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[54] **TERTIARY MONO OLEFIN EXTRACTION WITH MIXED ACIDS**

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[51] **Int. Cl.** **C07c 11/00**

[58] **Field of Search** ..... 260/677 A, 677 S, 681.5 R

[56] **References Cited**

UNITED STATES PATENTS

1,941,267	12/1933	Morrell	208/224
1,941,267	12/1933	Morrell	208/255
2,515,006	7/1950	Hudson	260/677 R
2,530,332	11/1950	Hudson	260/677 X
3,231,632	1/1966	Friedli et al.	260/677 S

FOREIGN PATENTS OR APPLICATIONS

683,322	3/1964	Canada	260/677 A

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[57] **ABSTRACT**

A liquid refinery hydrocarbon stream containing tertiary olefins is contacted with a mixture of sulfuric acid, water and at least one aliphatic monocarboxylic acid to extract the tertiary olefins from the hydrocarbon stream in an acid extract which may be further reacted directly, or treated to remove the tertiary olefins or the tertiary alcohols in concentrated form.

3 Claims, No Drawings

TERTIARY MONO OLEFIN EXTRACTION WITH MIXED ACIDS

BACKGROUND OF THE INVENTION

The use of strong polybasic mineral acids or organic acids or mixtures thereof for the selective extraction of tertiary olefins from a hydrocarbon stream is well known. For example, U.S. Pat. Nos. 2,007,159 and 2,007,160 teach the use of polybasic mineral acids such as sulfuric or phosphoric acid, or, in certain instances, the use of monobasic acids such as hydrochloric acid or organic acids such as benzenesulfonic acid or the sulfonic acids of the homologs of benzene. U.S. Pat. No. 2,515,006 teaches the use of a mixture of sulfonic acids modified by the presence of a polybasic mineral acid-acting substance such as sulfuric acid or phosphoric acid. U.S. Pat. No. 2,530,332 teaches the separation of certain tertiary monohexenes from other tertiary monohexenes, using polybasic mineral acids or mixtures thereof, organic sulfonic acids or mixtures thereof, or mixtures of polybasic and organic sulfonic acids. U.S. Pat. No. 1,941,267 teaches the use of a mixture of sulfuric acid, acetic acid and water for vapor-phase removal at temperatures from 250° to 600°F. of color and gum formers from hydrocarbon oil of motor fuel boiling range without removing unduly large percentages of monoolefins. A new method is desired which does not use the expensive sulfonic acids and is specific for tertiary olefins, resulting in greater tertiary olefin extraction than obtained with sulfuric acid-water extraction.

SUMMARY OF THE INVENTION

The method of the present invention comprises contacting a refinery liquid hydrocarbon stream containing tertiary olefins, with a mixture of sulfuric acid, water and at least one aliphatic monocarboxylic acid in liquid phase to extract tertiary olefins from the hydrocarbon stream. The extraction process results in greater tertiary olefin extraction than obtained with dilute sulfuric acid alone.

DESCRIPTION OF THE INVENTION

A first step toward economic utilization of refinery hydrocarbons is separation by close fractionation into isomeric groups wherein substantially all of the hydrocarbons in a group have about the same number of carbon atoms. A next step is the separation of various hydrocarbons within an isomeric group by methods depending upon a marked difference in reactivity of the various hydrocarbons. For example, acetylenes, diolefins and other hydrocarbons more highly unsaturated than monoolefins may be removed by reaction with copper salts or by other methods known to those skilled in the art. Of the major remaining compounds, tertiary monoolefins and normal monoolefins are successively less reactive with sulfuric acid, and saturated hydrocarbons (paraffins and cycloaliphatics) are practically inert. The same scale of decreasing reactivities has been found to exist for the mixed acids of the present invention.

The method of the present invention comprises contacting a liquid refinery hydrocarbon stream containing tertiary olefins with a mixture of sulfuric acid, water and at least one aliphatic monocarboxylic acid in liquid phase to extract the tertiary olefins from the hydrocarbon stream. More specifically, the method of the present invention comprises contacting a liquid refinery hydrocarbon stream containing at least tertiary monoolefins with a mixture of sulfuric acid, water and at least one aliphatic monocarboxylic acid in liquid phase to extract the tertiary monoolefins from the hydrocarbon stream.

The hydrocarbon stream is preferably a C_4 to C_6 carbon compound fraction, more preferably a C_4 to C_5 fraction. Tertiary olefins are those mono-or diolefins containing in the molecule a double-bonded carbon atom attached to three other carbon atoms, i.e., the four valences of a tertiary carbon atom are occupied by three other carbon atoms. Examples of tertiary olefins include C_4 compounds such as isobutene; C_5 compounds such as 2-methyl-1-butene, 2-methyl-2-butene, isoprene and the like; and C_6 compounds such as 2-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, and the like. The hydrocarbon stream generally contains from about 0.2% to about 50% by weight, more often from about 1% to about 35% by weight, of said tertiary olefins.

The extraction mixtures are mixtures of sulfuric acid and at least one aliphatic monocarboxylic acid with water. The monocarboxylic acids have from 2 to 6 carbon atoms. More preferred are acetic or propionic acids or mixtures thereof. Even more preferred is acetic acid. Hydrochloric acid and/or nitric acid cannot serve as strong acid replacements for sulfuric acid, since they form undesirable stable compounds with tertiary olefins. The mixture contains about 44% to about 71% by weight of sulfuric acid and from about 1% to about 50% by weight of the weak acid, with the remainder being water. The water is present in a molar ratio of water to olefin of at least 1.5/1 and constitutes the difference between the total acid percentage and 100% of the mixture. More preferably, the mixture contains from about 2% to about 26% by weight of the weak acid. The weight ratio of acid-water mixture to the hydrocarbon stream is at least 0.7/1, more preferably at least 1/1. The extraction is performed at a temperature of from about − 10°C to about 50°C, more preferably from about 0°C to about 30°C, and still more preferably from about 0°C to about 10°C.

Any convenient liquid contacting technique may be used for tertiary olefin extraction in a batch or continuous operation. Tertiary olefins are absorbed effectively by the mixture to form an acid liquor extract which may then be subjected to a reversion agent such as naphtha at a temperature of from about 20°C to about 80°C, more preferably from about 22°C to about 50°C, to recover the extracted tertiary olefins themselves or the tertiary alcohols in concentrated form as is known in the art. Controlled steam stripping may also be used but is less desirable, since it dilutes the acid. Alternatively, the acid extract may be heated further to polymerize the olefins to their dimers, trimers, higher oligomers or to their polymeric form. The extract may also be used directly in effecting chemical reactions between the tertiary olefins and other compounds. Other methods of treating and using the extract are known to those skilled in the art.

The method of the present invention does not use the expensive sulfonic acids of the prior art. This method results in greater tertiary olefin extraction than does use of a sulfuric acid and water mixture where sulfuric acid is of like concentration.

The corrosive effect of the treating mixtures may be overcome to some extent by controlling sulfuric acid concentration and by the use of acid-resisting metals or suitable linings of the contacting apparatus. For example, the apparatus may be lined with silicate mixtures and cements using water glass, fire clay and the like, or the apparatus may be lined with various enameling compositions.

The tertiary olefins extracted by the process of the present invention are useful in many organic syntheses and polymerization reactions. For example, isobutene is used in the production of isooctane, butyl rubber and polyisobutene resins. 2-methylbutene-2 or 2-methylbutene-1 may be dehydrogenated to isoprene, which may be polymerized to cis-1,4-polyisoprene (synthetic natural rubber), useful in tires and other rubber goods.

The following examples illustrate the present invention more fully. Tertiary amylene extractions were carried out in 500 cc. glass reactors equipped with 600 RPM stirrers and placed in a constant temperature bath. About 150 cc of acid and about 100 cc of hydrocarbon feedstock (containing 19.7% and 23.4% tertiary amylene in Example 1 and Example 2 respectively) were added to each reactor and stirred for three hours. Analyses of hydrocarbon feedstocks are shown in Table 1. The acid-hydrocarbon phases were separated using a separatory funnel and analyzed for tertiary olefin content by gas chromatography. The date (see Table 2) shows substantially greater tertiary olefin extraction solubility with a mixture of sulfuric acid, acetic acid and water than with a mixture of sulfuric acid and water. The acid liquor extract is then contacted with naphtha at 40°C to recover the tertiary olefins in concentrated form.

TABLE I

Hydrocarbon Feedstock Components	Approximate Wt.% Ex.1	Ex.2
C_1 to C_4 compounds	2.6	1.7
Isopentane	37.6	47.8
n-pentane and 3-methyl-1-butene	10.7	8.7
1-pentene	4.6	3.2
2-methyl-1-butene	5.1	7.0
Trans-2-pentene	8.3	7.8
Cis-2-pentene	6.3	8.2
2-methyl-2-butene	14.6	14.7
Isoprene	0	1.7
Cyclopentene	1.1	0
C_6 and higher	6.7	0

TABLE 2

	Ex. 1		Ex. 2	
Acid Mixture Composition (Wt%)				
Sulfuric Acid	61	60	61	60
Acetic Acid	10	0	15	0
Water	29	40	24	40
Temperature, °C	0	0	0	0
Mol% Tertiary Olefin in Acid	45	21	31	20
Mol% Tertiary Olefin in Hydrocarbon	55	79	59	80
Equilibrium Constant(1)	0.82	0.26	0.70	0.25

(1)Equilibrium Constant = (Mols Tertiary Olefin in Acid/Mols Tertiary Olefin in Hydrocarbon)

I claim:

1. A process for extracting tertiary mono olefins from a liquid refinery C_4 to C_6 hydrocarbon stream wherein said stream is contacted with a mixture containing (A) from about 44% to about 71% by weight sulfuric acid, (B) from about 1% to about 50% by weight of at least one aliphatic monocarboxylic acid containing from 2 to 6 carbon atoms, and (C) water in a molar ratio of water to olefin of at least 1.5/1, said water making up the difference between total acid percentage and 100% of said mixture, the weight ratio of said mixture to said hydrocarbon stream is at least 0.7/1, and mixture is contacted with said hydrocarbon stream at a temperature in the range from about −10°C to about 50°C.

2. A process of claim **1** wherein said hydrocarbon stream is selected from the group consisting of C_4 to C_5 compound fractions, said mixture contains from about 2% to about 26% by weight of an aliphatic monocarboxylic acid selected from the group consisting of acetic acid and propionic acid, the weight ratio of said mixture to said hydrocarbon stream is at least 1/1, said mixture is contacted with said hydrocarbon stream at a temperature of from about 0°C to about 30°C, and thereafter separated from said acid.

3. A process of claim **2** wherein said hydrocarbon stream is a C_5 compound fraction, said aliphatic monocarboxylic acid is acetic acid, said hydrocarbon stream is contacted with said mixture at a temperature of from about 0°C to about 10°C and thereafter separated from said mixture, and said tertiary monoolefins are thereafter recovered from said acid mixture.

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