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[54] **PREPARATION OF IMPROVED MOTOR FUELS CONTAINING FURAN ANTIKNOCKS**

[75] Inventors: **Richard S. Stearns,** Malvern, Pa.; **Robert M. Thompson,** Wilmington, Del.

[73] Assignee: **Sun Ventures, Inc.,** Pa.

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[51] **Int. Cl.**[2] **C01L 1/14**

[58] **Field of Search** ..... 44/63; 252/386; 260/346.1 R

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Primary Examiner—Delbert E. Gantz
Assistant Examiner—Andrew H. Metz
Attorney, Agent, or Firm—George L. Church; Donald R. Johnson; Stanford M. Back

[57] **ABSTRACT**

The octane rating of gasoline alkylate may be improved by separating therefrom 2,4- and 2,5-dimethylhexanes ("DMH") and subjecting said DMH to the following combination of steps: (1) oxidizing the DMH to form the corresponding hydroperoxides; (2) reacting of the hydroperoxides with propylene to yield the corresponding diols plus propylene oxide; and (3) dehydrating of the diols to produce 2,2,5,5-tetramethyltetrahydrofuran ("TMTHF"), which product is then added to the gasoline alkylate, thereby improving its octane rating. In addition, valuable propylene oxide is recovered as a by-product.

14 Claims, No Drawings

PREPARATION OF IMPROVED MOTOR FUELS CONTAINING FURAN ANTIKNOCKS

BACKGROUND OF THE INVENTION

This invention relates to a novel method for improving the octane rating of motor fuels. More particularly, this invention relates to a novel composition and a multi-step process for preparing the same by converting dimethylhexanes obtained from gasoline alkylate to 2,-2,5,5-tetramethyltetrahydrofuran, and returning said tetrahydrofuran to the gasoline alkylate in order to upgrade the same.

It is known that the presence of dimethylhexanes in motor fuel alkylate is detrimental to its octane rating, as demonstrated by the fact that their removal improves its octane number by about two units. Removal of these compounds is alone not a satisfactory answer to this problem since the cost of the alkylate is increased by these processing steps, which cost is not offset by the value of the dimethylhexanes (DMH) in their recovered state.

Accordingly, development of a method whereby the recovered DMH can be converted to a more valuable product, and particularly one which when added to the gasoline alkylate would increase its octane number, would be highly advantageous to the motor fuel art.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that dimethylhexanes recovered from conventional gasoline alkylates may readily be converted to the corresponding 2,2,5,5-tetramethyltetrahydrofuran, a compound which is known to increase the octane number of motor fuels. As a by-product of this process there is also recovered propylene oxides, or like olefin oxide depending upon the olefin reactant selected.

Thus, in accordance with this process there is carried out the following combination of steps:

1. a gasoline alkylate, i.e. a C_5–C_9 alkylate, boiling in the range of from about 80° to 270°F is distilled in order to recover 2,4- and 2,5-DMH;
2. the DMH mixture is then oxidized with oxygen to form the corresponding 2,4- and 2,5-DMH hydroperoxides;
3. the peroxides thus obtained are reacted with a C_4–C_8 monoolefin to yield the corresponding DMH alcohol together with the corresponding olefin epoxide;
4. the DMH alcohol is dehydrated to produce 2,2,5,-5-tetramethyltetrahydrofuran which is added to the alkylate.

DETAILED DESCRIPTION OF THE INVENTION

In the first step, a gasoline alkylate containing from about 6 to 8 percent by volume of 2,4- and/or 2,5-DMH's is distilled in a conventional manner, i.e. at a temperature of about 228° to 230°F in order to recover the DMH compounds. Desirably, as much DMH should be removed as is practicable, and in any event the remaining gasoline alkylate should contain not more than about 2 percent residual DMH. The gasoline alkylate charge stock to which the process generally pertains is that alkylate containing C_4–C_9 hydrocarbons which boils in the range of from about 80° to 270°F, and which is conventionally obtained by sulfuric acid or hydrofluoric acid alkylation.

The DMH mixture recovered therefrom is then oxidized in a known manner to produce the corresponding dihydroperoxides. This is conveniently achieved by oxidizing the DMH with oxygen at temperatures of about 235° to 290°F., preferably about 240° to 280°F, with low conversions per pass, i.e. about 15 to 25 percent per pass, and preferably about 20 percent, using no catalysts, but employing a peroxide or hydroperoxide initiator, such as dimethylhexyl hydroperoxide itself.

The dihydroperoxides thus obtained may then be reacted with a C_3–C_8 monoolefin, preferably propylene, to yield the corresponding DMH diol and olefin oxide, such as propylene oxide. This epoxidation reaction is desirably carried out in accordance with the method described in J. Org. Chem. 35, p. 1839 (1970), i.e. with an excess of olefin over hydroperoxide, desirably in a mole ratio of about 3:1 to 1.5:1 of olefin to hydroperoxide, and preferably about 2:1, using a catalyst such as molybdenum hexacarbonyl at temperatures of from about 75° to 95°C, preferably at about 85° to 90°C. The catalyst should be present in amounts of about 4×10^{-5} to 1×10^{-4} moles per 0.5 mole of olefin. The product mixture when, e.g., propylene is employed as the olefin, comprises 2,4- and 2,5-DMH diol and propylene oxide, which mixture is conveniently separated by distillation.

In the final step of the process the dimethylhexane diols are dehydrated to form 2,2,5,5-tetramethyltetrahydrofuran and water. This dehydration is readily achieved by contacting the diols with a catalyst such as aniline hydrobromide, at temperatures of about 100° to 130°C and recovering the TMTHF. The catalyst is generally employed in amounts of about 0.1 g. per mole of diol.

The TMTHF thus obtained is then blended with the original gasoline alkylate from which the DMH had been removed to obtain a gasoline composition containing at least about 1 percent by volume of said TMTHF, preferably about 1.5 to 3.0 percent, and not more than about 2 percent unreacted DMH. When compared with the octane number of the original alkylate containing the 2,4- and/or 2,5-DMH, the overall effect of removing these latter compounds and converting them to TMTHF is to raise the octane number of the gasoline alkylate by a total of about 3–3.5 units. It will be understood, of course, that additional furan obtained from sources other than the original hexanes may also be employed to increase the furan content of the alkylate if so desired.

In a further embodiment of this invention, it is also contemplated that the DMH hydroperoxides described above may themselves be used as octane improvers. That is to say, these hydroperoxides are also able to increase the octane number of a motor fuel alkylate, so that if desired, rather than convert the DMH compounds to TMTHF, the intermediate hydroperoxides may be employed as octane improvers instead. However, it is preferred to convert the hydroperoxide to TMTHF because of the inherent stability of this latter compound.

The process of this invention will now be illustrated in the following examples.

EXAMPLE 1

Distillation of Sulfuric Acid Alkylate Product

One gallon of gasoline alkylate obtained from conventional sulfuric acid alkylation, and containing about 7 percent by volume of a mixture of 2,4- and 2,5-

dimethylhexane was distilled on a Podbilniak still with a 25 mm × 36 inch column containing heli-grid packing and an efficiency of 30 plates at a 30 to 1 reflux ratio. A hydrocarbon fraction boiling between 213° to 233°F, and weighing 160 grams, was isolated. VPC analysis showed this fraction to contain 47 percent 2,5-dimethylhexane, 28 percent 2,4-dimethylhexane, together with 16 percent 2,2,3-trimethylpentane and some higher octane alkylates.

EXAMPLE 2

Oxidation of the 213°–233°F Distillate Fraction

In an apparatus similar to that described by F. F. Rust, J. Am. Chem. Soc., 79, 4000 (1957), oxygen was passed through the hydrocarbon fraction containing 47 percent 2,5- and 28 percent 2,4-DMH at 120°C with a pressure of 30 psi. The formation of hydroperoxides of the dimethylhexanes was followed iodimetrically. After about a 20 percent conversion of DMH, the reaction was stopped and the residual hydrocarbons were flashed off and recycled two more times. After three passes, 85 g. of the dihydroperoxide product was obtained, along with 100 g. of the hydrocarbon fraction containing the 2,2,3-trimethylpentane and higher alkylates.

EXAMPLE 3

Epoxidation of Propylene Using Oxidized Alkylate

The dihydroperoxides were charged in a 1 liter Parr reactor, along with 0.1 g. of $Mo(CO)_6$ and 44 g. of propylene (10 percent excess). The mixture was heated with stirring to 110°C. After 1 hour the reaction mixture was cooled to room temperature and the product analyzed for hydroperoxide conversion and epoxide formation by VPC. There was a 97 percent conversion of the hydroperoxides to 2,4- and 2,5-dimethylhexane diols; 48 g. of propylene oxides was recovered by distillation at low temperatures in vacuo and washed with thiosulfate solution to remove any traces of hydroperoxide.

EXAMPLE 4

Dehydration of the 2,4-Dimethylhexane-2,4-diol and 2,5-Dimethylhexane-2,5-diol

The residue comprising the DMH diols was distilled in the presence of aniline hydrobromide. 2,2,5,5-tetramethyltetrahydrofuran began forming slowly at 111.5°C and continued until the temperature reached 125°C; 52.0 g. of the TMTHF derivative was obtained.

EXAMPLE 5

Blending of 2,2,5,5-Tetramethyltetrahydrofuran and Residue Hydrocarbon in the Original Alkylate

The 52 g. of TMTHF and the 100 g. of the hydrocarbon fraction from the oxidation step were combined and blended with the original alkylate from which it was obtained. The blended material was then tested for anti-knock characteristics. It was found to have an octane rating of 99.2, 3.3 numbers over the original of 95.9.

What is claimed is:

1. A process for improving the octane rating of a gasoline alkylate containing at least 6 percent by weight of a mixture of 2,4- and 2,5-dimethylhexanes which comprises the steps of:

a. separating at least about 4 percent of said dimethylhexanes from said alkylate;

b. oxidizing the dimethylhexanes with oxygen to form the corresponding 2,4- and 2,5-dimethylhexane dihydroperoxides;

c. reacting said hydroperoxides with a C_3–C_8 monoolefin to form a mixture of the corresponding dimethylhexane diols and olefin oxide, and recovering said olefin oxide from said mixture;

d. dehydrating said dimethylhexane diols to form 2,2-,5,5-tetramethyltetrahydrofuran; and

e. combining said tetrahydrofuran with said gasoline alkylate from which the dimethylhexanes had been removed.

2. The process according to claim **1** wherein the monoolefin is propylene and the recovered olefin oxide is propylene oxide.

3. The process according to claim **1** wherein the mole ratio of olefin to hydroperoxide is about 3:1 to 1.5:1.

4. The process according to claim **1** wherein the reaction of the olefin with the hydroperoxide is carried out in the presence of a catalyst.

5. The process according to claim **4** wherein the catalyst is $Mo(CO)_6$.

6. The process according to claim **1** wherein the dimethylhexane diols are dehydrated in the presence of a dehydration catalyst.

7. The process according to claim **6** wherein the catalyst is aniline hydrobromide.

8. A process for the preparation of 2,2,5,5-tetramethyltetrahydrofuran which comprises the steps of:

a. oxidizing 2,4- and 2,5-dimethylhexane with oxygen to form 2,4- and 2,5-dimethylhexanedihydroperoxide;

b. reacting said hydroperoxides with a C_3–C_8 monoolefin to form a mixture of the corresponding dimethylhexane diols and olefin oxide, and recovering the olefin oxide from said mixture;

c. dehydrating said dimethylhexane diols to form 2,2-,5,5-tetramethyltetrahydrofuran.

9. The process according to claim **8** wherein the monoolefin is propylene and the recovered olefin oxide is propylene oxide.

10. The process according to claim **8** wherein the mole ratio of olefin to dihydroperoxide is about 3:1 to 1.5:1.

11. The process according to claim **8** wherein the reaction of the olefin with the hydroperoxide is carried out in the presence of a catalyst.

12. The process according to claim **8** wherein the catalyst is $Mo(CO)_6$.

13. The process according to claim **8** wherein the dimethylhexane diols are dehydrated in the presence of a dehydration catalyst.

14. The process according to claim **8** wherein the catalyst is aniline hydrobromide.

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