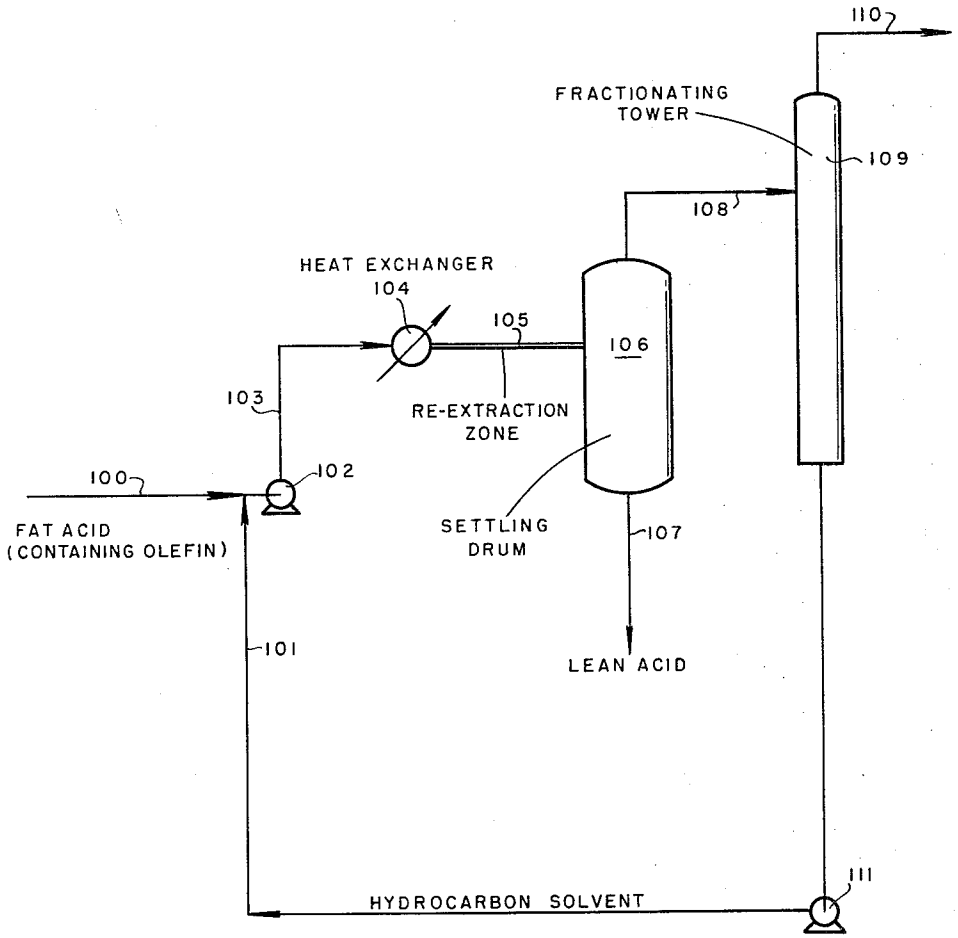
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RE-EXTRACTION METHOD

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RE-EXTRACTION METHOD

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The present invention is directed to a method of maximizing the efficiency of re-extraction in recovering tertiary olefins from concentrated acid extracts. More particularly, the present invention is directed to a method of maximizing re-extraction rates when recovering tertiary isoamylenes and tertiary isohexenes from a fat sulfuric acid extract while minimizing losses due to polymerization by maintaining the acid and hydrocarbon phases exclusively in concurrent flow during the re-extraction step.

By the practice of the present invention, polymer formation is substantially reduced, and the contact time required for recovery of a given amount of tertiary olefins is reduced by a factor of about 10 from that required by the practice of prior art methods. Accordingly, for a unit of given capacity, smaller re-extraction facilities are required by the practice of the present invention with concomitant savings in capital investment and operating expenses.

By the practice of the prior art, fat acid extracts containing tertiary isoamylenes and tertiary isohexenes are re-extracted by contacting the fat acid with a liquid hydrocarbon solvent in a contacting zone having means for agitating the acid and hydrocarbon solvent into intimate contact during the entire re-extraction process. Under these conditions, the entire acid and hydrocarbon inventory within the re-extraction zone is agitated into a homogeneous, or substantially homogeneous phase, resulting in at least a portion of the acid from which some of the tertiary olefin has been recovered being passed back into contact with the fat acid, thereby reducing the effective concentration of olefin in the fat acid during the re-extraction process. As has been surprisingly found by the practice of the present invention, by passing the fat acid and re-extraction solvent in concurrent flow during re-extraction, thereby preventing this type of back-mixing of the acid phase, a higher rate of re-extraction may be obtained with resultant low contact time requirement, and diminution of polymer losses in the re-extraction step.

In the practice of the preesnt invention, tertiary olefins such as isoamylene and isohexene are selectively extracted from an admixture of hydrocarbons by contacting the admixture at a temperature within the range of about 20° F. to 80° F. with sulfuric acid having a concentration within the range from about 60 to about 75% by weight, to obtain a fat acid extract containing olefins dissolved therein to the extent of from 10 to 40% by weight. This fat acid extract is, according to the practice of the present invention, contacted under re-extraction conditions in concurrent flow with a re-extraction solvent hydrocarbon.

The solvent hydrocarbon used in the re-extraction step of the present invention is one which suitably is not reactive with or soluble in the sulfuric acid to any great extent, and which has a boiling point substantially above or below the boiling point of the tertiary olefin to allow separation of the olefin and solvent hydrocarbon by simple distillation. Suitable solvent hydrocarbons are n-heptane, n-octane, and isooctane.

The ratio of solvent hydrocarbon to fat acid extract, according to the present invention, may range from 10 to 0.1, preferably from 3 to 1.

The temperature of re-extraction, according to the present invention, is suitably above 90° F., in order that a

substantial percentage of the tertiary olefin dissolved in the fat acid may be re-extracted. A preferred temperature range for isoamylenes is from 100° to 150° F. For isohexenes, the preferred temperature range is from 100° to 150° F. Higher temperatures may lead to substantial losses by polymerization.

The present invention may be practiced under atmospheric pressure, super- or subatmospheric pressures. The only limitation of pressure is that the pressure and temperature conditions must be such that the hydrocarbon solvent and tertiary olefin are maintained susbtantally in the liquid phase during the re-extraction process.

As stated, the acid to be used as the acid phase in the fat acid extract is suitably sulfuric acid having a concentration from 60 to 75% by weight. The fat acid extract may suitably contain the tertiary olefins in concentrations between 10 and 40% by weight.

The re-extraction, according to the present invention, is accomplished in a contact time from about 0.1 to about 10 minutes. The re-extraction time is determined by measuring the residence time from the point at which the admixture reaches the re-extraction temperature until the point at which the separation into an acid phase and a hydrocarbon phase of the re-extracted mixture is made. The concurrent flow must be maintained at substantially all times during which the admixture is at the re-extraction temperature and before separation into the acid phase and hydrocarbon phase.

The elongated re-extraction zone may suitably comprise a long run of pipe, having a length-to-diameter ratio of at least 10:1, with a linear velocity within the re-extraction zone sufficient to prevent back-mixing therein. Preferably, the re-extraction zone is unobstructed, although a small amount of obstruction for the purpose of maintaining the hydrocarbon and acid phases in admixture may be incorporated so long as back-mixing and stagnant areas are not thereby produced.

A preferred mode of practicing the present invention is set forth in the drawing, wherein the single figure is an illustration of one method of obtaining the admixture of solvent and fat acid, utilizing a centrifugal pump.

Referring now to the drawing wherein a preferred mode is illustrated, fat acid is introduced by way of line **100**, containing from 10 to 35% dissolved olefin, and is admixed with hydrocarbon solvent introduced by way of line **101**. The combined stream is passed through centrifugal pump **102**, wherein intimate mixing is obtained. The combined stream in intimate admixture is passed from the pump **102** by way of line **103** into heating means such as a heat exchanger **104**, wherein the temperature of the admixture is raised to a temperature of about 90° F. or higher. From the heater **104**, the hot mixture of acid and hydrocarbon solvent is passed by way of a re-extraction zone **105**, which is suitably a pipe run sized in length and diameter to provide a residence time sufficient for the olefin to pass from the acid into the solvent in substantial amounts. The residence time is determined from the point at which the admixture enters the heater until the stream is discharged into a settling drum **106**. From the drum **106**, lean acid is withdrawn by way of line **107**, and the hydrocarbon solvent, containing the tertiary olefin, is passed by way of line **108**. The hydrocarbon solvent is separated from the olefin in fractionating tower **109**, the olefin passing overhead as a light stream **110** with the hydrocarbon being passed from the tower **109** by way of line **101**, for recycle to the pump **102**. It will be apparent from a consideration of the drawing that the olefin is continually and incrementally removed from the acid as it passes sequentially from the entrance to the heater **104** into the settling drum **106**. By maintaining the acid and solvent exclusively in concurrent flow, the lean acid is prevented from back-mixing with the

fat acid. This allows the re-extraction rates to be unexpectedly increased.

Any suitable means for obtaining the intimate mixture of fat acid and re-extraction hydrocarbon solvent may be used. For example, the two streams may be passed through an orifice plate incorporator, baffle plate incorporator, etc., instead of being passed through the impeller of a centrifugal pump.

Further, it should be noted that rather than passing the admixture of acid and solvent through the heater **104**, the hydrocarbon solvent may be heated before admixture with the acid extract to a temperature sufficient to bring the admixture to the desired re-extraction temperature.

By the practice of the present invention, as has been heretofore stated, the effective re-extraction rate has been increased by a factor as great as 10. As exemplary of the increased re-extraction efficiency, the following tabulation is presented.

TABLE I

	Run 1 Back-mixing	Run 2 Present Invention
Temperature, ° F	90	90
Isoamylene recovery, percent	69.5	67.0
Driving force	0.15	0.12
Re-extraction rate, $\frac{lb.MeC_4^=}{lb.H_2SO_4\text{-}hr.}$	0.65	4.78
Polymer formed, wt., percent	14.0	0.3

The back-mixing comparison run was carried out by using a stirred reactor with complete mixing during heating, and is set forth below as Example 1. The run according to the present invention was carried out by using a centrifugal pump for mixing the acid and solvent, then passing the mixture through a steam jacketed heater in order to reach the re-extraction temperature. The steam jacketed heater comprises an elongated tube.

As will be seen by comparison of the two runs, both were carried out at approximately the same temperature and with aproximately the same driving force. The driving force is indicative of the concentration difference between the olefin in the hydrocarbon within the re-extraction zone and the olefin which would be present in the hydrocarbon phase at equilibrium with the acid under the same temperature. It is apparent that the re-extraction rate of the present invention, 4.78 pounds of isoamylene per pound of sulfuric acid per hour, is about seven times as great as that which is accomplished while using a stirred re-extraction type process.

Examples

In obtaining the data by exemplary runs, two methods of performing the re-extraction were used.

First, in order to provide a comparison with the re-extraction methods using the prior art teachings, the re-extraction of a fat acid extract was accomplished in a heated re-extraction kettle fitted with a mechanical stirrer (Examples 1 and 3). The fat acid and a solvent re-extraction hydrocarbon (heptane) were continuously passed into the re-extraction kettle and stirred constantly during an average residence time of 32 minutes in Example 1 and 26 minutes in Example 3. The hydrocarbon-acid admixture was continuously removed and passed to a settler, from whench lean acid was withdrawn as a lower phase and a hydrocarbon stream was recovered as the upper phase. The hydrocarbon phase was caustic washed, water washed, and fractionated to recover an isoamylene product stream and a heptane solvent stream which was recycled into the reaction kettle. The data on these comparison Examples 1 and 3 are shown in Table II, along with the runs made according to the practice of the present invention as set forth below.

Examples 2, 4, and 5 were accomplished according to the practice of the present invention wherein the re-extraction is accomplished during concurrent flow without back-mixing. The re-extraction in these runs was accomplished by admixing a fat acid extract with a solvent heptane stream and passing the admixture through a centrifugal pump wherein mechanical mixing energy was applied to give an intimate mixture of acid and extracting solvent. The mixture from the centrifugal pump was passed in concurrent flow through a jacketed, elongated tubular heater to raise the temperature of the mixture to the re-extraction temperature. From the tubular heater, the admixture was passed into a settler where the hydrocarbon and acid phases were separated. The residence time, as indicated in Table II, was measured from the point of introduction into the heater until introduction into the settler. The data from Examples 2, 4, and 5 are set forth in Table II in comparison with Examples 1 and 3.

It should be noted that Examples 1 and 2 are tabulated in detail in Table I as well as in Table II.

TABLE II

Example	1	2	3	4	5
Type	Back-mixing	Nonback-mixing	Back-mixing	Nonback-mixing	Nonback-mixing
Acid Strength, wt. percent	65	65	65	65	65
Feed:					
Isoamylenes in Acid	24	20.3	13	18.5	23
Isoamylenes in Hydrocarbon	0	6.6	0	1.6	0
Re-extraction:					
Temperature, ° F	90	90	100	100	120
Reisdence Time, Min	32	3	26	4	3
HC/Acid, wt	1.0	2.0	0.5	1.7	1.3
Effluent:					
Isoamylenes in Acid	5.5	7.7	1.5	5.0	7.2
Isoamylenes in Hydrocarbon	8.5	12.1	10.4	13.3	10.2
Isoamylenes recovered, percent	69.5	67.0	68.3	76.9	70.4
Polymer formed, wt. percent	14.0	0.3	21.5	0	3.6

By comparing the results of Examples 1 and 2, shown in Table I as well as Table II, it is seen that for comparable isoamylene recovery, utilizing almost identical driving rates and identical temperatures, the present invention involves a residence time of only about one-tenth of that involved in the method of the prior art. Further, by the practice of the present invention, the polymer formation has been reduced to only about 0.3% as compared to 14% in the comparison run. Thus, the advantages of the present invention are manifest.

Examples 3 and 4 set forth a comparison of the practice of the present invention with that of the prior art at 100° F. Although the isoamylene recovery is not substantially the same, as in Examples 1 and 2, an indication of the efficiency of the present invention is seen in the fact that only 4 minutes residence time is required at a higher isoamylene recovery by the practice of the present invention as compared to 26 minutes residence time required by the practice of the prior art. By the practice of the prior art method, 21.5% polymer is formed during the recovery of 68.3% methyl butene, while no polymer is formed by the practice of the present invention in recovering 76.9% methyl butene. Thus, it is seen that

the practice of the present invention gives a higher olefin recovery and lower polymer formation while requiring less than one-sixth of the residence time as is required by the practice of the prior art.

Example 5 is presented to show that even at elevated temperatures, 120° F., the practice of the present invention can be used to give high olefin recovery (70.4%) while forming only a minor amount of polymer (3.6%). It should be noted that at the elevated temperatures, with only 3 minutes residence time required, a very high recovery of methyl butene is still obtained.

In the above examples, it should be noted that the practice of the present invention gives much higher re-extraction rates than that of the prior art, as is exemplified in the need for only a very short contact time for equivalent, or nearly equivalent, olefin recovery. This is important in allowing the use of much smaller facilities to treat a given quantity of fat acid. Great savings in investment and operating expenses are thus obtained.

By the practice of the present invention, re-extraction temperatures within the range of 90° to 175° F. may be used, with a preferred range of 100° to 150° F. Residence times from about 0.1 to about 10 minutes may be used, preferably from about 0.5 to about 5 minutes. The ratio of solvent hydrocarbon to acid may range from 10 to 0.1, preferably from 3 to 1. The concentration of extracting acid is not critical in the practice of the present invention, but preferably is maintained within the range of 60 to 75% by weight. Since the re-extraction is to be accomplished in the liquid phase, the pressure is not critical so long as sufficient pressure is imposed upon the system at the re-extraction temperature to maintain the hydrocarbon phase in the liquid phase.

Applicants have shown the essence of the present invention by numerous examples and a recitation of a preferred and best mode. However, the scope of the invention should not be determined by the specific modes shown, but rather by the scope of the appended claims.

We claim:

1. A method of maximizing the driving force and the recovery of a tertiary olefin from a sulfuric acid extract which comprises admixing said acid extract with a solvent hydrocarbon at a temperature below the re-extraction temperature, heating the admixture to the re-extraction temperature, passing said acid extract and solvent hydrocarbon at said re-extraction temperature in concurrent flow in said admixture through a re-extraction zone having an *L/D* ratio within the range from about 10:1 to 100:1, whereby back-mixing of the acid phase is substantially prevented, separating the re-extracted mixture after a re-extraction residence time within the range from about 0.1 to about 10 minutes into a lean acid phase, and a hydrocarbon phase, and recovering said tertiary olefin from said hydrocarbon phase, said acid extract and said solvent hydrocarbon being maintained in concurrent flow at all times after being heated to the re-extraction temperature and until said separation into said lean acid phase and said hydrocarbon phase.

2. A method in accordance with claim **1** wherein the tertiary olefins are isoamylenes and the re-extraction temperature is 100° F. to 150° F.

3. A method in accordance with claim **1** wherein the tertiary olefins are isohexenes and the re-extraction temperature is 100° F. to 150° F.

4. A method in accordance with claim **1** wherein the solvent hydrocarbon comprises heptane.

5. A method in accordance with claim **1** wherein the solvent-to-acid ratio is within the range from about 10:1 to about 0.1:1.

6. A method in accordance with claim **1** wherein the re-extraction temperature is within the range from about 90° F. to about 175° F.

7. A method of recovering tertiary olefins from an extract of 60 to 75 wt. percent sulfuric acid which comprises admixing said extract with a solvent hydrocarbon liquid at a solvent-to-acid ratio from 10:1 to 0.1:1 and at a temperature of 20° F. to 80° F., passing said admixture through an incorporating zone whereby an intimate admixture of solvent hydrocarbon and acid extract is obtained, heating said intimate mixture to a temperature within the range from about 90° to about 175° F., passing said solvent hydrocarbon and acid extract in intimate admixture in concurrent flow through an elongated re-extraction zone, separating said mixture into a hydrocarbon phase and an acid phase, and recovering said tertiary olefin from said hydrocarbon phase, said acid extract and said solvent hydrocarbon being maintained in concurrent flow at all times after being heated to 90° F. to 175° F. and until said separation into said acid phase and said hydrocarbon phase.

8. A method in accordance with claim **7** wherein said tertiary olefins are isoamylenes.

9. A method in accordance with claim **8** wherein said tertiary olefins are isohexenes.

10. A method in accordance with claim **7** wherein said solvent hydrocarbon has a boiling point substantially different from said tertiary olefins, and said tertiary olefins are recovered from said solvent phase by distillation.

11. In the re-extraction of a tertiary olefin from a sulfuric acid extract wherein the acid extract is contacted in the liquid phase at a re-extraction temperature with a liquid hydrocarbon re-extraction solvent at a solvent-to-acid ratio from 10:1 to 0.1:1, the process which comprises

admixing said acid extract and said liquid re-extraction solvent at a temperature below the re-extraction temperature to obtain an admixture,

heating said admixture of acid extract and re-extraction solvent to the re-extraction temperature,

passing said heated acid extract and re-extraction solvent through an elongated re-extraction zone in concurrent flow and in said admixture during a residence time of 0.1 minute to 10 minutes,

and thereafter separating said admixture into a lean acid phase and a hydrocarbon phase,

said acid extract and said re-extraction solvent being maintained in concurrent flow at all times after being heated to the re-extraction temperature and before separation into said lean acid phase and said hydrocarbon phase,

whereby back-mixing of the acid phase is substantially prevented and the driving force for re-extraction is maximized.

12. A method in accordance with claim **11** wherein the tertiary olefin is tertiary isohexene.

13. A method in accordance with claim **11** wherein the tertiary olefin is an isoamylene.

14. A method in accordance with claim **12** wherein the solvent is n-heptane.

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