United States Patent [19]

Rollmann et al.

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[54] **PROCESS FOR THE PRODUCTION OF GASOLINE**

[75] Inventors: **Louis D. Rollmann; John C. Zahner,** both of Princeton, N.J.

[73] Assignee: **Mobil Oil Corporation,** New York, N.Y.

[22] Filed: **May 30, 1974**

[21] Appl. No.: **474,496**

[52] **U.S. Cl.** **44/56**

[51] **Int. Cl.**[2] **C10L 1/18**

[58] **Field of Search** ..... 260/643 D; 44/56

[56] **References Cited**

UNITED STATES PATENTS

3,846,088 12/1971 Brown et al. 44/56

Primary Examiner—Daniel E. Wyman
Assistant Examiner—Y. Harris-Smith
Attorney, Agent, or Firm—Charles A. Huggett; Michael G. Gilman

[57] **ABSTRACT**

Reduction of bromine number of cracked gasolines by etherifying the iso-olefin content thereof with excess methanol followed by the addition of a small amount of water to extract the excess methanol remaining after the etherification. The water-methanol phase can be conventionally resolved and the fractions thereof recycled.

4 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF GASOLINE

This invention relates to the production of gasoline. It more particularly refers to the production of gasolines which are less reactive with air and therefore less of a pollution hazard.

It is known to produce gasoline by blending a variety of similarly boiling hydrocarbon fractions e.g. C_5 to about 400°F. These fractions include virgin naphtha, reformate (reformed naphtha), cracked gasoline, coker gasoline, pyrolysis gasoline and the like. Some gasoline fractions have significant olefins content and while olefins have relatively high blending octane values, they also are reactive with air to produce smog formers as well as other pollutants.

In view of this situation, it has become the practice, in some areas of the country, to treat gasolines so as to reduce their smog forming potential. In this regard it is known to hydrotreat gasolines in order to remove at least some of the worst smog-producing constituents thereof. Such hydro-treating is relatively mild but is severe enough to saturate the olefin content of the gasoline. It is unfortunate that many high octane olefins are thus converted to lower octane paraffins. The overall effect is therefore to make cleaner, lower octane number gasoline.

It is known that low molecular weight ethers, particularly branched chain ethers, have very high octane numbers and are in general excellent gasoline blend stocks. Proposals have therefore been made to convert light olefins, particularly isobutylene, to a gasoline boiling range material by etherifying such with a lower alcohol, preferably methanol, in contact with a strong acid catalyst (see U.S. Pat. No. 3,726,942 as being exemplary of such art in this field). Converting isobutylene to t-butyl methyl ether can be an attractive alternative to alkylation of the isobutylene particularly in refineries where isobutane, required for alkylation, is in short supply or where alkylation capacity is insufficient to accommodate all of the C_3 and C_4 olefins generated in cracking processes. Converting isobutylene to t-butyl methyl ether further serves the purpose of increasing the total gasoline pool by adding into it non-gasoline constituents, e.g. methanol and isobutylene.

It has also been proposed to reduce the bromine number of cracked gasoline through etherification (see U.S. Pat. No. 3,482,952) of a portion thereof. This patent states that the C_4 to C_6 fraction of the effluent of a cracking process, commonly separated into light gas (C_4) and stabilized (C_5^+) gasoline streams, contains the major portion of the tertiary olefins and that a "high degree" of improvement in the present gasoline product is obtained when (this complete) fraction . . . is etherified. The patent states that, "If wider boiling ranges of materials are used, the improvement in octane rating is substantially decreased, rapidly approaching that of the whole untreated gasoline blend." Therefore, this reference discloses cutting unstabilized cracked gasoline to produce a C_4–C_6 fraction and a heavier fraction; etherifying the C_4–C_6 fraction with a lower alcohol and a strong acid catalyst; and then recombining the etherified fraction with the heavier fraction. In a preferred embodiment, the etherified fraction is subjected to alkylation before being recombined with the heavier fraction. In a further preferred embodiment, the ether containing fraction is split into an ether-lean and an ether-rich fraction; the ether-lead fraction is alkylated and all fractions recombined.

It will be clear that from an economics point of view, it is most desirable to subject a gasoline, or for that matter, any other product to as little processing as possible consistent with achieving the desired results. In the case at hand, the problem being attacked in the art, and here, is to reduce the olefins content of cracked gasoline in order to reduce the pollution hazard thereof, while at the same time, upgrading the quality and/or quantity of gasoline so produced. An added desiratum is to carry out these purposes with as little treatment and as few operations as possible.

It is therefore an object of this invention to provide a novel process of reducing the bromine number of gasoline.

It is another object of this invention to provide an improved process for reducing the olefins content of stabilized cracked gasoline.

Other and additional objects of this invention will become apparent from a consideration of this entire specification including the claims hereof.

In accord with and fulfilling these objects, one aspect of this invention resides in a process comprising: etherifying a cracked gasoline boiling in the range of C_5 to about 400°F and having a bromine number of at least about 40 with a stoichiometric excess of methanol (based on tertiary olefin) in the effective presence of a strong acid catalyst; separating a gasoline product having a reduced bromine number, an increased ether content and free methanol from said catalyst; adding about 10 to 100 volume percent, based upon the volume of methanol, of water to said product; partitioning said methanol to said water; and separating a gasoline fraction of substantially reduced methanol content from an aqueous phase having a methanol content of at least 50 volume percent.

While this invention is principally directed to treating whole, i.e. C_5^+, unsaturated gasoline in order to reduce the bromine number thereof, it is also applicable to treating portions of a full range cracked or coker or pyrolysis gasoline is only a portion. A critical feature of this invention lies in the methanol treatment of a gasoline boiling range fraction, not a lighter, e.g. C_4^-, fraction. There is a special problem which is encountered when a C_5^+, gasoline boiling range olefinic stream is etherified which does not occur when lighter olefins are etherified with methanol. Whereas with light olefins it is possible to judiciously choose catalyst and operating conditions so as to etherify with substantially stoichiometric reactant proportions at relatively low temperatures, with gasoline boiling range tertiary olefins the etherification conditions are much more difficult (because of equilibrium and reaction rate considerations) and require a marked excess of etherifying methanol. Etherifying with excess methanol requires that the ether and excess methanol containing product be resolved so as to separate at least most of the methanol therefrom.

The requirement for recovery of excess methanol in the gasoline product suggests inquiry into the light olefin etherification art for techniques to accomplish this. It will be found that separation of excess methanol from the etherification product of isobutylene is conventionally carried out by a combination of distillation to separate the hydrocarbons, on the one hand, from the ether and alcohol on the other hand. The hydrocarbon distil-

late contains a small amount of residual methanol which can be removed by water washing. The ether and the methanol are separated by water partitioning using a very large excess of water.

In treating an ether containing C_5^+ gasoline fraction containing unreacted methanol, separation of the alcohol by distillation is not feasible because of the formation of azeotropes and because of the proximity of the boiling points of methanol and portions of the gasoline fraction. It has been found, however, that this excess methanol can be separated from the etherification product by simply adding a small amount of water, i.e. about 2 to 15 percent, to the product, partitioning the methanol into the minor water phase and then separating the phases. It is most surprising that when an etherification product is so treated, even a rather large content of methanol up to about 25%, will partition into the rather small amount of water so completely, at least about 90%, and that the ethers will remain almost completely in the gasoline phase. Practice of the instant resolution process provides for at least 90% separation of the free methanol from the gasoline and removing less than 10% of the ether from the gasoline while reducing the bromine number of the gasoline by at least about 10% and by as much as about 40%.

Etherification catalysts are strong acids, for example, hydrofluoric acid, sulfuric acid, aluminum chloride, boron trifluoride, sulfonated coals or other solid materials such as resinous phenol-formaldehyde, coumarone-indene-cyclopentadiene, styrene-divinyl benzene and the like. Solid catalyst particle size may vary over a wide range, e.g. 10 to 400 mesh, and may comprise about 0.5 to 50 weight percent of the reaction zone contents. Etherification space velocities of about 0.5 to 10 LHSV are suitable at temperatures of about 100° to 300°F, and preferably between about 150° and 220°F.

The following Examples are illustrative of the practice of this invention without being limiting thereon. Parts and percentages are by weight unless expressly stated to be on some other basis.

EXAMPLE 1

A mixture of 80 volume % light fluid catalytically cracked C_5^+ gasoline having a bromine number of 98, and 20 volume of methanol is contacted with a sulfonated styrene-divinyl benzene solid catalyst at 176°F, 300 psig and 3 WHSV to produce a product containing 16% methanol in addition to various methyl ethers and C_5^+ hydrocarbons. After separation of the liquid product from the solid catalyst, 4 volume percent water is admixed whereupon a phase separation occurs. The oil phase contains 1.7% methanol, has a bromine number of 74 and is acceptable as a gasoline blend stock. This oil phase represents a liquid yield of 103.2%, based upon the gasoline charged and has a clear research octane number of 95.9 compared to 94.6 for the fed gasoline. The aqueous methanol phase contains less than 1% ether.

EXAMPLE 2

The procedure of Example 1 is repeated except that 15 volume percent water is admixed with the liquid product from the solid catalyst. After phase separation the oil phase contains 1.0% methanol. The aqueous methanol phase contains less than 0.5% ether.

What is claimed is:

1. In the process of improving the quality of an olefinic gasoline boiling range fraction containing, C_5^+, gasoline boiling range, tertiary olefin and having a bromine number of at least about 40 by contacting such with a stoichiometric excess of methanol, based on tertiary olefin, at about 100° to 300°F in the effective presence of an acid etherification catalyst to produce a product, having a bromine number at least 10% lower than the Bromine number of the olefinic gasoline feed, comprising gasoline boiling range hydrocarbons, ethers and free methanol; the improvement, whereby removing said methanol from said product, which comprises admixing said product with about 2 to 15% water; partitioning said methanol into a water phase and said ether into an oil phase; and separating said water and oil phases.

2. The improved process claimed in claim **1** wherein the etherification is carried out at about 150° to 220°F.

3. The improved process claimed in claim **1** wherein said stoichiometric excess of alcohol is up to about 500%, based on tertiary olefin.

4. The improved process claimed in claim **1** wherein said gasoline comprises pyrolysis gasoline, coker gasoline, cracked gasoline or mixtures thereof.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,902,870

DATED : September 2, 1975

INVENTOR(S) : LOUIS D. ROLLMANN and JOHN C. ZAHNER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line "the ether-lead fraction" should be --the ether-lean fraction--

Signed and Sealed this

twenty-fifth Day of *November 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks