Sept. 13, 1966 W. R. EDWARDS ETAL 3,272,886

PRODUCTION OF NORMAL PENTENES

Filed Nov. 4, 1963

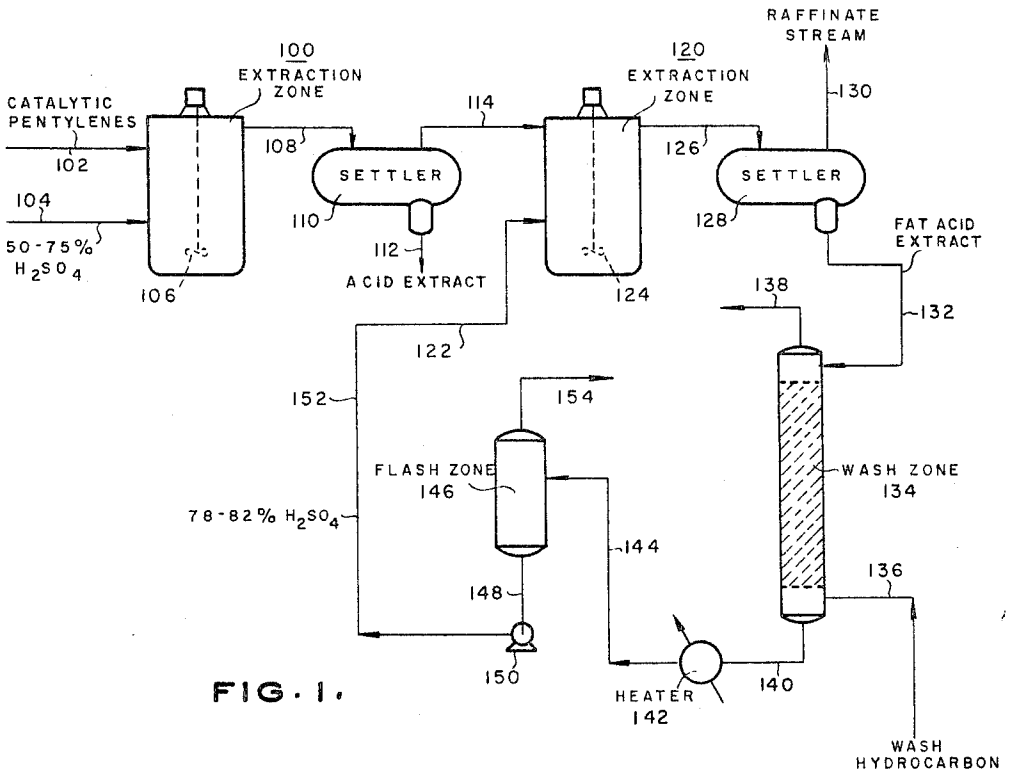


FIG. 1.

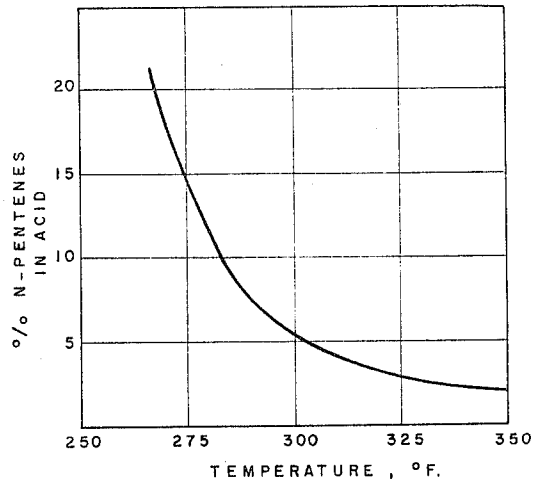


FIG. 2.

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United States Patent Office 3,272,886 Patented Sept. 13, 1966

3,272,886

PRODUCTION OF NORMAL PENTENES

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Filed Nov. 4, 1963, Ser. No. 321,256
3 Claims. (Cl. 260—677)

The present invention relates to a process of obtaining normal pentenes of high purity. More specifically, the present invention relates to a process of obtaining normal pentenes from a catalytic pentene stream by a two-stage extraction followed by thermal, indirect heating regeneration without dilution. All of this is more clearly set forth hereinafter.

Heretofore, normal pentenes have been recovered from an admixture with their isomeric hydrocarbons by contact with sulfuric acid of varying concentrations. In Patent 2,128,971, Robert E. Snow discloses a method of obtaining normal pentenes by first selectively extracting the tertiary amylenes from the admixture, then submitting the remaining mixture to a second extraction step wherein the normal pentenes are absorbed into the extracting acid. The extracting acid is diluted and refluxed in order to obtain the normal pentenes as a product. However, by the Snow process, large amounts of the normal pentenes are lost to polymer, or, in avoiding polymerization, it is necessary to regenerate only a small portion of the normal pentenes from the extracting acid. An additional disadvantage is the fact that the dilute acid which results from the practice of the Snow process renders the process uneconomical since the acid must be reconstituted before use. By the process of the present invention, the acid strength is maintained undiluted and the acid need not therefore be reconstituted before reuse.

It is a further discovery that the acid strength must be maintained within a particular range for use in the extraction step so that during regeneration a substantially pure product and a higher regeneration efficiency may be obtained with minimal losses to polymerization. It has been found that the acid strength must be maintained between the range of 78% and 82% by weight H_2SO_4. If a concentration of less than 78% is used, the extraction step is not optimized since the amount of olefin which is absorbed by the acid is lessened considerably when the acid strength drops below that level. At above 82 weight percent sulfuric acid concentration, the losses of pentene to polymer upon regeneration become uneconomically large. Thus, the acid must be maintained within that concentration range. The present invention will be more clearly understood by reference to the drawings wherein:

FIG. 1 is a schematic diagram showing the flow process of the present invention; and

FIG. 2 is a curve representing the percent normal pentene remaining in the acid at various temperatures of regeneration.

Turning now to FIG. 1, the process is seen to include a first extraction zone **100**, into which catalytic pentylenes are introduced by way of line **102**, and 50 to 70 weight percent sulfuric acid is introduced by way of line **104**. Within the zone **100**, the pentylene stream and sulfuric acid are placed in intimate admixture by mixing means **106**. At the end of a residence time of about 0.1 to about 4 hours at a temperature of about 20° F. to about 70° F., the stream is discharged by way of line **108** into settler **110**, from whence the acid extract is discharged by way of line **112**, containing all of the tertiary olefins which were in the catalytic pentylene stream.

A tertiary olefin-free catalytic pentylene stream is discharged from settler **110** by way of line **114** and is passed

into second-stage extractor **120**, where it is contacted with a 78% to 82% sulfuric acid which is introduced by way of line **122**, and the admixture is kept in intimate contact by mixing means **124**. After a residence time from 1 to 6 hours at a temperature of 20° F. to 50° F., the stream is discharged from the contacting zone **120** by way of line **126** and discharged into a settler **128**. In the settler **128**, the raffinate stream which comprises virtually no olefins and comprises mostly paraffins is discharged by way of the line **130**, while the fat acid extract is discharged by way of line **132** containing the normal pentene and a certain amount of dissolved paraffin hydrocarbons. The paraffin hydrocarbons are removed from the fat acid extract in the wash zone **134**, where the fat acid extract is contacted in countercurrent flow over a packed bed. The wash hydrocarbon is introduced by line **136** and may comprise suitably a hydrocarbon which boils at a widely different range from the normal pentene in the fat acid.

Suitable wash hydrocarbons are n-heptene, n-octane, isooctane, etc., on the high-boiling end, or propane or butane on the low-boiling side. The wash hydrocarbon which contains the normal pentanes and isopentanes is discharged from wash zone **134** by way of line **138**. The extract is discharged by way of line **140** and is heated by indirect heat exchange within the heater **142** to a final temperature of 275° F. to 325° F. at a minimum heating rate of about 1000° F. per minute. The fat acid is not diluted prior to the heating in the heater **142**.

Within the heater **142** the normal pentenes are released from the fat acid extract and are discharged in admixture with a substantially olefin-free regenerated acid by way of line **144** and introduced into the flash zone **146**, from whence the acid is removed by way of line **148** and recycled by way of pump **150** and lines **152** and **122** for use in the second extraction zone **120**.

The normal pentenes stream is withdrawn from the flash zone **146** by way of line **154** as a substantially purified stream.

Thus, it is seen that a relatively straight forward process is provided which requires a minimum of operating equipment and produces a normal pentene stream of high purity while suffering minimum losses to polymerization.

Referring now to FIG. 2, the importance of the high temperature to which the fat acid extract must be heated is shown by the curve. Note that at about 275° F., the amount of normal pentene remaining in the acid is only about 13%. Thus, the temperature should be raised at least to that value in order to obtain the high regeneration which is necessary in an economic process.

At temperatures of 325° F. and above, the sulfuric acid itself begins to suffer degradation in amounts which render it uneconomical to operate at these temperatures. Thus, the temperature range should be maintained within about 275° F. to about 325° F.

In order to establish the criticality of the acid concentration, a number of runs were made under substantially identical conditions except for the acid concentration. The process was generally as follows. The catalytic pentylenes were contacted with sulfuric acid having a strength of 75% for the removal of tertiary olefins, and the raffinate was contacted with sulfuric acid at a temperature of 20° F. to 50° F. for 2 to 4 hours in order to extract the normal olefins into the acid phase. The extract phase was separated from the raffinate and washed with a paraffin hydrocarbon (isooctane) at a temperature of about 60° F. This washing operation removed the dissolved C_5 paraffin from the acid extract, which was then passed through the heat exchanger and heated to a final temperature of around 300° F. at a heating rate of 3000° F. to 5000° F. per minute. The results of these runs are set forth in Table I below.

TABLE I

Runs	1	2	3	4
Extraction of n-Pentene:				
Acid, wt. percent H_2SO_4	75	79	81	85
Contact Time, hrs	3	2	2	2
Temperature, ° F	32	32	32	32
Extract, wt. percent olefin	9	30	34	41
Regeneration:				
Heating Rate, ° F./min	-------	-------	5,000	3,600
Final Temperature, ° F	-------	-------	308	298
Percent Regeneration	-------	-------	87	84
Polymer formation, percent	-------	-------	13	24

Referring to Table I it is seen first by a comparison of the figures relating to extraction of normal pentene that the amount of normal pentene extracted into the acid increases with acid strength. At 75% sulfuric acid concentration, however, the amount of normal pentene which is absorbed is only 9 weight percent. At 79% this has more than tripled to give 30 weight percent normal pentenes in the acid phase. Thus, it would appear that the minimum level of 78 weight percent sulfuric acid concentration would be the determinative factor. However, by comparison of the figures shown in the regeneration step, at 85% concentration, 24% of the olefin was polymerized and lost to polymer; whereas at 81% concentration, the loss was only 50% of that, being 13%. However, it is to be noted that the amount of olefin regeneration which is accomplished also appears to be a function both of the acid concentration and of the temperature to which the acid was heated. Thus, the higher concentration must be heated to high temperatures in order to obtain regeneration of the normal pentene, which apparently leads to the higher loss of polymer.

In order to show the operability of the process and to disclose a preferred mode of practicing it, the following run was made.

Example 1

A sample of catalytic pentylene was contacted with 65% H_2SO_4 at 32° F. to remove 2-methylbutene-1 and 2-methylbutene-2. The product was distilled. The raffinate was then distilled to remove most of the 3-methylbutene-1. A normal pentene concentrate was obtained having the following composition:

	Weight, percent
n-Pentene	38.1
Isopentene	1.4
C_5 paraffins	60.5

1575 g. of the normal pentene concentrate was contacted with 1200 g. of 80.7 weight percent H_2SO_4 for 4 hours at 32° F. while being agitated by propeller agitators. The hydrocarbon raffinate was removed and the acid extract was washed twice with 140 g. of n-hexane. The purified acid product then contained 24 weight percent olefin.

The washed extract (1093 g.) was then regenerated by heating to 318° F. at a heating rate of 5000° F. per minute to yield 197 g. of hydrocarbon containing 10% polymer. The acid phase contained 5 weight percent olefin, representing a regeneration of 95%. The C_5 product contained 96.8% normal olefins.

Having disclosed the present invention in great detail, including a preferred mode of practicing it, what is desired to be covered by Letters Patent should be limited not by the specific examples herein given, but rather by the appended claims.

We claim:

1. A method of producing high-purity normal pentene which comprises
contacting a catalytic pentylene stream containing tertiary pentenes, normal pentenes, and C_5 paraffins with H_2SO_4 having a weight concentration of 50% to 75%
at a temperature of 20° F. to 70° F.
a ratio of acid-to-hydrocarbon stream of 10:1 to 1:10
and a residence time of 0.1 to 4 hours,
whereby a tertiary pentylene-free raffinate is obtained,
contacting said raffinate with H_2SO_4 having a concentration of 78 to 82 weight percent
at a temperature of 20° F. to 50° F.,
a ratio of acid to first raffinate of 10:1 to 1:10,
and a residence time of 1 to 6 hours,
whereby a normal pentene-containing fat acid extract is obtained,
washing said flat acid by contact with a wash hydrocarbon stream at a temperature of 20° F. to 50° F.,
said wash hydrocarbon boiling within a range substantially different from said normal pentene,
and indirectly heating said washed fat acid extract without dilution to a final temperature of 275° F. to 325° F.,
and at a rate of at least 1000° F. per minute,
whereby a substantially pure normal pentene stream is obtained with only minimal losses to polymer.

2. A method of producing normal pentene which comprises
contacting a hydrocarbon stream containing tertiary pentylenes, normal pentylenes and C_5 paraffins with H_2SO_4 having a concentration of 50 to 75 weight percent
at a temperature of 20° F. to 70° F.
and a residence time of 0.1 to 4 hours,
whereby a tertiary pentylene-free raffinate is obtained,
contacting said raffinate with H_2SO_4 having a concentration of 78 to 82 weight percent
at a temperature of 20° F. to 50° F.
and a residence time of 1 to 6 hours,
whereby a normal pentene-containing fat acid extract is obtained,
washing said fat acid by contact with a wash hydrocarbon stream,
and indirectly heating said washed fat acid without dilution to a final temperature of 275° F. to 325° F.,
and at a rate of at least 1000° F. per minute.

3. A method of producing high-purity normal pentene which comprises
contacting a hydrocarbon stream containing tertiary pentylenes, normal pentylenes, and C_5 paraffins with H_2SO_4 having a concentration of 50 to 75 weight percent to obtain a tertiary pentylene-free raffinate,
contacting said raffinate with 78 to 82 weight percent H_2SO_4 at a temperature of 20° F. to 50° F. to obtain a normal pentene-containing fat acid extract,
and indirectly heating said fat acid extract without dilution to a final temperature of 275° F. to 325° F.,
and at a rate of at least 1000° F. per minute.

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