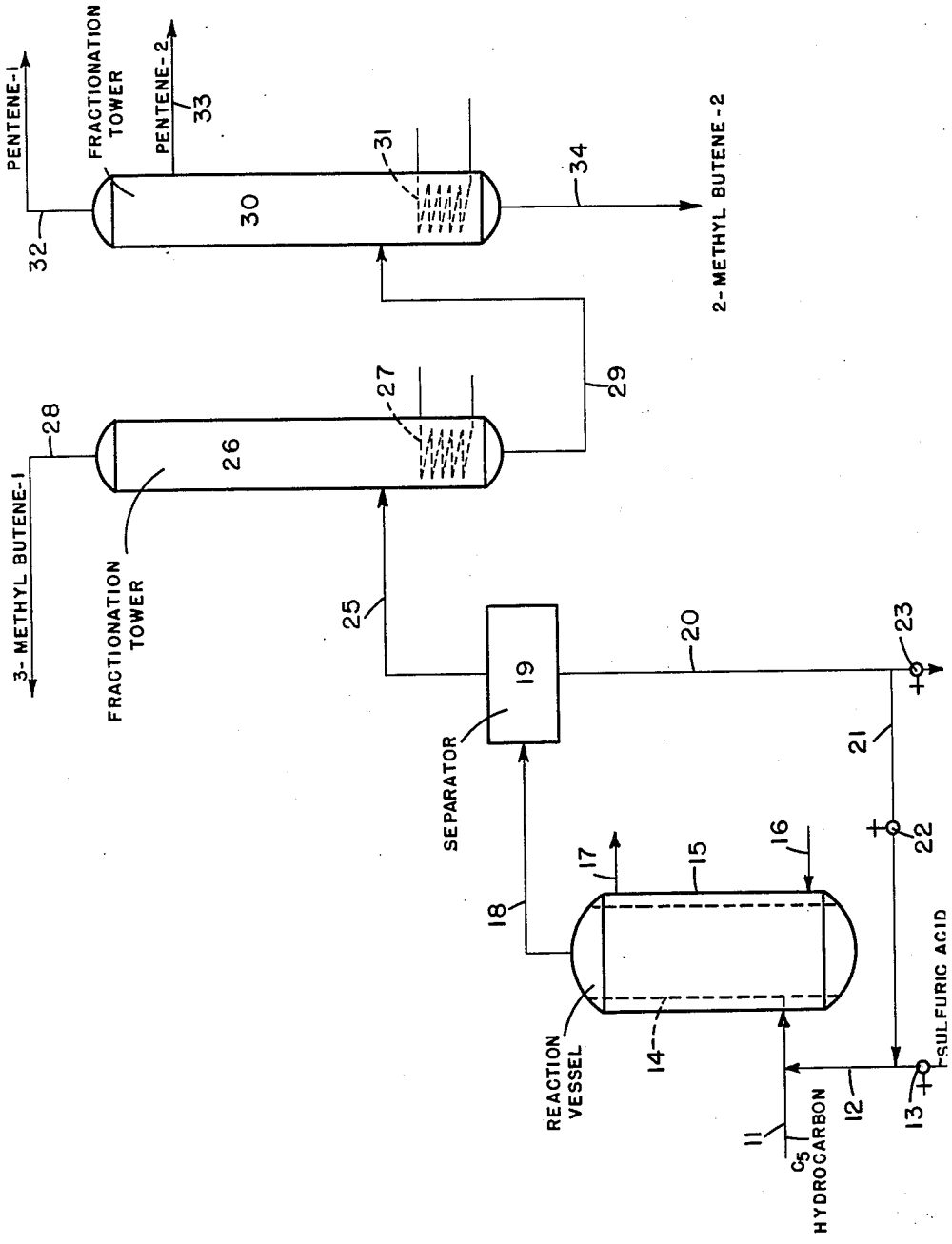
March 8, 1949. R. L. HEINRICH 2,463,873

SEPARATION OF PENTENE-1 FROM ITS MIXTURES WITH OTHER C_5 OLEFINS

Filed Oct. 3, 1947



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Patented Mar. 8, 1949 2,463,873

UNITED STATES PATENT OFFICE

2,463,873

SEPARATION OF PENTENE-1 FROM ITS MIXTURES WITH OTHER C_5 OLEFINS

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Application October 3, 1947, Serial No. 777,702

6 Claims. (Cl. 260—677)

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The present invention relates to the separation of straight chain alpha olefins from mixtures with branched chain olefins. More particularly, the invention is directed to the separation of pentene-1 from its mixtures with other olefins having five carbon atoms in the molecule.

The production of synthetic lubricants and other polymers from olefinic hydrocarbons generally requires a feed stock comprising substantially olefins having a double bond in the alpha position and having all of the carbon atoms arranged in a straight chain. If the double bond is in the beta position or if the carbon atoms are not arranged in a straight chain, the quality of the polymer, when used as a synthetic lubricating oil, will be seriously impaired. Now that the supplies of crude petroleums from which high quality lubricating oil is produced is decreasing, it becomes increasingly important to produce synthetic lubricating oils of high quality to supply the deficiency in the natural lubricating oils which is becoming more and more apparent.

Unfortunately, pentene-1 is not obtained from petroleum hydrocarbons as a pure compound. It is usually produced as a result of cracking and other conversion operations or dehydrogenation operations and, besides pentene-1, there may be produced cis and trans pentene-2, 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2. The boiling points of the several olefinic hydrocarbons having five carbon atoms in a molecule are such that a separation of pentene-1 may be made from pentene-2 by distillation. Similarly, 3-methylbutene-1 may be separated from the C_5 olefinic mixture by distillation. Similarly, it is possible, by modern fractionating techniques, to separate 2-methylbutene-2 from its mixtures with other hydrocarbons. However, the separation between pentene-1 and 2-methylbutene-1 is quite difficult due to the proximity of the boiling points of the olefinic hydrocarbons. The following table gives the boiling points of the olefinic hydrocarbons having five carbon atoms in the molecule:

	°F.
Pentene-1	86.0
Cis pentene-2	98.6
Trans pentene-2	96.3
2-methylbutene-1	87.9
3-methylbutene-1	65.9
2-methylbutene-2	101.3

Separation among the olefinic hydrocarbons by isomerization is also difficult because, according to the prior art methods, pentene-1 has the tendency to isomerize to pentene-2 and 2-methylbutene-2. Thus, instead of obtaining the pure pentene-1 as desired, all one would obtain would be pentene-2, which is an undesirable feed stock for the production of synthetic lubricating oils.

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Therefore, it is the main object of the present invention to provide a method for separating straight chain alpha olefins from branched chain olefins.

Another object of the present invention is to separate pentene-1 from its mixtures with other C_5 carbon atom olefins.

A further object of the present invention is to provide a process wherein an olefinic mixture, including olefins having five carbon atoms, may be separated into pure compounds.

The objects of the present invention are achieved by isomerizing a mixture including pentene-1 and 2-methylbutene-1 under controlled conditions such that the pentene-1 is substantially unaffected while the 2-methylbutene-1 is isomerized to 2-methylbutene-2.

In accordance with the present invention, a mixture of C_5 olefins, including pentene-1 and 2-methylbutene-1, is subjected to contact with sulfuric acid having a concentration in the range from about 40% to 70% H_2SO_4 at a temperature in the range from about 40° to 100° F. for a contact time ranging from about 5 to about 60 minutes. Under these conditions, the pentene-1 and the pentene-2 in the mixture are unaffected and the 2-methylbutene-1 is largely isomerized to 2-methylbutene-2. Reference to the foregoing table will show that the separation among the olefins may then be accomplished by simple distillation employing modern fractionating techniques which allow separation among compounds having boiling points within 2 or 3 degrees.

The invention will now be illustrated by reference to the drawing in which the sole figure presents a preferred mode of practicing the invention.

Referring now to the drawing, numeral 11 designates a charge line through which a C_5 hydrocarbon fraction may be introduced into the system. This fraction includes olefinic hydrocarbons having five carbon atoms in a molecule and contains pentene-1 in admixture with 2-methylbutene-1. The feed stock may also include paraffinic hydrocarbons, but for purpose of simplifying the description, it is assumed that the hydrocarbon fraction flowing into the system through line 11 is substantially free of paraffinic hydrocarbons. The olefinic fraction in line 11 is admixed with sulfuric acid, having a strength

in the range given, which is introduced into the system by way of line 12, controlled by valve 13. The mixture of olefinic hydrocarbon and sulfuric acid may be contacted in a reaction vessel 14 which may be provided with suitable internal equipment which allows intimate contact between the C_5 olefinic fraction and the sulfuric acid. The temperature conditions in reactor 14 are maintained within the critical range and reactor 14 is of sufficient size to allow a residence time sufficient for the isomerization of 2-methylbutene-1 to 2-methylbutene-2 to go to completion.

Since olefins in the presence of sulfuric acid have a tendency to polymerize, it may be necessary to provide a cooling system for the reactor 14. Therefore, reactor 14 may be provided with a jacket 15 through which a cooling fluid may be circulated around the reactor through inlet pipe 16 and outwardly through outlet pipe 17. This cooling fluid may be a low-boiling hydrocarbon fraction or other refrigerant.

As mentioned before, reactor 14 may be equipped with internal contacting equipment which may include baffle plates, bell cap plates, and the like and as a result, the hydrocarbons and olefins may issue from the reactor 14 by line 18 as an emulsion which is discharged thereby into a settler 19 where, under the influence of gravity, a separation betwen the hydrocarbon constituents and the acid constituents of the emulsion may be effected. The sulfuric acid separated from the emulsion in separator 19 discharges therefrom by line 20 and may be recycled to the reactor by line 21, controlled by valve 22, which connects into line 12. From time to time it may be desirable to withdraw a portion of the acid separated from the emulsion in separator 19 and under these conditions, valve 23 in line 20 may be opened allowing the acid to discharge to a recovery system not shown. When acid is withdrawn from the system, it may be desirable to replace it by an equivalent amount of fresh acid and this may be done by opening valve 13 connecting line 12 to a source of fresh sulfuric acid not shown.

The hydrocarbon phase separated in separator 19 may be discharged therefrom by line 25 into a fractionation tower 26 which is provided with a heating means illustrated by a coil 27 for adjustment of temperature and pressure conditions therein. Conditions are adjusted in fractionation tower 26 to allow the recovery of an overhead fraction comprising substantially 3-methylbutene-1 by line 28. The boiling point of 3-methylbutene-1 is such that it may be easily separated from the other olefinic hydrocarbons having five carbon atoms in a molecule by distillation. The remaining C_5 olefins in the mixture discharge from fractionating tower 26 by line 29 into a second fractionation tower 30 which, similar to fractionation tower 26, is equipped with a heating means illustrated by a coil 31. Differing from fractionating tower 26, fractionating tower 30 should be a highly efficient fractionating tower having a large number of theoretical plates to allow separation among pentene-1, pentene-2, and 2-methylbutene-2 resulting from the isomerization of 2-methylbutene-1. The fractionating tower 30 may be a series of fractionating towers provided the fractionation towers are of sufficient efficiency to allow the desired separation. For purposes of illustration, it wil be assumed that fractionating tower 30 is a single, highly efficient fractionating tower which will allow separation among the C_5 olefins remaining in the mixture. Pentene-1, which boils at about 86° F., is removed overhead from fractionating tower 30 by line 32, a mixture of cis and trans pentene-2, boiling at about 97° F., is removed as a side stream by line 33, and 2-methlybutene-2, boiling at about 101° F., is removed as a bottoms fraction by line 34. It will thus be seen from the foregoing description taken with the drawing that a method has been provided for separating the various olefins ordinarily contained in a C_5 olefinic mixture.

If it is desired to obtain the 2-methylbutene-1, then the 2-methylbutene-2 may be subjected to a separate treatment with sulfuric acid since the isomerization of the 2-methylbutene-1 to 2-methylbutene-2 is an equilibrium reaction.

In order to illustrate further the practice of the present invention, a number of runs were made in which hydrocarbon mixtures, including pentanes and the several C_5 olefinic hydrocarbons, were subjected to treatment in accordance with the present invention. In the first run, a C_5 hydrocarbon fraction, including pentanes and the several C_5 olefins, was contacted with 70% H_2SO_4 at a temperature in the range between 70° and 80° F. for 30 minutes at atmospheric pressure. Five volumes of hydrocarbon were employed for every volume of 70% sulfuric acid. In the second run, a temperature in the range between 78° and 83° F. was employed for contact time of 30 minutes at atmospheric pressure with five volumes of hydrocarbon being employed with every volume of 70% sulfuric acid.

The third run comprised a feed stock including only the C_5 olefins. Atmospheric pressures were used and a temperature in the range between 60° and 70° F. was maintained with the acid contacting the hydrocarbon for 30 minutes. In this run 2 volumes of hydrocarbon were contacted with every volume of 70% sulfuric acid.

Composition, Mol Percent	Run No. 1		Run No. 2		Run No. 3	
	Charge	Product	Charge	Product	Charge	Product
Pentanes	80.0	80.9	84.3	84.3	0.0	0.0
3-Methylbutene-1	3.2	0.9	0.7	0.0	0.2	0.4
Pentene-1	10.2	11.7	6.8	5.8	48.3	51.5
2-Methylbutene-1	5.7	0.9	7.2	3.4	51.1	2.0
Pentenes-2	0.0	0.8	0.2	0.8	0.4	0.5
2-Methylbutene-2	0.0	3.8	0.7	4.7	0.0	5.6
Olefin Absorbed by H_2SO_4		1.0		0.9		40.0
Total	100.0	100.0	100.0	100.0	100.0	100.0

It will be noted from an examination of the data in the foregoing table that in run No. 1 the 2-methylbutene-1 concentration was reduced to 0.9% while the 2-methylbutene-2 concentration rose to 3.8%, indicating that the 2-methylbutene-1 was isomerized to 2-methylbutene-2. It will be further observed that the pentene-1 concentration did not change significantly, while the pentene-2 concentration rose to 0.8%, indicating that only a small amount of pentene-1 was isomerized to pentene-2.

In run No. 2 the pentene-1 concentration was reduced by only 1.0% while the pentene-2 concentration increased by 0.6%. On the other hand, the 2-methylbutene-1 concentration decreased 3.8% and the 2-methylbutene-2 concentration increased from nothing to 4.7%. The decrease in 3-methylbutene-1 concentration in both runs indicates that this olefin is isomerized to some extent to 2-methylbutene-2 at about the same rate as 2-methylbutene-1 is isomerized to 2-methylbutene-2. In run No. 3, in which a substantially olefinic hydrocarbon feed stock was employed, the 2-methylbutene-1 concentration was reduced from 51.1% to 2.0% while the 2-methylbutene-2 concentration increased from nothing to 5.6%. The pentene-1 concentration was not appreciably changed and the pentene-2 concentration increased only 0.1%. It is apparent that a large amount of the 2-methylbutene-1 has been absorbed in the acid. However, the 2-methylbutene-1 may be recovered therefrom by well-known means. It is apparent from the foregoing runs that satisfactory isomerization of 2-methylbutene-1 to 2-methylbutene-2 may be obtained. It is also apparent from the data that the presence of pentanes as a diluent in the reaction may be beneficial in the practice of the present invention in the mode illustrated with respect to the drawing. When pentanes are present, it may be desired to remove, as described, the 3-methylbutene-1 by line **28**, the pentanes by line **32**, pentene-1 by line **33**, and to separate pentene-2 from 2-methylbutene-2 in a third fractionation tower, not shown. In any event, the separation of paraffins from olefins may be easily accomplished.

In practicing the present invention, it may be desirable to obtain from a petroleum fraction containing olefins a fraction boiling in the range from about 55° to 95° F. including pentane and the C_5 olefins. This mixture may be subjected to contact with 40–70% sulfuric acid at a temperature in the range from 40° to 100° F. for a time up to about 60 minutes. The amount of acid employed of the strength given may vary from about 10 volumes of hydrocarbon to 1 volume of acid to about 1 volume of hydrocarbon to 1 volume of acid. Under these conditions, the pentene-1 is not appreciably isomerized and the 2-methylbutene-1 is substantially isomerized to 2-methylbutene-2.

It is important that the temperature and the strength of the acid be carefully controlled. If the temperature should be allowed to rise appreciably, the pentene-1 may be isomerized to pentene-2 thus defeating the whole purpose of the invention. If the strength of the acid is allowed to increase appreciably, the olefins may be polymerized and undesirable products obtained.

Under the conditions where a mixture of pentenes and C_5 olefins are employed, the pentene-1 may be separated from the pentanes by solvent extraction or azeotropic or extractive distillation if the fraction should include substantial quantity of isopentane, which boils at the boiling of pentene-1.

The nature and objects of the present invention, having been fully described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for separating pentene-1 from its mixtures with other C_5 olefins which comprises contacting an olefinic mixture containing pentene-1 and 2-methylbutene-1 with sulfuric acid having a strength in the range from 40% to 70% H_2SO_4 at a temperature in the range from 40° to 100° F. for a time in the range between 5 and 60 minutes to form a reaction product and to cause isomerization of 2-methylbutene-1 to 2-methylbutene-2, separating sulfuric acid from the reaction product, and subjecting the reaction product to distillation to recover substantially pure pentene-1.

2. A method for separating pentene-1 from a hydrocarbon fraction including paraffin hydrocarbons having 5 carbon atoms in the molecule and containing pentene-1 and 2-methylbutene-1 which comprises contacting said hydrocarbon fraction with sulfuric acid having a strength in the range from 40% to 70% H_2SO_4 at a temperature in the range from 40° to 100° F. for about 30 minutes to form a reaction product, separating the reaction product from the sulfuric acid and subjecting the reaction product to a separation treatment to recover substantialy pure pentene-1 therefrom.

3. A method for recovering substantially pure olefins from a C_5 olefinic hydrocarbon fraction containing pentene-1, pentenes-2, 2-methylbutene-1, 2-methylbutene-1, and 2-methylbutene-2 which comprises contacting said olefinic fraction with sulfuric acid having a strength in the range from 40% to 70% H_2SO_4 at a temperature in the range from 40° to 100° F. for about 30 minutes to form a reaction product and to cause selective isomerization of 2-methylbutene-1 to 2-methylbutene-2, separating sulfuric acid from the reaction product, subjecting the reaction product to distillation and separately recovering by distillation 3-methylbutene-1, pentene-1, pentenes-2, and 2-methylbutene-2.

4. A method for separating pentene-1 from its mixtures with other C_5 olefins which comprises contacting an olefinic mixture containing pentene-1 and 2-methylbutene-1 with 70% sulfuric acid at a temperature in the range between 60° and 85° F. for about 30 minutes to form a reaction product and to cause isomerization of 2-methylbutene-1 to 2-methylbutene-2, separating sulfuric acid from the reaction product, and subjecting the reaction product to distillation to recover substantially pure pentene-1.

5. A method for separating pentene-1 from its mixtures with other C_5 olefins which comprises contacting an olefinic mixture containing pentene-1, pentenes-2, 2-methylbutene-1, 3-methylbutene-1, and 2-methylbutene-2 with sulfuric acid having a strength in the range from 40% to 70%, said olefinic mixture being employed in an amount in the range between 1 volume and 10 volumes for every volume of sulfuric acid, at a temperature in the range from 40° to 100° F. for about 30 minutes to form a reaction product and to cause isomerization of 2-methylbutene-1 to 2-methylbutene-2, separating sulfuric acid from the reaction product, and subjecting the reaction product to distillation to recover substantially pure pentene-1.

6. A method for separating pentene-1 which comprises contacting an olefinic mixture including substantial amounts of pentene-1 and 2-methylbutene-1 with sulfuric acid having a strength in the range between 40% and 70% H_2SO_4 at a temperature in the range between 40° and 100° F. for a time in the range between 5 and 60 minutes to form a reaction product and to cause isomerization of 2-methylbutene-1 to 2-methylbutene-2 while the pentene-1 is sub-

stantially unaffected, and subjecting the reaction product to distillation to recover substantially pure pentene-1.

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