Patented Mar. 27, 1951 2,546,180

UNITED STATES PATENT OFFICE

2,546,180

METHOD OF MAKING MOTOR FUEL

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No Drawing. Application September 17, 1945, Serial No. 616,797

1 Claim. (Cl. 196—78)

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The present invention is a continuation in part of my copending application Serial Number 436,019, filed March 24, 1942, now Patent No. 2,384,866, and relates to a method of treating liquid hydrocarbon containing substantial qualities of undesirable unsaturates usually resulting from oil pyrolysis with or without catalysts and boiling within the range from about 80 degrees to 800 degrees F. and, thus, includes within its scope commercial cracked gasolines, Diesel fuels and light distilled burning or range oils such as kerosene.

The unsaturated hydrocarbon content, as contained in cracked gasoline, or the lower boiling distillate (80° F.–400° F.) as usually used as motor fuel in spark fired Otto cycle motors, represents a valuable component because of its high anti-knock character. It has the disadvantage that it forms gums in storage and in the motors. The unsaturated content is substantial and may range from 20–60%, dependent upon the method of cracking. Where the cracking has been conducted with catalysts the quantity of unsaturates present may be somewhat less than this indicated, however catalytically cracked hydrocarbon will be similarly improved by the treatment according to the present invention.

For ordinary automobile motors, cracked gasoline in present day practice is treated by polymerization, filtration through clay, or by dilute acid washing to remove a portion of the most active gum-forming components which, incidentally, are of the most valuable anti-knock character. The remainder of the fuel is then doped with strong anti-oxidants to prevent oxidation over a period of a few months to allow marketing. Such fuel is not entirely gum-free and must often be used with special heavy solvents to keep the gum in suspension and remove it together with occluded carbon from the combustion chambers. This product, therefore, represents a refiner's compromise to lose as little of the fuel as possible while stabilizing it to a degree only satisfactory for quick use in commercial transportation.

This fuel is not susceptible to substantial improvement in anti-knock value by doping with lead tetraethyl because of its unsaturated hydrocarbon content. Hence, it cannot be used in aviation motors both because it cannot be doped to the super high octane anti-knock value required for high compression aviation motors and because the gum-forming unsaturated constituents cannot be adequately stabilized for aviation

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motor requirements wherein any gum deposition could not be tolerated.

It has been the practice for aviation fuel blends to avoid use of the present great bulk fuel supply of cracked gasoline because of its unsaturated character and to rely largely upon special synthetic isoparaffins formed from alkylation and hydropolymerization of the C_3—C_4 fraction of the byproduct gases produced in gas oil cracking. Hence, the high anti-knock aviation fuel supply has substantially been restricted to the 1 or 2 per cent of waste gas by-product of the normal cracked gasoline motor fuel supply. The synthetic isoparaffins must be blended with a fuel base which must be specially refined and is of poor anti-knock character and of relatively limited supply. Such fuel base may be obtained from gasolines cracked with catalysts but only after removal of unsaturates which represents a loss.

In the cracked higher boiling naphtha fractions of the kerosene type, unsaturated hydrocarbon components are undesirable for both Diesel fuel and burning oil purposes not only because of the gum-forming character but also because, in the case of Diesel fuel, the high anti-knock unsaturates are undesirable because they do not burn properly in the Diesel cycle of combustion, resulting in a lower cetane number of the fuel and in the case of burning oils, the unsaturates burn with a smoky flame, resulting in carbon and soot deposition. Thus, it is desirable to replace unsaturates in any type of motor fuel or burning oil with saturated products.

In its broadest aspect the present invention embraces the treatment of unsaturated cracked petroleum naphthas boiling in the gasoline, Diesel fuel, and burning oil range to remove the unsaturated constituents and converting all or a substantial portion thereof to branched chain paraffinic hydrocarbon.

The unsaturates are first extracted from cracked naphtha by treating the naphtha with an extraction medium such as strong mineral acids, for example, 65–100% H_2SO_4, or with other known extraction solvents such as liquid sulfur dioxide, phenol, furfural, "Chlorex," polyglycol ethers, etc. or mixtures thereof by conventional dual extraction processes.

In operating the present process, this extract may be acted on in its entirety as hereinafter described to convert all of the active components to branched chain paraffinic hydrocarbon.

It is preferable, however, to first fractionate the extract to produce a low or high boiling fraction, depending upon the particular fuel for which

it is intended. For example, for high anti-knock spark-fired motor fuel, the lower boiling fraction from 80° to 200° or 80° to 150° F. would be preferred in order that the product, when converted to branched chain paraffinic hydrocarbon, will boil in lower boiling range desirable for this type of fuel. It will be apparent that if the so-called "safety" high flash point fuel were specified, a higher boiling fraction of extract boiling from 125 to 250° F. would be used. For use in Diesel fuels and burning oils, the use of the higher boiling fractions from 200° F. to the end point of 500 to 800° F. would be preferred.

It is further desirable to extract from any particular fraction the more readily reactable unsaturates, for example, the tertiary olefins, so that a higher yield of branched chain paraffinic hydrocarbon may be produced by more rigid control of reaction conditions upon easily reactable olefins as distinguished from the less easily reactable unsaturates, each being subjected to optimum reaction conditions for its type. Tertiary olefins are readily separated by treating the original extract or fraction thereof with 60–65% H_2SO_4 or a selective solvent such as phenol. In an alternative method, suitable catalysts, such as BF_3, boron fluoride, in alcohol or acetic acid solution may be used which reacts selectively with only the tertiary olefins, the secondary or less reactive olefin being reacted at a later stage or discarded.

The extract or fraction according to the present invention is now alkylated with methane or ethane gas to effect substantial saturation thereof. According to this method of alkylation the extract is treated with methane and hydrogenation catalysts at low temperatures 100–600° F. and high pressures so that free methyl radicals produced as intermediates are caused to add to the extract.

Not only do the olefins otherwise wasted provide a source from which the saturated hydrocarbon may be prepared for blending with motor fuels, but the very method of obtaining the olefin by extraction from the naphtha provides a saturated blending base fuel containing no undesirable olefins, a characteristic which makes the present process of outstanding value for preparation of 100 plus aviation fuels.

It will be apparent that the aromatic content of the extract may similarly be desirably converted to the type of derivatives set forth above, but since it is a desirable fuel component particularly in gasolines, it may be separated and returned to the raffinate without treatment.

Example

A raw vapor phase cracked gasoline boiling from 80 to 400° F. was extracted with liquid sulfur dioxide according to the Edeleanu process. After removal of sulfur dioxide, the extract was fractionated to obtain a cut boiling from 80 to 175° F. Alternatively the entire extract may be treated or extracts of unsaturated petroleum fractions of higher or lower boiling ranges.

Any such olefine preferably a high volatile fraction rich in tertiary olefines is reacted in a hydrogen exchange reaction sometimes known as intermolecular hydrogenation with gaseous hydrocarbon such as methane, ethane or propane, preferably methane, by reacting the extract with an excess of methane for hydrogenation thereof in the presence of aluminum chloride at about 600° F. and high pressures 60 to 100 atmospheres. The catalyst is carried on an inert carrier such as silica, alumina or diatomaceous earth which has been treated with dry hydrogen chloride and minor quantities of activating metals such as reduced nickel or platinum. The efficiency and degree of alkylation depends on the time of contact, the contact being short and rapid for select fractions such as tertiary olefines, but a fraction containing aromatics takes longer. For purposes herein the extract is contacted with the catalyst at a 10 to 20% rate and 5 to 12% for an aromatic fraction (weight of extract per weight of catalyst per hour). The saturated gas is used in preferably two or three times the molecular ratio required for saturation by alkylation but a larger excess up to 10 times may be used and the extract vapors and methane are passed under the conditions stated over the catalyst. The reaction product is separated from unreacted portions by extraction and the raffinate is reblended with the original raffinate. The extract may be fractionated and recycled to the reactor after proportions are readjusted, or it may otherwise be treated according to other unsaturated treatments herein or discarded. Where higher temperatures are used, i. e. up to 800° F., alkylation is effected in higher yield, but side reactions such as polymerization of the olefine also takes place at a higher yield tending to destroy its utility as recycle stock. Where mixtures of methane with higher alkanes such as ethane and propane are used a progressively lower temperature may be used ranging from 400 to 600° F. and if the higher molecular weight gas is used alone (propane) it is desirable to use the lower temperature or 300 to 400° F.

Having thus described my invention, I claim:

Process of treating olefines comprising passing a mixture thereof with an excess of methane over a catalyst comprising aluminum chloride and activating metals selected from the group consisting of nickel and platinum on a carrier at a temperature from 400 to 800° F. and a pressure of 60 to 100 atmospheres.

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