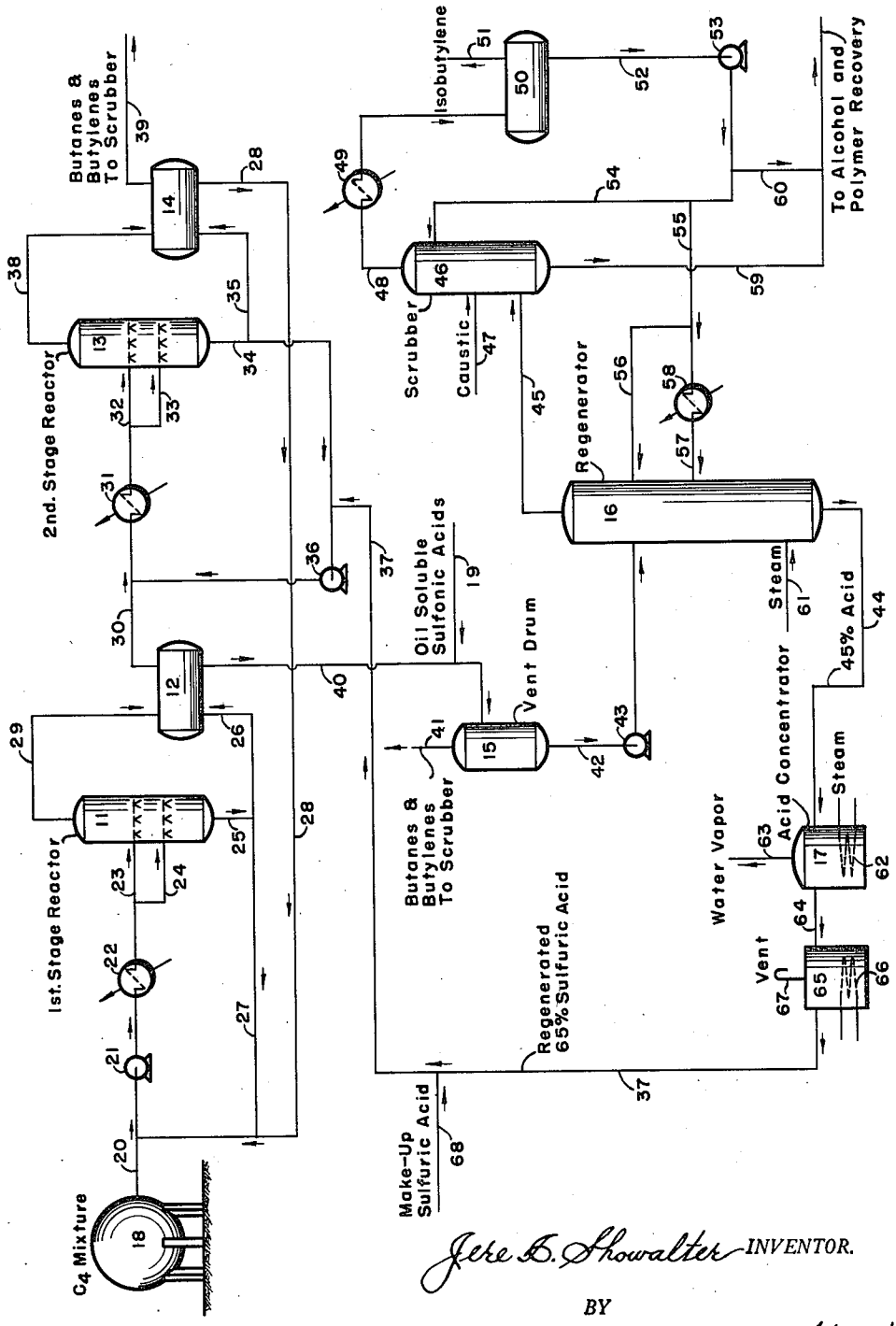
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PROCESS FOR RECOVERING OLEFINS FROM A HYDROCARBON STREAM

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PROCESS FOR RECOVERING OLEFINS FROM A HYDROCARBON STREAM

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6 Claims. (Cl. 260—677)

The present invention is directed to a method for concentrating relatively weak sulfuric acid which has been previously employed for treating hydrocarbons.

More particularly, the present invention is directed to a process comprising the treatment of low molecular weight hydrocarbons including olefins with sulfuric acid to form an extract, the recovery of absorbed and reacted hydrocarbons from the extract and the concentration of the recovered acid wherein oil soluble sulfonic acids are employed to prevent foaming of the extract and of the sulfuric acid undergoing concentration.

It is conventional to the art to recover low molecular weight olefins from a hydrocarbon mixture by contacting the mixture with 65% sulfuric acid. As an example of a typical operation, a hydrocarbon feed stock including normal butane, isobutlyene and normal butylene may be brought into contact with sulfuric acid in a reaction zone under a pressure substantially in excess of atmospheric in order to form an extract. The pressure on this extract is reduced to substantially atmospheric in a vent drum with the resultant release of the butanes and butylenes previously absorbed therein. The extract is then sent to a regenerator where polymers and alcohols resulting from the reaction of the sulfuric acid with the hydrocarbon mixture are separated as overhead fractions and the acid is concentrated to a 45% strength. The acid is removed from the regenerator to an acid concentrator where its strength is increased to 65% and then returned to the reaction zone of the system. In conventional operations, a substantial foaming is encountered in the vent drum, the regenerator and in the acid concentrator and this foaming requires these portions of the system to be operated at a rate below that which may be employed when foaming is eliminated.

In accordance with the present invention foaming in the vent drum, regenerator and acid concentrator is eliminated by adding small amounts of oil soluble sulfonic acids to the sulfuric acid being circulated in the system. The oil soluble sulfonic acids are preferably added to the extract as it is being passed from the reaction zone to the vent drum, but alternatively the oil soluble sulfonic acids may be added to the stream of sulfuric acid flowing through other portions of the system.

Perhaps the best known method of forming oil soluble sulfonic acids is in the refining of lubricating petroleum oils or white oils. When refining petroleum oils, in order to obtain white oils or highly refined lubricating oils, it is common to treat the starting petroleum stock with fuming sulfuric acid in order to eliminate undesirable components. The petroleum sulfonic acids resulting from such treatment may be divided into two general types; green acids which are characterized as being water soluble and mahogany acids which are characterized as being oil soluble. The oil soluble mahogany sulfonates conventionally obtained as a by-product in the refining of white oils and lubricating oils may conveniently be employed as the oil soluble sulfonic acids employed in the present invention to prevent the foaming of the sulfuric acid extract and the sulfuric acid in the recovery of the sulfuric acid from the extract.

The invention will now be described in greater detail in conjunction with the drawing in which the single figure is in the form of a flow sheet illustrating a preferred modification of the present invention.

In the drawing a first stage reactor is designated by 11, a first stage settling drum by 12, a second stage reactor by 13, a second stage settling drum by 14, a vent drum by 15, a regenerator vessel by 16 and an acid concentrator vessel by 17. The mixture of feed hydrocarbons is passed to the system from a vessel 18.

The system shown in the drawing may be described generally as involving a reaction zone, an acid regenerating zone and an acid concentrating zone. The reaction or absorption zone is divided into two stages, with hydrocarbons flowing through the first and second stages in sequence, and sulfuric acid passed into the second stage and forming an extract therein, the extract taken from the second stage and enriched in the first stage, and the resulting extract from the first stage sent, in turn, through acid regeneration and acid concentration zones. The hydrocarbon feed passes first through first stage reactor 11, and then through second stage reactor 13. Regenerated acid is fed into second stage reactor 13 and forms an extract therein and this extract is fed to first stage reactor 11 to serve as the absorption liquid therein. The enriched extract passes from reactor 11 to settling vessel 12 and is taken from settling vessel 12 through vent drum 15, regenerator 16, and acid concentrator 17, where the acid is restored to its original condition and returned to second stage reactor vessel 13. The vent drum 15 is arranged between settling vessel 12 and regenerator tower 16 in order to allow the release of pressure from the extract before it is sent to the regenerator tower.

In order to prevent foaming of the acid in vent drum 15, regenerator 16 and acid concentrator 17 an oil soluble sulfonic acid is added to the circulating stream of acid. In the drawing the means for adding the acid is indicated as inlet line 19 which adds the sulfonic acids to the extract being sent from first stage settling drum 12 to vent drum 15.

As a typical example, the mixture of hydrocarbon in vessel 18 may consist of 50% of iso and normal butane, 32% normal butylene and 18% isobutylene. This hydrocarbon mixture is passed from vessel 18 via line 20 in which is arranged pump 21 and heat exchanger 22 and discharges through distributing lines 23 and 24 into first stage reactor vessel 11. The liquid from the bottom of reactor vessel 11 is withdrawn through line 25 and the stream split, with a portion passing through line 26 to first stage settling drum 12 and the remainder being recycled to line 20 via line 27. To the extract flowing through line 27 is added extract withdrawn from the second stage settling drum 14 by line 28. The extract withdrawn from drum 14 and the extract withdrawn from first stage reactor vessel 11 are mixed in line 27 and the mixture of extract is then discharged into the hydrocarbon stream in line 20.

It is convenient to operate first stage reactor vessel 11 at a temperature of 100° F. and at a pressure of 140 pounds per square inch. The admixture of the extract comprising sulfuric acid with the hydrocarbon mixture in line 20 usually results in such a rise in temperature that it is necessary to cool the mixture with heat exchanger 22 in order to maintain the temperature in reactor vessel 11 at approximately 100° F. The hydrocarbon vapors in first stage reactor vessel 11 which are not absorbed or do not react with sulfuric acid therein are removed as overhead via line 29 and are discharged into the upper portion of first stage settling drum 12. The unabsorbed hydrocarbons from first stage settling drum 12 are passed through line 30 containing heat exchanger 31 and are discharged through lines 32 and 33 into second stage reactor vessel 13. Extract from the lower portion of second stage reactor vessel 13 is withdrawn via line 34 and the stream split with a portion passing through line 35 to second stage settling drum 14 and the remainder passing through pump 36 and discharging into the hydrocarbon stream passing through line 30. Regenerated sulfuric acid is discharged into stream 34 through line 37.

Unabsorbed and unreacted hydrocarbon vapors from second stage reactor vessel 13 pass through line 38 to second stage settling vessel 14 and the unreacted and unabsorbed hydrocarbons from vessel 14 comprising principally iso and normal butane and normal butylenes are withdrawn from outlet line 39. It is convenient to operate second stage reactor vessel 13 at a temperature of 70° F. and under a pressure of 135 pounds per square inch and in order to maintain these temperature and pressure conditions in vessel 13 it will usually be necessary to employ a cooling medium in heat exchanger 31 in order to remove heat resulting from the mixing of hydrocarbons with sulfuric acid in line 30.

With a pressure in first stage reactor vessel 11 of approximately 140 pounds per square inch and in second stage reactor vessel 13 at approximately 135 pounds per square inch the pressure in first stage settling drum 12 is also approximately 135 pounds per square inch. In order to recover hydrocarbons from the extract in settling vessel 12 and regenerate the sulfuric acid used as the extracting agent, it is desirable first to release the pressure on the extract and subsequently subject the extract to a heating operation. In the drawing the extract from settling vessel 12 is withdrawn through line 40 to vent drum 15 where the pressure is released to atmospheric by vent line 41. Extract is withdrawn from vent drum 15 via line 42 and pump 43 and discharged into regenerator tower 16. Hydrocarbons in vaporous condition are removed from tower 16 as overhead via outlet 45 and passed into scrubber 46 where they are brought into contact with caustic introduced into the scrubber through inlet 47. The vapors from scrubber 46 are removed through outlet 48 and passed through cooler 49 to condense the high boiling constituents and the cooled mixture is discharged into accumulator 50. Uncondensed materials, principally isobutylene, are removed in gaseous form from the upper portion of accumulator 50 through outlet 51. Condensate is removed from vessel 50 through line 52 containing pump 53 and the stream split with a portion being passed through line 54 to serve as a scrubbing material in tower 46, another portion passing through lines 55 and again divided with one portion discharged through line 56 into an upper part of regenerator tower 16 and the remaining portion passing through line 57 containing heater 58 and discharged into regenerator 16 some distance below the point of discharge of line 56. Liquid is withdrawn from the bottom of scrubber 46 through line 59 and has added thereto condensate withdrawn from vessel 50 via line 52, pump 53 and branch line 60. The liquid mixture in line 59 includes alcohol and polymer and is withdrawn from the system to a suitable arrangement for recovering these valuable products.

It is desirable to operate regenerator tower 16 with a bottom temperature of approximately 240° F. and a top temperature of 160° F. In addition to the heat added to the tower by heat exchanger 58 heating the stream flowing through line 57, steam may be injected into the bottom of the tower through inlet 61.

Acid is withdrawn from the bottom of the regenerator tower 16 at a concentration of approximately 45% and is passed via line 44 to acid concentrator 17. In this vessel the acid is heated by steam passing through coil 62 and the water vapor driven from the acid is discharged through outlet 63. In concentrator vessel 17 the acid is concentrated to a strength of approximately 65% and is discharged through line 64 to vessel 65 containing cooling coil 66 and vent 67. The acid accumulated in vessel 65 is regenerated acid and is passed through lines 37 and 34 to the hydrocarbon stream passing through line 30 to second stage reactor vessel 13. In order to replace the acid lost in the operation, makeup acid may be introduced in the required amounts through inlet line 68 to the stream of regenerated acid.

When operating the reactor vessels 11 and 13 at temperatures and pressures of 100° F. and 140 pounds per square inch and 70° F. and 135 pounds per square inch, respectively, and with a feed stock having the composition given above, it will be found that good results may be obtained when withdrawing 235 gallons of feed per minute from vessel 18 and passing 1360 gallons of regenerated acid per minute through line 37 and into the hydrocarbon stream being passed to the second stage reactor vessel 13.

While I have disclosed the use of oil soluble sulfonic acids as such for eliminating foaming in vessels 15, 16 and 17, it is to be understood that as an alternative, I may form a solution of these acids in a suitable medium such as alcohol and admix the solution of the oil soluble sulfonic acids with the acid stream being circulated through the system. The amount of oil soluble sulfonic acids required to eliminate foaming in the acid recovery portion of the system is so small that it will usually be found more convenient to add the oil soluble sulfonic acid as a solution in order to regulate more precisely the quantity of oil soluble sulfonic acid being added to the circulating acid stream. When using oil soluble mahogany sulfonic acids, it will be found that amounts approximating .005 part per million of sulfonic acids in the sulfuric acid extract being passed to the vent drum will be sufficient to eliminate foaming in the drum as well as in the regenerator tower and acid concentrator. Such small amounts of acid may conveniently be added to the sulfuric acid extract by making a solution of the sulfonic acids in tertiary butyl alcohol with a concentration of one part in a thousand, and adding this solution to the sulfuric acid extract. It is to be understood that the sulfonic acids employed in the practice of the present invention have boiling points substantially above the boiling points of the low molecular weight hydrocarbon absorbed or reacted with the sulfuric acid. If desired the regenerated sulfuric acid being returned to the reaction zone may have mixed therewith the oil soluble sulfonic acids and the oil soluble sulfonic acids in view of their high boiling points will remain in the acid while it circulates through the first and second reactor stages and will be present in the sulfuric acid extract being passed to the vent drum and be effective to prevent foaming therein.

Having fully described the present invention, what I desire to claim is:

1. In a system for recovering olefin from a predominately C_4 hydrocarbon feed stock comprising olefins involving contacting the feed stock with sulfuric acid in a reaction zone under conditions to form an extract, the removal of the extract from the reaction zone to a regeneration zone where the extract is heated under a pressure substantially less than that in the reaction zone to cause vaporization of a major portion of the hydrocarbons from said extract and recovery of the sulfuric acid and the recycling of the recovered sulfuric acid to the reaction zone, the step of adding oil soluble sulfonic acids to the circulating sulfuric acid stream in sufficient amount substantially to eliminate foam in the regeneration zone.

2. A method in accordance with claim 1 in which the oil soluble sulfonic acids are added to the circulating sulfuric acid stream in sufficient quantity to maintain approximately .005 part of sulfonic acid per million parts of sulfuric acid extract passed to the regeneration zone.

3. In a process for removing olefins from a hydrocarbon stream comprising a substantial portion of C_4 hydrocarbons and appreciable amounts of olefins including the steps of contacting the stream with sulfuric acid in a reaction zone under conditions to form an extract and the treatment of the resulting extract in an acid regeneration zone to separate hydrocarbons from the acid and recover acid of approximately the same concentration as employed in the reaction zone, the step of adding to the extract being sent from the reaction zone to the regeneration zone oil soluble sulfonic acids.

4. A process in accordance with claim 3 in which the concentration of the added oil soluble sulfonic acids in the extract are present in amount of .005 part per million of the extract passed to the regeneration zone.

5. A method in accordance with claim 3 in which the oil soluble sulfonic acids are mahogany acids obtained from petroleum.

6. A method in accordance with claim 3 in which the oil soluble sulfonic acids are mahogany acids from petroleum and are added in the form of a solution of sulfonic acids in butyl alcohol to produce a concentration of .005 part per million of sulfonic acids in the sulfuric acid extract passed to the regeneration zone.

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