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TREATMENT OF SYNTHETIC GASOLINE

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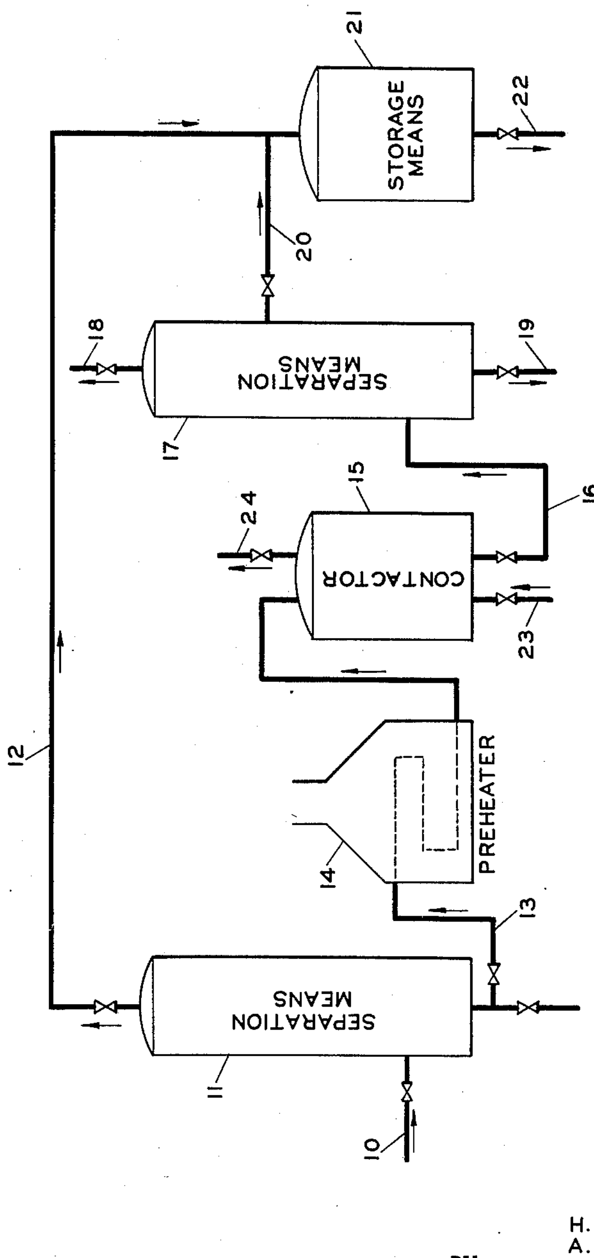

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TREATMENT OF SYNTHETIC GASOLINE

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This invention relates to a process for the production and treatment of motor fuel. In one of its more specific aspects, it relates to a process for the treatment of synthetic gasoline to improve its properties. Preferred embodiments of the invention relate to the treatment of a Fischer-Tropsch type synthetic gasoline to improve its properties.

The Fischer-Tropsch synthesis is a conversion process wherein mixtures of carbon monoxide and hydrogen are converted to hydrocarbons and lesser amounts of oxygen-containing materials over catalysts such as iron, cobalt, and nickel. Under proper conditions and with a suitable catalyst, the reaction may be so controlled that the hydrocarbons produced are principally straight chain olefins containing 5 to 12 carbon atoms per molecule. Such yields may be obtained by using an iron catalyst reduced from iron oxide, which contains minor quantities of potassium oxide and aluminum oxide. In such a procedure, minor amounts of oxygen-containing compounds such as alcohols, aldehydes, ketones, acids, and esters are produced. Certain of these materials are beneficial as components of gasoline, whereas others are detrimental. In particular, the C_1 to C_4 alcohols may be used to advantage in gasolines.

Other oxygen-containing materials, particularly those of long carbon chains and boiling above 90 to 95° C., have detrimental effects if included in gasoline. These oxygen-containing materials have low octane ratings, and the aldehydes are prone to decompose with resultant harmful effects on color, odor, and other properties of the gasoline. As an example of the detrimental effects of these high boiling oxygen-containing materials, there is normal amyl alcohol, which has a clear ASTM octane number of only 52.4. If these oxygen-containing materials are treated over catalysts which will remove organically combined oxygen, such as a natural clay reforming catalyst from the class consisting of bauxite, natural clays of the bentonitic type including montmorillonite, either plain or acid treated, and brucite, bauxite being preferred, to convert them to hydrocarbons, particularly olefins, their octane numbers may be raised. The olefin corresponding to normal amyl alcohol shows the improvement imparted by this treatment by having an octane rating of 77.1 which is 24.7 octane numbers above that of the alcohol. In addition to converting the oxygen-containing materials to olefins, shifting of the double bond and/or shifting of the carbon chain of the olefins

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to form more branched chain olefins, may result with improvement in octane rating and stability.

An object of this invention is to produce high quality motor fuel from hydrogen and carbon monoxide. Another object of this invention is to provide a method for improving gasoline. Another object is to increase the volume of gasoline range products from the Fischer-Tropsch synthesis. Another object is to improve the color and color stability of a Fischer-Tropsch gasoline. A further object is economy in the operation of a Fischer-Tropsch process to produce gasoline. Further objects and advantages of this invention will be apparent to one skilled in the art from the accompanying disclosure and discussion.

We have discovered that by separating a fraction boiling within the gasoline range from a Fischer-Tropsch synthesis and recovering a low boiling fraction below 90 to 95° C. and a high boiling fraction above 90 to 95° C., and by treating the high boiling fraction over a catalyst which will remove organically combined oxygen and isomerize olefins, and admixing the previously separated low boiling fraction with the treated high boiling materials, that a gasoline of improved octane rating and color is obtained. When a raw synthetic gasoline of the Fischer-Tropsch type is separated into fractions of gradually increasing boiling points, the color bodies and compounds of low stability and motor fuel value are found primarily in the high boiling fractions, that is, above about 90 to 95° C. The C_5 to C_7 fractions are colorless and tend to so remain, while the fractions of high molecular weight have excessive color and tend to darken upon standing, especially when exposed to light. Further, we have found that by operating in this manner, i. e., treating only the fraction boiling above 90 to 95° C., that a great saving in catalyst consumption is had thereby making for greater economy of operation.

In a preferred embodiment of the invention, a mixture of hydrogen and carbon monoxide, in a volume ratio of 2:1 is contacted with a Fischer-Tropsch type catalyst, particularly, a powdered iron catalyst made by reducing iron oxide containing 0.05 to 1.0 weight per cent potassium oxide (K_2O), and from 0.5 to 2.5 weight per cent aluminum oxide (Al_2O_3). Suitable reaction conditions are a temperature of 290 to 350° C., a pressure of 70 to 500 pounds per square inch, and a space velocity of 1000 to 4000 volumes of gas per volume of catalyst per hour. Products of this reaction are principally hydrocarbons along with smaller portions of oxygen-containing materials.

The bulk of the oxygen-containing materials, however, are found in an aqueous phase. The lower boiling of these materials, i. e., those boiling below about 90 to 95° C., may be recovered, if desired, as additional gasoline components.

A fraction of the total Fischer-Tropsch effluent produced as described above, boiling in the gasoline range, such as approximately 37 to 205° C., and containing both hydrocarbons and oxygen-containing materials, is recovered for treatment in accordance with this invention. This particular fraction is separated by suitable means into two portions, one boiling below 90 to 95° C. and another boiling above 90 to 95° C. The low boiling fraction comprises 40 to 50 volume per cent of the total gasoline fraction and contains hydrocarbons in the C_5 to C_7 range and lesser amounts of oxygen-containing materials of the C_1 to C_4 range. The high boiling fraction, comprising 50 to 60 volume per cent of the total gasoline fraction, is composed of C_8 and heavier hydrocarbons and minor portions of C_5 and heavier oxygen-containing materials. This high boiling fraction is treated over a stationary catalyst which will isomerize olefins and remove organically combined oxygen, such as bauxite, natural clays of the bentonitic type including montmorillonite, which are plain or acid treated, and brucite, bauxite being preferred, at a temperature which is preferably in the range of 316 to 427 C., a pressure of 0 to 200 pounds per square inch, and a liquid space velocity of 1 to 10 volumes per volume of catalyst per hour. Products from this treatment are separated, removing those materials boiling above and below the gasoline range. The resultant gasoline range materials are then blended with the untreated low boiling fraction producing an improved synthetic gasoline of full boiling range, reduced oxygen content, increased octane number, and improved color and color stability. Furthermore, the oxygen compounds contained in this finished product contribute to the high quality of the fuel.

A better understanding of our invention may be had by referring to the drawing which is a schematic flow diagram of a preferred embodiment.

A synthetic gasoline from a Fischer-Tropsch reaction is introduced through line **10** to separation means **11**, comprising one or more fractional distillation columns and associated equipment, where it is separated into a low boiling fraction and a high boiling fraction. The low boiling fraction containing hydrocarbons and oxygen-containing compounds is removed from separation means **11** through line **12** and passed to storage means **21**. The high boiling fraction is removed through line **13** and passed through preheater **14** to contactor **15** where it is contacted with a catalyst which will decompose oxygen-containing materials to their corresponding olefins, and which will isomerize olefins. Effluent from contactor **15** is removed through line **16** and passed to separation means **17**. Light materials boiling below the gasoline range are separated and removed through line **18**, and heavy materials boiling above the gasoline range are removed through line **19**. Gasoline range materials are removed through line **20** and passed to storage means **21** through line **12**, where they are admixed with the low boiling fraction removed from separation means **11** through line **12**. If desired, low boiling oxygen-containing materials in the C_1 to C_4 range may be separated from the aqueous phase of the Fischer-Tropsch effluent by means not shown, and passed to storage means **21** by further means not shown, where it is admixed with the other gasoline range components. Gasoline may be removed from storage means **21** through line **22**. To regenerate the catalyst, oxygen-containing regeneration gas is introduced to contactor **15** through line **23** at an elevated temperature, and passed countercurrent to the flow of materials which have been treated. Spent regeneration gas is removed from contactor **15** through line **24**.

Advantages of this invention are illustrated by the following example. The reactants and their proportions, and other specific ingredients are presented as being typical and should not be construed to limit the invention unduly.

Example

A Fischer-Tropsch synthesis gas mixture consisting of two volumes of hydrogen and one volume of carbon monoxide is reacted over a powdered iron catalyst promoted with 0.5 weight per cent potassium oxide (K_2O) and 1.5 weight per cent aluminum oxide (Al_2O_3) at a temperature of 300° C., a pressure of 250 pounds per square inch gauge, and a space velocity of 2500 volumes of synthesis gas per volume of catalyst per hour. From a charge of 3000 cubic feet of synthesis gas 3.5 gallons of C_3 and heavier hydrocarbons are produced of which 20 volume per cent is C_3 and C_4 hydrocarbons, 65 volume per cent are C_5 to 205° C. materials, 10 per cent are materials boiling between 205 and 371° C., and 5 per cent is residue boiling above 371° C. Of the gasoline range materials formed, 80 per cent are unsaturated. In addition to the 3.5 gallons of hydrocarbons formed, there are 5 gallons of aqueous layer formed. Of this layer, 8 volume per cent are oxygen-containing materials boiling below 100° C. The gasoline fraction that is recovered from the total Fischer-Tropsch product contains 10 per cent oxygen-containing materials.

The gasoline fraction boiling between 38 and 205° C. is separated by fractional distillation at 90 to 95° C. into two fractions, one boiling below and one boiling above the 90–95° C. cut point. The high boiling fraction is treated over bauxite at a temperature of 400° C., atmospheric pressure, and a liquid space velocity of 2 volumes per volume of catalyst per hour, removing oxygen-containing materials and isomerizing olefins. Of the fraction treated, 2 weight per cent are converted to gases and 3 weight per cent are converted to polymers boiling above the gasoline range. The treated materials within the gasoline range are combined with the low boiling fraction, the gasoline thus produced being stable, free of color, and of 70 to 75 ASTM clear and 80 to 90 Research clear octane ratings. The original untreated gasoline was unstable and had an ASTM clear octane rating of 55 to 65.

From the foregoing disclosure, discussion, and specific example, it is seen that a Fischer-Tropsch type gasoline of high olefinicity and containing oxygen-containing compounds is materially improved by treatment according to this invention, thus producing a higher grade motor fuel.

Although this process has been described and exemplified in terms of its preferred modifications, it is understood that various changes may be made without departing from the spirit and scope of the disclosure and of the claims.

We claim:

1. A process for the manufacture of an im-

proved synthetic gasoline from gasoline boiling range materials having a boiling point range from about 37° to 205° C. produced by a Fischer-Tropsch process for the manufacture of hydrocarbons from hydrogen and carbon monoxide which comprises; separating from said materials a first fraction containing oxygenated organic compounds and having a boiling range above 90°–95° C.; separating from said materials a second fraction containing oxygenated organic compounds and having a boiling range below 90°–95° C.; treating said first fraction at a temperature in the range 316°–427° C. with a reforming catalyst selected from the group consisting of bauxite, brucite and a natural clay of the bentonitic type to effect the removal of the chemically combined oxygen present in said first fraction; and admixing said treated first fraction with said second fraction having its same original composition to produce an improved synthetic gasoline.

2. The process according to claim 1 wherein the reforming catalyst is bauxite.

3. A process for the manufacture of an improved synthetic gasoline from gasoline boiling range materials having a boiling point range from about 37° to 205° C. produced by a Fischer-Tropsch synthesis of hydrocarbons from hydrogen and carbon monoxide employing an iron catalyst which comprises; separating from said materials a first fraction containing oxygenated organic compounds and having a boiling range above 90°–95° C.; separating from said materials a second fraction containing oxygenated organic compounds and having a boiling range below 90°–95° C.; treating said first fraction at a temperature within the range 316°–427° C., with a reforming catalyst selected from a group consisting of bauxite, brucite and a natural clay of the bentonitic type to effect the removal of the chemically combined oxygen present in said first fraction at a pressure in the range of 0–200 pounds per square inch atmospheric and a space velocity of 1–10 liquid volume of catalyst per hour and admixing said treated first fraction with said section fraction having its same, original composition to produce an improved synthetic gasoline.

4. The process according to claim 3 wherein the iron catalyst is promoted with minor amounts of potassium oxide and aluminum oxide.

5. The process for the manufacture of an improved synthetic gasoline from gasoline boiling range materials having a boiling point range from about 37° to 205° C. produced by a Fischer-Tropsch synthesis of hydrocarbons from hydrogen and carbon monoxide over an iron catalyst promoted with minor amounts of potassium oxide and aluminum oxide which comprises; separating from said materials a first fraction containing oxygenated organic compounds and having a boiling range above 90°–95° C.; separating from said materials a second fraction containing oxygenated organic compounds and having boiling range below 90°–95° C., treating said first fraction at a temperature in the range 316°–427° C. with bauxite to effect the removal of the chemically combined oxygen present in said first fraction, at a pressure in the range 0–200 pounds per square inch atmospheric and a space velocity in the range of 1–10 liquid volume of catalyst per hour and admixing said treated first fraction with said second fraction having its same original composition to produce an improved synthetic gasoline.

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