while uncondensed gases are preferably recycled to the reaction zone by means of line 21 and compressor 22. The liquid product removed by means of line 20 is fractionated to obtain a motor fuel product and a heavy product which may be recycled to zone 15.

The process of the present invention may be widely varied. The invention essentially comprises destructively hydrogenating feed oils and simultaneously hydrogenating oxides of carbon by controlling the temperature and the pressure conditions within a single reaction zone and utilizing a particular catalyst whereby these simultaneous reactions are secured. Although the reaction is not entirely understood, it is my belief that the oxides of carbon react with hydrocarbon constituents or hydrocarbon fragments as well as with the hydrogen under the conditions in my reaction. The feed oil preferably comprises a relatively high boiling oil, as, for example, one which boils in the range from about 400 F. to about 700° F.

The oil and the oxides of carbon are contacted in the reaction zone at a temperature in the range from about 500° F. to about 800° F. and at a pressure in the range from about 100 pounds per square inch to about 3,000 pounds per square inch, and higher. The catalysts employed in the reaction zone are metals of the iron group, preferably supported on suitable carriers, such as acid treated bentonites, silica-alumina gels, and silica-magnesia gels. These carriers may or may not be treated with hydrogen fluoride or another suitable fluoride.

These catalysts consist essentially of metallic nickel, cobalt or iron deposited upon highly active cracking catalysts such as "Super-Filtrol," aluminum silicate, synthetic impregnated or plural gels of silica and alumina, silica and magnesia, or silica and alumina and magnesia, or acid-treated clays of the bentonitic and montmorillonitic type. The quantity of metal in the catalyst may be between 1 and 15% by weight and is preferably between 2% and 10% by weight. The active carrier may or may not first be treated with fluorine, hydrofluoric acid, fluosilicic acid, or other fluorine compounds. A particularly desirable catalyst comprises nickel supported on a hydrogen fluoride treated bentonite clay which has been subjected to sulfuric acid treatment before hydrogen fluoride treatment.

The catalyst may be prepared by impregnating the active carrier with a solution of a soluble salt of the metal, preferably the nitrate, then extruding or otherwise shaping the plastic mass so obtained and drying the extruded mass in a steam oven at about 300–400° F. If the nitrate has been used for impregnation, some nitric acid as well as oxides of nitrogen will be evolved in this drying operation. Thereafter the dried mass is heated in a furnace to a temperature between 500° F. and 800° F. for a period of 10 to 12 hours or more in order to decompose the remaining nitrates. This results in a catalyst comprising the metal oxide deposited on the carrier. The metal oxide is then reduced to the metal by circulating hydrogen over the catalyst while the temperature is gradually raised to between about 600° F. and 900° F. This reduction treatment may take place in the reaction vessel in which the catalyst is to be used and immediately following complete reduction the hydrogenation may be begun by introducing the oil feed. In some cases it is found that the activity of these catalysts may be increased still further by treating the metallic catalyst prepared in the manner just described with sulfur-containing gases, such as hydrogen sulfide, and then subsequently removing the sulfur by treatment with hydrogen or hydrogen and a sulfur-free oil.

The preferred gas for the reaction is one obtained by the reformation of methane with steam. The principal products of this reaction are carbon monoxide and hydrogen with only a small amount of carbon dioxide. The hydrogen concentration of the gas mixture is about 4 to 5 times that of the carbon monoxide so that sufficient hydrogen is available for destructive hydrogenation as well as for the Fischer Synthesis. The latter reaction uses from 1 to 2 times as much hydrogen as carbon monoxide depending on the catalyst and conditions used. In the usual destructive hydrogenation process, hydrogen is obtained by reforming methane with steam to produce a mixture of carbon monoxide and hydrogen. The former is oxidized to carbon dioxide which is then scrubbed out to leave pure hydrogen. In the present process the oxidation and scrubbing processes are eliminated and, in addition, part of the carbon ordinarily lost as carbon dioxide is converted to useful hydrocarbons.

In order to illustrate my invention further, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

A cycle stock of low sulfur content and about 43° A. P. I. gravity boiling in the kerosene range and produced in the destructive hydrogenation of a naphthenic kerosene was charged to a bomb with 40 weight percent of a catalyst consisting of 7% metallic nickel supported on an HF treated acid-activated clay. Carbon monoxide was then added to the bomb in the proportion of 0.48 mol of carbon monoxide per mol of hydrocarbon based on the average molecular weight of the hydrocarbon fraction. The carbon monoxide used contained 14% carbon dioxide. Electrolytic hydrogen was then added to bring the gage pressure at room temperature to 900 pounds per square inch. The bomb was then sealed and heated to a temperature of 600° F. which temperature was maintained for a period of twelve hours. The liquid product obtained from the

reaction had an A. P. I. gravity of 53.1. This increase in gravity may be taken as a measure of the extent of the conversion of the liquid feed. Analysis of the products showed that carbon monoxide had reacted to the extent of 0.15 mol per mol of feed. Only 0.02 mol of methane per mol of liquid feed were produced thus showing that the carbon monoxide was converted to higher boiling hydrocarbons. Small amounts of methane are produced in destructive hydrogenation processes when no carbon monoxide is added.

Example 2

The above experiment was repeated with the exception that the amount of carbon monoxide added was 0.28 mol per mol of feed and hydrogen was added to make the total pressure at room temperature 1,450 pounds per square inch. The A. P. I. gravity of the liquid product in this case was 63.1 and the amount of carbon monoxide reacted was 0.22 mol per mol of feed which is equivalent to 79% of the carbon monoxide added. The quantity of methane produced was 0.03 mol per mol of feed.

Example 3

In a third experiment the carbon monoxide used was scrubbed with ascarite to remove carbon dioxide. The amount added was 0.29 mol per mol of feed. The total pressure at room temperature was 1,400 pounds. Otherwise the conditions were the same as given for Example 1. The A. P. I. gravity of the product in this case was 61.4. The amount of carbon monoxide reacted was 0.25 mol per mol of feed. The amount of methane produced was 0.11 mol per mol of feed.

Example 4

In a comparative run in which no carbon monoxide was added and in which the total pressure was 1,700 pounds at room temperature, the A. P. I. gravity of the liquid product obtained was 66.1. The quantity of methane produced was 0.01 mol per mol of feed.

What I claim as new and wish to protect by Letters Patent is:

1. In a process for the catalytic destructive hydrogenation of hydrocarbon oils in the presence of hydrogen and carbon monoxide at temperatures of about 500 to 800° F. and pressures of about 100 to 3,000 lbs./sq. in., the improvement which comprises contacting the hydrocarbon oil at said temperatures and pressures with a metallic iron group catalyst and supplying approximately 0.3 to 0.5 molecular weights of carbon monoxide per molecular weight of hydrocarbon and an amount of hydrogen about 4 to 5 times as great as the amount of carbon monoxide, whereby the hydrocarbon oil is destructively hydrogenated and carbon monoxide is simultaneously converted into hydrocarbons having more than one carbon atom per molecule.
2. The process set forth in claim 1 in which said catalyst comprises a metal of the iron group supported on a siliceous carrier.
3. The process set forth in claim 1 in which said catalyst comprises nickel.
4. The process set forth in claim 1 in which said catalyst is supported on a hydrogen halide-treated clay of the bentonitic and montmorillonitic type.
5. The process set forth in claim 1 in which said oil is a petroleum oil boiling in the range from about 400° F. to about 700° F.

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