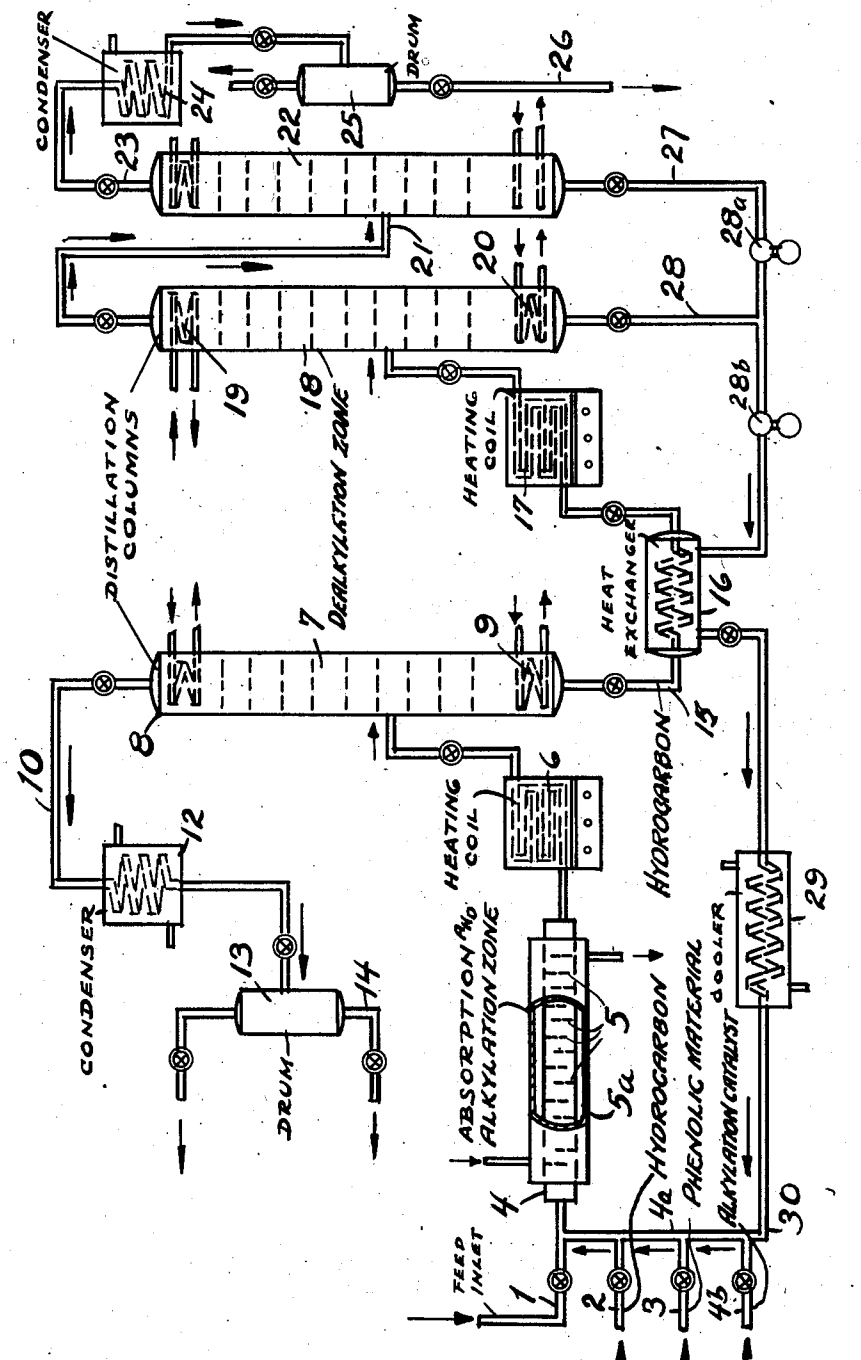
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PROCESS FOR SEGREGATING VALUABLE HYDROCARBON CONSTITUENTS

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PROCESS FOR SEGREGATING VALUABLE HYDROCARBON CONSTITUENTS

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The present invention relates to the art of the segregation of certain unsaturated hydrocarbons from mixtures with other hydrocarbons of closely similar boiling points, and more specifically to the separation and purification of tertiary olefins from their mixtures with normal or secondary olefins or from saturated hydrocarbons.

The process will be understood from the following description and drawing. The drawing is a semi-diagrammatic view in sectional elevation showing the flow of the various materials employed in the process.

Tertiary olefins, such as isobutylene and isoamylene, occur together with many other olefins, both normal and secondary, as well as saturated hydrocarbons, in cracked hydrocarbon oil fractions, and it has been for some time desirable to develop a cheap, effective method for segregating the tertiary olefins from other constituents in narrow boiling cuts. In the lower molecular weight ranges, for example, in the so-called C_4 and C_5 cuts, which comprise those hydrocarbons having 4 and 5 carbon atoms respectively in the molecule, separation can be accomplished by distillation but due to the close boiling points, this is a very difficult and expensive operation. Better results have been obtained by chemical means; for example, isobutylene has been selectively extracted from normal butenes and butanes by solution in 65% to 75% sulfuric acid. Acids of this strength absorb the tertiary olefin without substantially affecting the normal olefins or paraffins, and the iso-olefin can be recovered from the acid liquor by dilution and distillation.

Another method of accomplishing the same result employs a mixture of phenols, cresols and the like along with a minor amount of mineral alkylation acid by means of which the reactive tertiary olefins are caused to unite with the phenolic material to form an alkylated phenol. The unaffected hydrocarbons may be distilled off from this product and the residue, which consists of the alkylated phenol, is then heated to effect the dealkylation so that the tertiary olefin is then collected and the phenol returned.

This method is not entirely satisfactory because of the fact that the yield is not as high as might be desired due to several factors; first, polymerization of the tertiary olefin; second, the fact that some tertiary olefins are distilled over along with the unalkylated fractions of the feed stock and, third, because of the difficulty in completely removing the absorbed tertiary olefin from the phenolic material in the recovery step. The present invention involves an improvement over the above mentioned process by which increased yields may be obtained.

Referring to the drawing, numeral 1 denotes a line through which the hydrocarbon feed is introduced. For purposes of illustration, a refinery C_4 cut from cracking operations will be taken but it will be understood that a C_5 cut or other mixture of hydrocarbons including tertiary olefins might be taken equally well for purposes of illustration. The cut is preferably a rather narrow boiling fraction, such as can be readily produced in ordinary refinery equipment without great difficulty. The feed stock is preferably fed in liquid phase and sufficient pressure is imposed to maintain it throughout the absorption step.

In addition to the feed stock, a second liquid hydrocarbon of a higher boiling point than the original feed stock, but boiling below the boiling point of the phenolic material used, is also supplied by the pipe 2. The nature of this hydrocarbon, which is termed the "added hydrocarbon" will be more specifically disclosed later. A suitable absorption medium, which for the present will be described as a phenolic material, is added through a pipe 3 and the mixture of these three materials is passed through an absorption zone 4 by way of a common leader pipe 4a. An alkylating catalyst supplied by pipe 4b is small in amount and it is preferably also added to the leader. This mixture of ingredients now passes through the absorption zone 4 in liquid phase. Any particular design for the absorption zone may be employed in which all of the ingredients are mixed thoroughly and given sufficient time for reaction. As shown in the drawing, the reaction zone is merely a pipe fitted with baffles 5 and a jacket 5a through which a cooling medium may be circulated, since there is considerable heat evolved in the alkylation step. The conditions are such that only the tertiary olefins are caused to alkylate the phenolic material, the other olefins passing through substantially unaffected. The reaction product is discharged through a heating coil 6 and into a distillation column 7 which is provided with a refluxing coil 8 and a reboiling coil 9 at its lower end. In this fractionating zone, the uncombined hydrocarbons, namely the butanes and the normal butenes, are distilled overhead through a pipe 10, condensed in a condenser 12 and collected in the drum 13 through which they may be withdrawn as a liquid, by pipe 14. From the base of the tower 7, the residue containing the alkylated phenolic material and the added hydrocarbon along with a small amount of alkylation catalyst passes by pipe 15 through a

heat exchanger 16 and a second heating coil 17 and thence into a stripping tower 18. This tower is similar to tower 7 containing the refluxing coil 19 and reboiling coil 20. It will be understood that in this tower, the temperature is raised to a sufficient point to cause the dealkylation of the alkylated phenol and the distillation overhead not only of the tertiary olefins but also of the added hydrocarbon. The vaporized substances removed by a pipe 21 and discharged into a secondary tower 22 which is similar to those shown above and is devised to make a close fractionation between the tertiary olefin and the higher boiling added hydrocarbon. The tertiary olefin is taken overhead by a pipe 23, is condensed in 24 and collected in 25. It is withdrawn as a liquid by a pipe 26. The added hydrocarbon is withdrawn from the base of tower 22 by a pipe 27 and is passed by a pump 28a for recirculation. It is preferably joined by the stripped phenolic material from tower 18 which is added by pipe 28 and the mixture formed by the materials flowing through pipes 27 and 28 then passes through the heat exchanger 16, through a cooler 29 and by a pipe 30 back to the leader 4a and the absorber 5. Thus it will be seen that the phenolic material, the added hydrocarbon and the alkylation catalyst are continually circulated through a closed system and used over and over again to treat fresh quantities of the C_4 cut which is continually added and resolved into components consisting on the one hand of the tertiary olefins and on the other of a mixture of olefins and saturated C_4 hydrocarbons.

In the operation of the present process, it will be understood that the absorbent material is of a phenolic nature. Phenol itself may be used for this purpose or a cresol, or a mixture of cresols with or without other phenols. An advantageous absorption medium consists of a mono-tertiary phenol such as tert-butyl phenol or tert-amyl phenol. Simple phenol has been found capable of readily absorbing three molecules of isobutylene and of readily evolving two molecules thereof so that in effect even when operation is begun with simple phenol after a while the absorption medium is largely mono-tert-butyl phenol which has proved to be a very satisfactory mode of operation. If dealkylation conditions maintained are sufficiently drastic, however, all tert-butyl groups can be removed and the monobutyl phenol converted back to phenol. The materials during absorption are maintained, as indicated above, preferably in the liquid phase at temperatures between about 60° and 100° C., and a complete absorption of the tert-olefin can be accomplished in from 20 to 120 minutes, depending on the amount of tert-olefin in the feed stock, the ratio of absorption agent to the feed stock and other conditions. It is found desirable to provide about .33 to 1.0 mols of phenolic material for each mol of iso-olefin to be absorbed although even higher ratios may be used. The alkylation dealkylation catalyst is preferably a mineral acid, such as concentrated sulfuric or concentrated phosphoric acid, but other acid reacting catalysts such as potassium acid sulfate or phosphate may also be used, as well as benzene or phenol-sulfonic acids or some of their salts. The amount of the alkylation catalyst is small indeed, for example from 0.1 to 10 mol per cent thereof based on the phenol or equivalent material employed, and with otherwise good conditions about one mol per cent of the catalyst is quite effective in quickly effecting the alkylation of the phenolic material without causing any substantial polymerization of the tertiary olefin.

An important feature of the process is the presence of the so-called added hydrocarbon which, as stated above, should be a relatively stable material boiling conveniently above the boiling range of the feed stock and below the phenolic material so that it may be on the one hand readily separated from the unabsorbed constituents of the feed stock by the first distillation step and from the regenerated tertiary olefin and likewise readily separated from the phenolic material in the regeneration step. When isobutylene is recovered from C_4 cuts, pentane is an admirable material to employ but other materials may be used as well, for example hexane, di-isobutylene and other equivalent materials. The added hydrocarbon is preferably added at the inlet of the absorber 4 so that it may be present during the absorption. When so used it tends to slow down the alkylation reaction, making the control easier, and tends to prevent excess polymerization of the C_4 olefins. It may, however, be added to the reaction mixture just after the absorption is complete. The amount of the added hydrocarbon can be varied over quite a range, say from 10 to 100%, by volume, based on the amount of phenolic material, but from 40 to 60% is generally quite satisfactory.

After the absorption is complete, the first step is the distillation of the normal olefins and the saturated hydrocarbons contained in the feed stock. This distillation is carried out preferably under pressure so that the products may be collected in liquid phase without the use of refrigeration and with the C_4 cut this distillation may be accomplished under super-atmospheric pressure, say 40 to 60 pounds gauge. The head temperature of the still will be about 43° C. and the bottom temperature about 82° C. In any case, the bottom temperature of this first distillation should not be above about 100° C., in order to prevent a partial dealkylation and loss of the tertiary olefin. The residue from the first distillation consists of the phenol-tertiary olefin alkylate, the acid catalyst and the added hydrocarbon and this mixture, which forms a single phase, is passed into the second distillation column or the regenerator. This distillation column is likewise preferably held under pressure and the temperature is raised sufficiently high to not only cause the dealkylation of the phenol but also to distill off not only the tertiary olefin but likewise cause the distillation of the added hydrocarbon. The actual temperature therefore depends on the boiling point of the added hydrocarbon, the extent of alkylation of the phenol and other conditions. With pentane and using a pressure of say 50 to 70 pounds gauge, the maximum temperature will be about 250° C. When working at lower pressures, below 50 pounds, lower temperatures, in the range of 150 to 200° C. are adequate. In cases where the phenol is combined with 2 to 3 molecules of olefin in the absorption step, regeneration temperatures as low as 100 to 110° C. suffice at pressures close to atmospheric. The added hydrocarbon rapidly sweeps the tertiary olefin out of the phenol as soon as it is released and prevents loss on the one hand from incomplete dealkylation and on the other from polymerization during the regeneration step.

The third distillation step is also preferably accomplished under pressure so as to permit the tertiary olefin to be collected in liquid phase at

cooling water temperature. In this last still, the separation is made between the tertiary olefin and the added hydrocarbon and from the nature of the separation required, it will be readily understood that the added hydrocarbon should conveniently boil above the boiling point of the tert-olefin to be segregated. The closer the added hydrocarbon boils to the tertiary olefin the more difficult this separation will be. In any case, a mixture of the phenolic material removed from tower 18 and the added hydrocarbon taken from tower 22 are returned or recycled for further reaction. As indicated before, the phenolic material which also contains the alkylation catalyst is returned to the inlet of the reactor 4. The added hydrocarbon is also preferably returned to the same point but may be returned to the inlet of the heating coil 6, if desired.

As a specific example of the operation of the process, a mixture of meta and para cresols and a C_4 cut containing 18–19% isobutylene was continuously fed into and through a steel reaction drum at 85 to 90° C. Pressure sufficient to maintain the reactants in liquid phase was provided and the reactor was of size to give a time of throughput of about 1 hour. The mixture fed consisted of 5 mols cresol to 1 more of isobutylene and about .2 mol per cent of cresol sulphonic acid based on the cresols was included in the feed.

As the reaction mixture emerged from the chamber it was continuously admixed with one-half of its value of mixed pentanes and this mixture sent to a distillation tower which was under 3 atmospheres pressure (abs.) and distillation of the C_4 hydrocarbon was effected using a maximum temperature of 95 to 100° C. Practically no decomposition of the alkyl phenol was noted during this distillation.

The debutanized mixture was now distilled in a regeneration tower with a maximum temperature of 200° C. and under atmospheric pressure. From the top of the tower a mixture of pentane and regenerated isobutylene was recovered while the regenerated cresol and catalyst were drawn off of the tower from the bottom and reused for further absorption of isobutene. The regenerated isobutene and the pentanes were separated by distillation and the pentane reused as before. A careful balance showed that 93.7% of the isobutene fed to the system was recovered and the product contained 97.2% isobutene.

The present invention is not to be limited to the segregation of any particular tertiary olefin nor to the use of any particular phenolic material nor to any particular alkylation catalyst or added hydrocarbon, but only to the following claims in which it is desired to claim all novelty inherent in the invention.

We claim:

1. An improved process for recovering tertiary olefin from tertiary alkylated phenolic material, which comprises heating the alkylated material in order to produce the tertiary olefin and produce a dealkylated material in the presence of an added hydrocarbon having a boiling temperature between that of the olefin recovered and the dealkylated phenolic material, whereby the tertiary olefin and the added hydrocarbon are distilled from the dealkylated phenolic material, and thereafter separating the tertiary olefin and the added hydrocarbon by fractional distillation.

2. An improved process for recovering tertiary olefins from an alkylated phenolic material, which comprises heating the alkylated material to a dealkylating temperature to produce a tertiary olefin and a dealkylated phenolic material, while in the presence of an added hydrocarbon having a boiling point between that of the tertiary olefin and the phenolic material, and also in the presence of an acidic dealkylation catalyst, whereby the tertiary olefin and the added hydrocarbon are distilled from the dealkylated material, and separating the tertiary olefin and the added hydrocarbon by fractional distillation.

3. Process according to claim 2 in which the added hydrocarbon is employed in an amount of 10 to 100% of the volume of the phenolic absorbent.

4. An improved process for recovering tertiary olefins from hydrocarbon mixtures of similar boiling range containing tertiary olefins which comprises admixing with the hydrocarbon feed a phenolic material and, a minor amount of an alkylation catalyst, whereby the tertiary olefin alkylates the said phenol, distilling off the unalkylated hydrocarbons contained in the feed stock at a temperature below that at which dealkylation takes place, and while in the presence of an added hydrocarbon boiling between the tertiary olefin and the phenolic material, regenerating the tertiary olefin by heating the tertiary alkylated phenol to a dealkylating temperature and distilling the tertiary olefin and the added hydrocarbon from the regenerated phenolic material, then separating the regenerated tertiary olefin from the added hydrocarbon by fractional distillation and returning the phenol and the hydrocarbon for reuse.

5. Process according to claim 4 in which the added hydrocarbon is a saturated hydrocarbon and it is present during the alkylation step.

6. Process according to claim 4 in which the added hydrocarbon is a saturated hydrocarbon and it is added to the alkylation product.

7. An improved process for recovering isobutylene from its mixtures with other C_4 hydrocarbons which comprises agitating the C_4 hydrocarbons in the liquid phase with a phenolic absorbent and a small amount of an alkylation catalyst while in the presence of an added hydrocarbon having a boiling point between that of the C_4 hydrocarbons and the phenolic absorbent, whereby the isobutylene is chemically combined with the phenolic absorbent to form an alkylated phenolic product, distilling the uncombined C_4 hydrocarbons originally in the feed at a temperature below that at which dealkylation takes place, heating the alkylated phenolic product while still in the presence of the added hydrocarbon and the alkylation catalyst to a temperature between about 100° and 250° C., whereby the phenolic substance is dealkylated, removing the regenerated tertiary butylene and the added hydrocarbon as vapors from the phenolic absorbent and separating the isobutylene from the added hydrocarbon by fractional distillation, collecting the isobutylene and recirculating the said added hydrocarbon along with the phenolic absorbent to the process.

8. Process according to claim 7 in which the phenolic solvent is mono-tertiary butyl phenol.

9. An improved process for recovering tertiary amylenes from their mixtures with other C_5 hydrocarbons which comprises agitating the C_5 hydrocarbons in the liquid phase with a phenolic absorbent and a small amount of an alkylation catalyst while in the presence of an added hydrocarbon having a boiling point between that of the C_5 hydrocarbons and the phenolic absorbent, whereby the tertiary olefins are chemically combined with the phenolic absorbent to form an

alkylation product, distilling the uncombined C_5 hydrocarbons originally in the feed at a temperature below that at which dealkylation takes place, heating the alkylated phenolic absorbent while still in the presence of the added hydrocarbon and the alkylation catalyst to a temperature between about 100° and 250° C., whereby the phenolic substance is dealkylated producing tertiary amylenes and a dealkylated phenolic absorbent, removing the regenerated tertiary amylenes and the added hydrocarbon as vapors from the phenolic absorbent and separating the tertiary amylenes from the added hydrocarbon by fractional distillation, collecting the former and recirculating the latter along with the phenolic absorbent to the process.

10. Process according to claim 9 in which the phenolic absorbent is mono-tertiary amyl phenol.

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