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METHOD OF RECOVERING ALIPHATIC LACTONES

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This invention relates to an improved method of recovering aliphatic lactones and other valuable materials from pyroligneous products.

The present application is a continuation in part of our prior application Serial No. 330,198, filed April 17, 1940.

It has been found, as is more particularly described in the copending application referred to, that pyroligneous acid residues contain appreciable amounts of valuable lactones and phenols and may be recovered from other components of the pyroligneous acid. Such a treatment involved the treatment of the crude pyroligneous acid to separate a fraction containing the lactones and phenols substantially free from methanol and acetic acid and the fractionation of this lactone and phenol-rich fraction by steam distillation. By such steam distillation the mixed lactone-phenol fraction was separated into a water soluble portion containing the lactones and a portion substantially insoluble in water which contained the phenols.

As a result of further experimentation on such final or ultimate fractionation certain phenomena were observed and based upon such observations an improved method and apparatus for separating a lactone-rich and a phenol-rich fraction was devised.

It was found that when a fraction or extract of pyroligneous material having a boiling range of from about 185° to 220° C. was subjected to steam distillation the separation, although attainable, was quite slow and required excessive amounts of steam. Upon thorough investigation it was found that in the initial stage of the operation two liquid phases are present. One phase, which is substantially aqueous, consists of water containing the dissolved lactones together with minor amounts of water insoluble impurities, including phenols which while ordinarily considered substantially insoluble in water are somewhat soluble in hot dilute aqueous lactone solutions. The other liquid phase consists largely of phenols and other water insoluble materials together with lactones and a minor proportion of water. When the described two liquid phases are co-existent the vapor tension of the water insoluble materials remains high and they steam distill quite rapidly from the mixture. However, as the distillation proceeds the proportion of water insoluble material progressively diminishes and a point is reached at which the two liquid phases are completely miscible. At this point the undistilled water insoluble materials dissolve in the hot aqueous lactone solution with a concomitant reduction in the vapor tension of such water insoluble materials. Because of this, further distillation proceeds at a greatly diminished rate such that a prolonged distillation period is required for complete separation of the water-insolubles from the aqueous lactone solution.

In the course of experimentation to accelerate the distillation it was ascertained that when the steam distillation was continued to a point where complete miscibility occurs at a predetermined temperature, as for example at 100° C., separation of the two phases may be established by cooling the liquid system. It was further discovered that if the aqueous lactone solution is separated from the stratified water-insoluble phase and is replaced with fresh water the two phases are no longer miscible at the temperature of boiling water and hence steam distillation in this second stage proceeds rapidly.

The aqueous lactone solution which is separated at an intermediate stage in the distillation as above described, can readily be concentrated and purified by simple fractional distillation. Since the concentration of the water insoluble materials in this fraction is quite low, these are carried over with the steam resulting from heating the lactone solution.

It will thus be seen that the new type of fractionation is based upon the discovery of special phase relationships existent in the system and comprises in effect a two stage treatment in the second stage of which the inherent characteristics of the then existing conditions of coefficient distribution is modified to secure a markedly increased distillation and sharp fractionation. The improved method thus involves the separation of lactones from the water-insoluble material occurring with them by means of a primary distillation by steam to remove the water-insoluble materials, the continuance of this distillation until the residual liquid phases become miscible, the separation and stratification of the erstwhile miscible phases, the separation of the lactone-rich fraction and the further distillation of the non-aqueous phase to complete the distillation. In this manner great economies in steam consumption are effected as compared to the earlier method of the simple steam distillation and a higher degree of purification of the lactones is attained.

The functioning of the process will be more readily comprehended from a consideration of an improved apparatus in which it may be carried out. Such apparatus is illustrated in dia-

grammatic form in the single figure of the accompanying drawing.

In the present description the starting material comprises a fraction or extract of pyroligneous material having a boiling range of between substantially 185° to 220° C. substantially free from methanol and acetic acid. Such fraction may be obtained as a result of selective solvent fractionation of pyroligneous acid as described in our copending applications Serial Nos. 326,112 and 326,113, filed March 26, 1940, or by fractional distillation of pyroligneous material as described in copending application Serial No. 330,198.

The apparatus comprises a continuous distillation column such as the bubble tower having an upper section 1 and a lower section 2 each of which are provided with the trays 3. Intermediate the sections 1 and 2 is the tap-off tray 4. The tower is provided with the inlet line 5 communicating with the upper section 1 at an intermediate point. The lower section of the tower is provided with any suitable heating means, such as the reboiler 6. Such lower section is also provided with the draw-off line 7 for withdrawing the fractionated lactones.

The top of the tower is provided with the vapor line 8 which is connected with the condenser 9. This may be any suitable air or liquid cooled condenser. At its outlet the condenser is connected to the continuous decanter 10 through the line 11. Line 11 is provided with the vent 12 to bleed off gas introduced into the tower for a purpose to appear.

In the decanter the condensate from condenser 9 is stratified into two layers; the aqueous layer is returned to the top of the tower through line 13 and the lower layer of water-insoluble material is withdrawn through the line 14. This line may be connected with the stripping column 15 provided with the heating means 16. This column is provided with the vapor line 17 communicating with the condenser 18. The aqueous condensate is fed to the decanter through lines 19 and 11 and the dehydrated water-insoluble material is withdrawn from the bottom of the column and passed to storage through line 20.

As previously indicated the process involves the special treatment of the liquid resulting from the primary distillation by cooling this liquid and thus separating it into two separable layers. As shown, this is effected by drawing off a liquid fractiop from the intermediate tray 4 through the line 30. Line 30 is connected with the water cooler 31 and the cooled liquid fraction is passed through the line 32 to continuous decanter 33. The aqueous layer which forms in decanter 33 is passed continuously through line 34 to the lower section 2 of the bubble tower and the lower water-insoluble layer is passed through line 35 to the surge drum 36.

The liquid collecting in drum 36 is withdrawn through line 37 and is forced by pump 38 through line 39 to the upper section 1 of the main distilling column. The pressure in drum 36 is equalized with the pressure in the tray 4 by means of the equalizing line 40. To prevent escape of steam through line 40 into the drum 36 a slow stream of gas may be introduced through branch 41. This gas is bled from the system through vent 12.

The removal of water from the system, as for example by passing the water-insoluble layer from decanter 10 to storage rather than to stripping column 15 may be compensated for by replenishment through water line 42.

In the preferred apparatus a second heating means is utilized in the tower. Preferably this is located at or adjacent the tray 4 and as shown may comprise a steam coil 43 on the tray 4. By regulating the quantity of steam passing through this coil a considerable load is taken off the reboiler 6 and an accurate control of the amount of material passing to the cooler 31 can be exercised. By such control the speed of circulation through the surge tank 36 and line 39 can be thus varied at will. Such a secondary heating means also permits the acceleration of the rate of steam distillation in the upper section 1 of the tower independently of the rate of distillation in the lower section.

The operation of the process will have been appreciated from the description of the apparatus. The pyroligneous material to be fractionated is charged to the column through line 5 and flows downwardly toward the base of the tower. During such passage it is heated by ascending steam evolved from the liquid heated by the reboiler 6. Mixed vapors comprised largely of the insoluble constituents and steam pass overhead through line 8 and are condensed in condenser 9. The condensate passes continuously to decanter 10 and is there separated into a layer comprised essentially of water and a layer comprised essentially of the water-insoluble constituents of the material being treated. The separated water layer is returned to the top of the tower and mixes with the fresh feed entering from line 5. At this zone of mixing two liquid phases exist, an aqueous phase containing the lactones separated from the water-insoluble materials and a water-insoluble phase containing lactones; the concentration of the lactones in the two phases depending upon the particular distribution coefficient existing.

As the mixed liquid phases flow downwardly in the tower they are contacted by the ascending steam and steam distillation ensues in consequence of which portions of the water-insoluble materials are carried upwardly in vapor form and are passed together with steam to the condenser and decanter. The water layer in the decanter, as described, is returned to the tower. The layer of water-insoluble materials usually contains a small amount of dissolved water. This layer is withdrawn through line 14 and may either be passed to storage or it may continuously be treated in the stripping column 15. If this layer is passed to storage the water which is removed with it may be replenished by an equivalent amount admitted through line 42. As previously noted, if it is desired to substantially completely remove the water from the water-insoluble layer it may be passed to the stripping column 15. In this stripping column the liquid portion may be heated by means of the heating coil 16 to distill out the water. The overhead vapors which may contain some entrained water-insoluble material are condensed in condenser 18 and returned to the decanter 10.

As the distillation in the main column proceeds the composition of the downwardly flowing liquid phases changes; the aqueous phase becomes enriched in lactones and the proportion of water-insoluble material progressively diminishes. As explained earlier as a result of the change in composition a point is reached when the two phases become substantially completely miscible in the heated condition and the rate of distilla-

tion is greatly lowered. The descending liquid thus arrives at the tray 4 substantially as a single phase.

At this particular stage of distillation, as explained, the temperature of the liquid is reduced in cooler 31 so as to re-establish the two phases which are then separated and retreated. As will be appreciated, by controlling the heating effected by coil 43 the transition from the two separate phases to the single phase can quite accurately be established with consequent acceleration in the complete distillation cycle.

The liquid fraction accumulating on tray 4 is drawn off through line 30 and is cooled in cooler 31 preferably down to about atmospheric temperature. The cooled liquid passing to decanter 33 separates into two layers, one layer consisting essentially of water with dissolved lactones and containing a minor percentage of water-insoluble materials and one layer consisting essentially of water-insoluble materials with some dissolved lactones.

The aqueous lactone layer is passed continuously through line 34 to an intermediate tray of the lower section 2 of the tower. In this section the aqueous stream is contacted with an ascending stream of steam and vapors of lactones. By fractionation in this section water is evaporated and the water-insoluble materials are steam distilled and pass into the upper section of the tower. The finished lactones accumulating in the base of the tower are continuously withdrawn through line 7.

The non-aqueous layer which spontaneously forms in decanter 33 is passed continuously to the surge tank 36 and is returned in the desired amount to an intermediate portion of the upper section of the main tower through line 39. The material recycled to the upper section of the tower from tank 36 is substantially immiscible with the hot water fed in through line 13 and consequently its contained water-insoluble constituents are steam distilled very rapidly.

It is to be noted by way of precaution that the character of the feed stock is important in the proper operation of the process. If the primary fractionation (i. e. fractionation of pyroligneous products) which produce the charging stock for this process was not efficient there is a tendency for the liquid accumulating in the surge drum to build up a relatively high concentration of high boiling water-insoluble substances, i. e. substances boiling above the maximum distillation point of the feed material. In such an event all or a portion of the material accumulating in the drum 36 may be withdrawn through the line 44 and passed back to the primary fractionating system so that these high boiling materials will be separated from the fraction which is selected for treatment under the present process.

It will be appreciated that the function of the decanters 10 and 33 is essentially to separate the phenol-containing and lactone-containing phase and to return these to the fractionating column. In ordinary circumstances the aqueous layer in each decanter is the lighter and hence the upper layer. There may be circumstances, as for example where the terpene hydrocarbons and other neutral oils predominate over the phenols in the steam distillate separated in the decanter 10 when such distillate may be lighter than water and hence become the upper layer. In any such circumstances it will be necessary only to reverse the piping arrangement shown in the drawing to insure the proper fractionation.

The efficiency of the process may readily be appreciated and evaluated from a consideration of a typical run. A fraction obtained by primary distillation of a benzol extract from the pyroligneous acid obtained by the destructive distillation of southern pine, and having a boiling range of 185° C. to 220° C. was subjected to steam distillation in an apparatus of the type described and according to the defined method. Water-insoluble materials were rapidly distilled from the top of the column and the lactones were continuously withdrawn from the bottom. It was found that steam consumption was less than 50 per cent of that required to secure complete separation in a simple column. The lactones which were recovered were completely soluble in cold water. The overhead distillate contained approximately 10 per cent of dissolved water and after dehydration was found to consist of a mixture of 75 per cent of phenols soluble in 10 per cent sodium hydroxide, 15 per cent of high boiling aliphatic acids and 10 per cent of neutral oils, largely terpene derivatives. Of the total feed stock approximately 25 per cent by volume was separated as a mixture of butyrolactone and valerolactone the other 75 per cent steam distilling from the top of the tower.

We claim:

1. A process of treating pyroligneous acid to recover valuable products therefrom which comprises separating from the acid a fraction boiling between substantially 185° C. and 220° C., subjecting such fraction to steam distillation to remove a predetermined percentage of contained water-insoluble materials as an overhead distillate, cooling the residual undistilled portion of the fraction to a degree sufficient to effect separation of two liquid phases comprising respectively a substantially aqueous phase and a substantially non-aqueous phase and subjecting the non-aqueous phase to steam distillation and the aqueous phase to fractional distillation.

2. A process of treating pyroligneous acid to recover valuable products therefrom which comprises separating from the acid a fraction boiling between substantially 185° C. and 220° C., subjecting such fraction to steam distillation to remove a predetermined percentage of contained water-insoluble materials as an overhead distillate, cooling the residual undistilled portion of the fraction to a degree sufficient to effect separation of two liquid phases and subjecting the separated phases to distillation under differential distillation conditions.

3. In the process of treating a pyroligneous fraction having a boiling range of between substantially 185° C. and 220° C., containing lactones and phenols and substantially free from methanol and acetic acid, that improvement which comprises passing the fraction to a distillation zone and steam distilling the fraction therein, withdrawing an overhead vaporous fraction from the zone comprised essentially of water-insoluble constituents of the said fraction, cooling the fraction to a degree sufficient to effect the separation of two liquid phases one of which is rich in water-insoluble material, returning the other liquid phase to the distillation zone; withdrawing the undistilled liquid portion containing essentially the water-soluble constituents of the entering fraction from the zone and cooling such portion to an extent sufficient to effect the separation of a layer relatively rich in water-insolu-

ble materials and a layer relatively poor in water-insoluble materials, fractionally distilling the layer poor in water-insoluble material in a distillation zone substantially free from said water-insoluble materials and recycling the water-insoluble rich layer to the first said distillation zone for redistillation therein.

4. A process of treating pyroligneous acid to recover valuable products therefrom which comprises distilling crude pyroligneous acid to separate a fraction containing lactones and water-insoluble materials, such as phenols and having a boiling range between substantially 185° C. and 220° C. and substantially free from methanol and acetic acid, subjecting such fraction to steam distillation to separate an overhead distillate rich in water-insoluble materials, cooling the undistilled portion of the fraction to separate therefrom additional amounts of the water-insoluble materials and fractionally distilling the remainder of the fraction to produce a purified fraction rich in lactones.

5. A process of treating pyroligneous acid to recover valuable products therefrom which comprises, distilling crude pyroligneous acid to separate a fraction containing lactones and water-insoluble materials such as phenols and substantially free from methanol and acetic acid, subjecting such fraction to steam distillation to separate an overhead distillate rich in water-insoluble materials, cooling the undistilled portion of the fraction to separate therefrom additional amounts of water-insoluble materials, and fractionally distilling the remainder of the fraction to produce a purified fraction rich in lactones.

6. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. and substantially free from methanol and acetic acid to separate lactones and relatively poor in water-insoluble materials from associated water-insoluble materials which comprises, steam distilling the fraction to separate a condensed fraction rich in water-insoluble materials and relatively poor in water-soluble materials and an unvaporized fraction rich in lactones and relatively poor in water-insoluble materials; cooling each fraction to a degree sufficient to effect separation of two immiscible layers; separating and recovering the water-insoluble rich layer from the condensed fraction and the lactone-rich layer from the unvaporized fraction.

7. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. and substantially free from methanol and acetic acid to separate lactones and relatively poor in water-insoluble materials from associated water-insoluble materials which comprises, steam distilling the fraction to separate a condensed fraction rich in water-insoluble materials and relatively poor in water-soluble materials and an unvaporized fraction rich in lactones and relatively poor in water-insoluble materials; cooling the condensed fraction to a degree sufficient to effect the stratification of two liquid phases, one of which is rich in water-insoluble materials and the other of which is substantially free of water-insoluble materials, separating and purifying the water-insoluble rich layer, cooling the unvaporized fraction to a degree sufficient to effect stratification of two liquid phases, one of which is relatively rich in lactones and separating and purifying the lactone-rich layer.

8. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. and substantially free from methanol and acetic acid to separate lactones from associated water-insoluble materials such as phenols which comprises, passing the fraction to a distillation column and steam distilling therein, withdrawing an overhead vapor fraction, condensing the vapor fraction and passing the condensate to a decanter to form two layers comprising an upper layer comprising essentially a layer of water soluble materials and a lower layer comprising essentially a layer of water-insoluble materials, withdrawing a layer enriched in water-insoluble materials and returning the aqueous layer to the upper portion of the column; withdrawing the unvaporized fraction of the entering material; cooling such unvaporized material and passing it to a decanter; returning the non-aqueous layer of material in the last named decanter to the upper part of the column and recovering the lactone enriched layer.

9. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. and substantially free from methanol and acetic acid to separate lactones from associated water-insoluble material, which comprises, passing the fraction to an upper section of a distilling column and steam distilling therein, passing overhead material through a condenser and thence to a decanter to form two layers one comprised largely of water-insoluble materials and the other comprising an essentially aqueous layer; withdrawing and recovering the layer of water-insoluble materials, returning the aqueous layer to the upper section of the column as a reflux liquid; withdrawing the unvaporized portion of the entering fraction from an intermediate section of the column, passing such portion through a cooler and thence to a decanter to effect the separation of two immiscible layers one of which is an essentially aqueous layer enriched in lactones and the other an essentially non-aqueous layer containing water-insoluble materials, returning the said non-aqueous layer to the upper section of the column for redistillation with fresh charge, returning the aqueous layer to the lower section of the column for redistillation and withdrawing a concentrated purified lactone fraction from the base of the tower.

10. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. and substantially free from methanol and low boiling fatty acids to separate lactones from associated water-insoluble materials, which comprises passing the fraction downwardly through a steam distillation zone, withdrawing overhead materials and fractionating such materials by cooling and decantation to produce a phenol-rich fraction substantially free from water, withdrawing unvaporized material from the zone, fractionating such material by cooling and decantation to produce a lactone-rich fraction substantially free from water-insoluble materials.

11. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. substantially free from methanol and low boiling fatty acids to separate lactones from associated water-insoluble materials which comprises steam distilling the material from a distilling zone wherein the lactones and water-insoluble materials exist as two liquid phases, continuing such distillation unit the water-insoluble phase is denuded of water-insoluble materials to the extent that the two phases become miscible, withdrawing the single liquid phase, cooling this material to a degree sufficient to effect the forma-

tion of an aqueous layer enriched in lactones and a relatively non-aqueous layer containing water-insoluble materials, recycling the non-aqueous layer to the distillation zone for additional distillation and withdrawing and concentrating the aqueous layer.

12. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. substantially free from methanol and low boiling fatty acids to separate lactones and associated water-insoluble materials, which comprises passing the fraction downwardly through a steam distillation zone, withdrawing overhead material and fractionating such materials by cooling and decantation to produce a phenol-rich fraction substantially free from water, withdrawing unvaporized material from the zone, fractionating such material by cooling and decantation to produce a lactone-rich fraction substantially free from water-insoluble materials and concentrating and purifying such lactone-rich fraction in a separate distillation zone.

13. A process of treating a pyroligneous fraction boiling between about 185° C. and 220° C. substantially free from methanol and low boiling fatty acids to separate lactones from associated water-insoluble materials which comprises passing the fraction downwardly through a steam distillation zone, withdrawing overhead material and fractionating such materials by cooling and decantation to produce a phenol-rich fraction substantially free from water, withdrawing undistilled material from the zone, fractionating such material by cooling and decantation to produce a fraction further enriched in lactones and then concentrating and purifying such fraction.

14. A process of fractionating an aqueous system containing lactones and phenols which comprises steam distilling the fraction for a predetermined time and less than that required for complete separation of lactones as an undistilled residue and phenols as an overhead distillate, withdrawing the undistilled material, cooling the withdrawn lactone-containing material to separate a lactone phase and a phenol phase and separately redistilling the separated phases.

15. A process of treating a pyroligneous acid fraction of the class described, said fraction boiling between substantially 185° C. and 220° C. and consisting essentially of lactones and phenols substantially free from fatty acids which comprises continuously passing the fraction to a distilling column and steam distilling it therein, continuously withdrawing an overhead fraction consisting essentially of water insoluble materials but containing a small percentage of water soluble materials, fractionating such overhead fraction to recover water insoluble components, returning the water soluble materials of said fractionated overhead fraction to the upper part of the distilling column, and continuously withdrawing the unvaporized portion of the pyroligneous fraction, cooling said withdrawn portion to form an aqueous and a substantially non-aqueous phase, separating the phases, returning the aqueous phase to the lower part of the column and withdrawing a substantially anhydrous water soluble lactone fraction from the base of the column.

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