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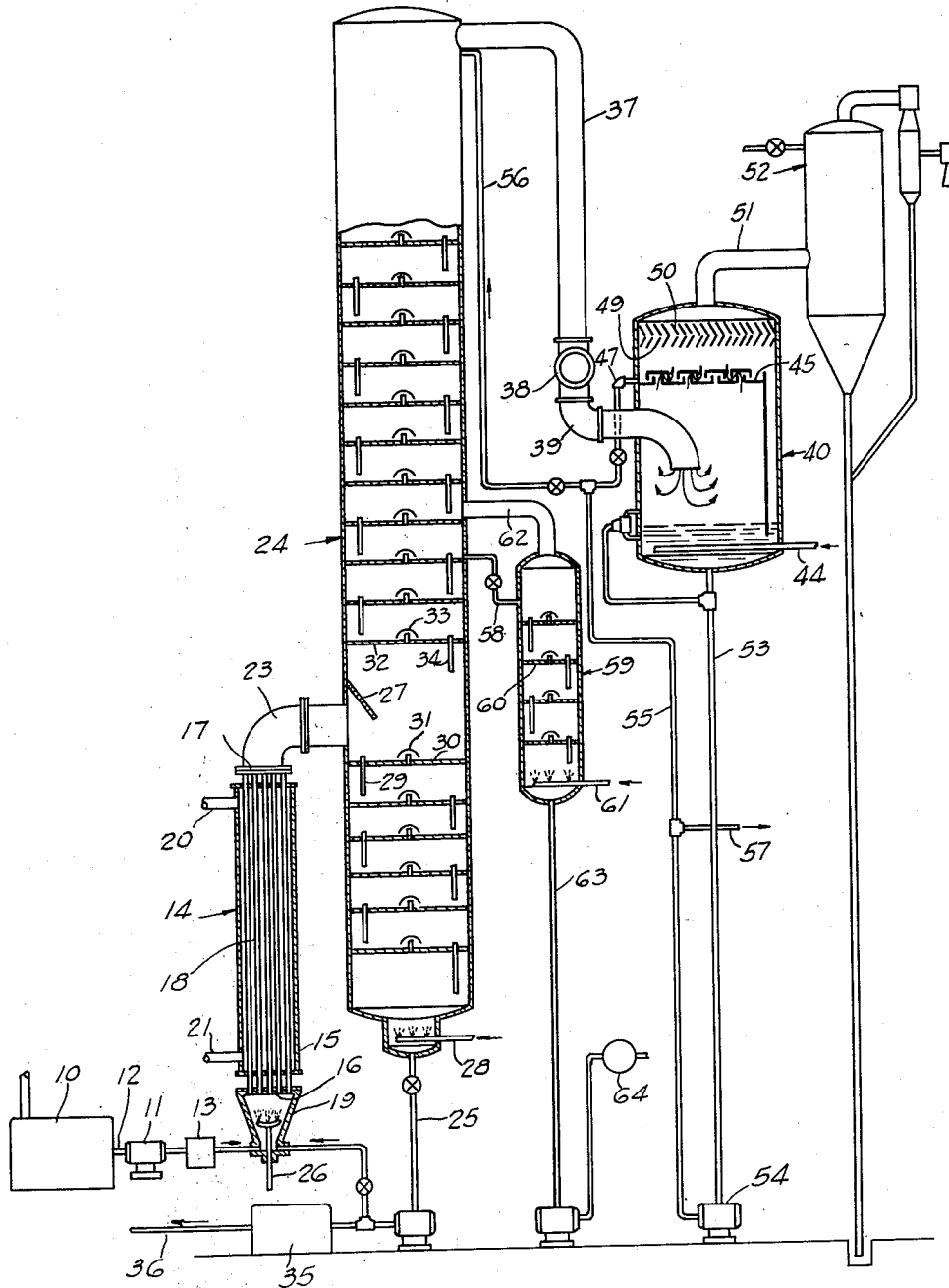
R. H. POTTS ET AL

2,224,925

FRACTIONAL DISTILLATION OF FATTY ACID MATERIALS.

Filed Oct. 13, 1939

2 Sheets-Sheet 1



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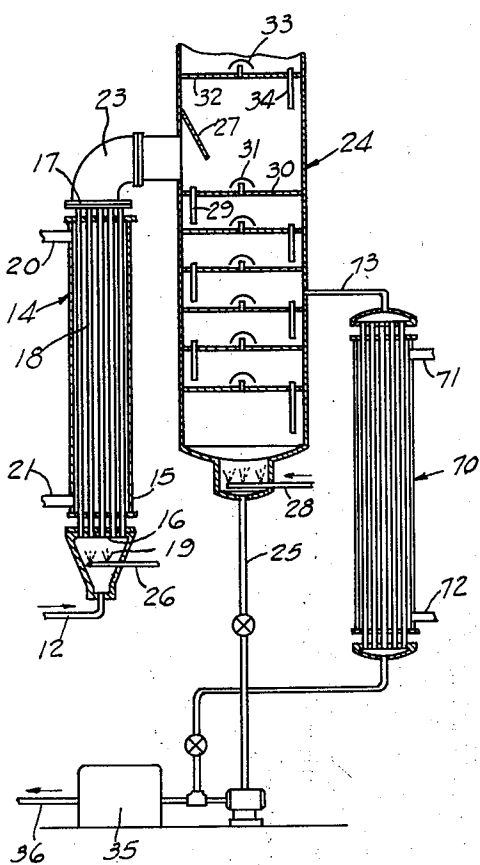


Fig. 2

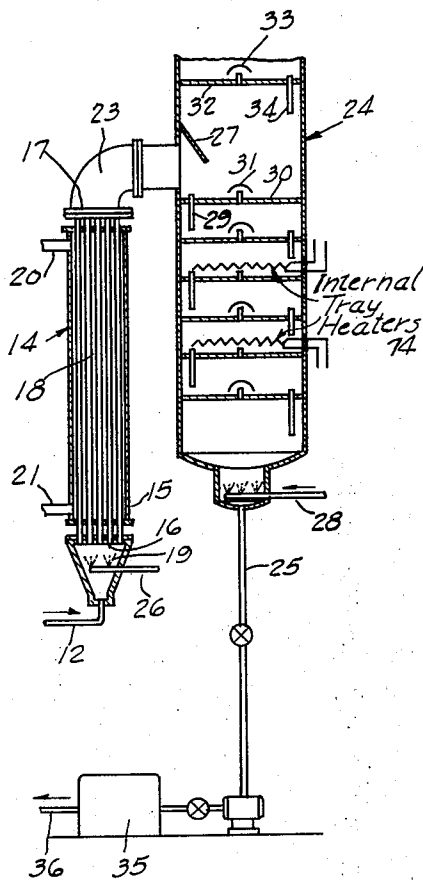


Fig. 3

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FRACTIONAL DISTILLATION OF FATTY ACID MATERIALS

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7 Claims. (Cl. 202—46)

This invention relates to the fractional distillation of fatty acid materials and particularly those materials containing also a quantity of neutral oil. The invention is concerned principally with an improvement involving the amount of steam introduced into the fractional distillation zones, a feature set forth in our copending application, Serial 96,732, of which the present application is a continuation in part.

In the treatment of oleaginous fatty acid materials it is necessary to separate the volatile fatty acids from the non-volatile glycerides, and to accomplish this in an efficient manner it has been found that the material must not only be heated to a temperature at which the fatty acids will vaporize at the vacuum employed, but some sort of mechanical stripping agent must be used. Since steam is economical and an excellent stripping agent, the art has employed it universally in the distillation of such materials. By passing superheated steam through the fatty acid material heat is added and also the vaporized fatty acids are carried away from the non-volatile material; thus the steam serves a double purpose, and prior fatty acid distillation processes have utilized both of these functions.

In this description the term "straight distillation" signifies the separation of volatile fatty acids from glycerides, impurities or other non-volatile matter, while the term "fractional distillation" signifies the separation of the volatile fatty acids themselves into separate fractions having different boiling points. Thus when oleaginous fatty acid materials are fractionally distilled not only is non-volatile matter separated from volatile fatty acids, but also volatile fatty acids of higher boiling points are separated from volatile fatty acids of lower boiling points.

Since in the fractional distillation of oleaginous fatty acid materials it is necessary to supply heat and to strip the volatile fatty acids from the non-volatile material, just as was true in the case of straight distillation, steam has heretofore been used in the art of fractional distillation as is shown in our prior Patent No. 2,054,096.

In the practice of the process set forth in our Patent No. 2,054,096, it was realized that the division between the different fatty acid fractions obtained was not as sharp as desired, that is, the high boiling fraction would contain a higher percentage of the lower boiling acids, and the low boiling fraction would contain a higher percentage of the high boiling acids, than

was desired. It is this problem to which this invention is particularly directed.

For sharper fractionation, those skilled in the art turn to adjustment of the trays in the fractionating tower. The addition of more trays serves to give sharper fractionation. It was found however, that this expedient was not the solution to the present problem, since by adding more trays a greater vacuum differential was created between the top of the fractionating column and the feed stock inlet. While with other materials this might have been immaterial, it had the effect of rendering the present process practically inoperative, since at the higher pressure near the inlet a higher temperature was required for vaporization, and this proved very injurious to the heat-sensitive unsaturated fatty acids.

We have discovered that by reducing the total amount of steam in the fractionating procedure to below one-half of the amount of feed stock, the sharpness of fractionation is greatly improved and the stripping function of the steam is retained to a satisfactory degree. When the amount of steam used is so reduced, the heat which it carries becomes insufficient to reboil the reflux liquid, and we have provided other means for supplying the necessary heat, as will be described later. With still more heat supplied otherwise than by steam, we have also found fractionation can be further improved greatly if the steam which is passed through the fractionation zones is reduced to an amount less than 25% of the amount of the feed stock.

A clear understanding of the advantages and benefits of the invention will be had after the following detailed explanation, taken in connection with the accompanying drawings in which:

Figure 1 is a schematic representation of an apparatus suitable for carrying out the improved process.

Figure 2 is a view showing another means of supplying heat to the fractionating column which might be substituted for that shown in Figure 1, and

Figure 3 is a view of still another means for supplying heat to the fractionating column which might be used instead of that shown in Figure 1.

The improved process is useful for the treatment of fatty acid stocks obtained from a great variety of oils of animal, marine or vegetable origin; but for clearness of understanding this detailed explanation will deal specifically with a feed stock known as "black acid foots," obtained from cottonseed oil and having a fatty

acid content of about 70 percent, the remainder being predominantly triglycerides.

In the preparation of the feed stock the foots material, which is a by-product of cottonseed oil refining by the alkali process, is acidulated with sulfuric acid to break the soap into fatty acid and the sulfate salt of the positive radical combined with the fatty acid. The mass then separates into an oil layer and a water layer, these layers being separately recovered. The fatty material thus obtained is called "black acid foots," and is the material which is specifically referred to hereinafter. The distillation of this type of raw material involves problems the solution of which is made more difficult because of the tendency of the fatty acids to decompose at the higher temperatures, the decomposition products rendering the materials viscous and of poor color and odor.

Referring particularly to Figure 1 of the drawings, the black acid foots, for example, are fed into the tank 10 from which the material is transferred by a pump 11 through line 12 and a preheater 13 to the bottom of a tube heater indicated generally at 14. The preheater 13 may be any type of a heat exchange apparatus for conserving heat and raises the temperature of the fatty acid and neutral oil mixture to the order of 350° F.

The heater 14 consists of a column 15 of substantial cross section and terminated by a bottom header 16 and a top header 17. A relatively large number of pipes or tubes 18 extend between headers 16 and 17 and provide openings through which the fatty acid materials being pumped into the conical chamber 19 may be passed.

Communicating with the top of the column 15 is a vapor inlet 20 into which passes a mixture of diphenyl and diphenyl oxide vapors heated to a temperature of about 600° F. These vapors pass downwardly through column 15 and about the tubes 18. The fatty acids rising in the tubes 18 cool the tubes to a temperature below the liquefaction temperature of the vapors in column 15 and the latter condense into a liquid upon the tubes, thereby imparting to the tubes their latent heat of liquefaction. The liquefied diphenyl and diphenyl oxide trickle down into the bottom of the fatty acid heater and are withdrawn through line 21 to a suitable heater, not shown, for re-vaporizing these materials.

This type of feed stock heating means is very satisfactory since the highest temperature to which the fatty acids are subjected is the temperature at which the diphenyl and diphenyl oxide mixture is liquefied. However, other heating agents may be employed and the heating unit for heating the continuously moving input of feed stock may take other forms.

The fresh feed stock from tank 10 enters the chamber 19 at a temperature of about 300° to 400° F., and is then passed through tubes 18 toward the outlet of the heater. Advantageously, superheated steam at a temperature of about 500° F., for example, may be introduced into the chamber 19 by the injector 26, in an amount of about 0.05 to 0.25 pound of steam per pound of feed stock. The introduction of steam at this point serves to increase the speed of travel of the feed stock through tubes 18, and sweep clean the interior surfaces of the tubes. However, the use of steam at this point is not essential to the process, and the invention can be practiced very satisfactorily without the use of steam in the tube heater.

The tubes 18 connecting with pipe 23 which is of greater cross sectional area than the combined cross sectional areas of the tubes 18, and the pipe 23, connects in turn with an intermediate portion of the fractionating column 24 beneath the baffle plate 27. The column 24 is maintained under a high vacuum and preferably as in the illustrated apparatus this vacuum is allowed to extend through pipe 23 and into the tubes 18. This feature gives an advantage in that by having the vacuum extend back into the tube heater vaporization may take place within the tubes thus enabling the latent heat of vaporization to be supplied as vaporization takes place, and eliminating the need for raising the materials to a temperature above their boiling points under the vacuum conditions. However, this improved process may be carried on without the use of vacuum in the tube heater and according to the process set forth in our issued Patent No. 2,054,096.

As the material passes upwardly through the heater tubes, the static pressure diminishes, the fatty acids are vaporized at least in part and the speed of flow becomes greater, being of the order of 150 to 155 feet per second when steam is employed in the tube heater. At the outlet of the tubes the partly vaporized material slows its movement upon entering the pipe 23 of larger cross section, and upon entering the fractionating column 24 the movement is again slowed down.

The vaporized portion of the feed stock is composed almost entirely of fatty acids having different boiling points. This volatile mixture of fatty acids is passed upwardly through the bubble caps 33, of the trays 32 positioned above the vapor inlet, while the liquid from the upper trays passes downwardly through the overflow lines 34. Thus there is maintained a series of pools or zones having progressively lower boiling points toward the top of the column.

The unvaporized portion of the stock entering column 24 and consisting mainly of neutral oil passes downwardly in the column through a series of zones a function of which is to strip this material of the entrained volatile fatty acids. This unvaporized portion passes through pipes 29 of the trays 30 toward the bottom of the column, while steam injected at the bottom of the column through line 28 passes upwardly through bubble caps 31, the steam serving to strip the volatile fatty acids from the glycerides and carry them upwardly with it through bubble caps 33. The temperature of the steam entering the bottom of the column is preferably of the order of 500° F. so that the bottom of the column is maintained at a temperature not detrimental to the highly unsaturated fatty acids being taken from the unvaporized material. The amount of steam injected is critical, and must not be in quantity which would be sufficient to supply the necessary heat to the column as has heretofore been the practice. The amount of steam however should desirably be sufficient to strip the oleaginous materials to a reasonable degree, and sufficient to supply a partial vapor pressure within the column so as to reduce the temperature at which the acids will vaporize under the static pressure conditions being maintained.

We indirectly heat the fatty acids within the fractionating tower to overcome the deficiency in the heat supplied by the reduced amount of steam and thus enable the necessary reboiling of reflux liquid. By the term "indirectly" we

mean in ways such as will be described in connection with the modifications illustrated in Figures 1, 2, and 3 of the drawings, but not through direct contact of a gaseous medium such as with steam or nitrogen gas.

In the apparatus illustrated in Figure 1 additional heat is indirectly supplied to the fractionating column by recirculating at least a part of the oleaginous bottoms withdrawn at the bottom of the column through line 25, through the tube heater 14 and back again through pipe 23 into the column. The recycled stock is taken from the bottom of the column 24 at a temperature of about 500° F. and during its passage through the tube heater is raised to the order of 550° F., so that through this circulation additional heat is imparted to the zones within the column, and the amount of heat so supplied may be regulated by controlling the amount of material recirculated through the heater 14. The part of the bottom materials from the column which is not recirculated through the tube heater is withdrawn in a residue tank 35 which may be emptied through the outlet line 36. If desired this residue may be again hydrolyzed and subjected to repeated treatment by the same process.

The volatile fatty acid mixture passing upwardly through trays 32 is met with a downwardly flowing stream of reflux liquid which preferably initially is composed of a condensate of a lighter fraction of fatty acid taken from adjacent the top of the fractionating column. This condensate flows downwardly across the bubble plates, and in travelling upward through the fractionating column the higher boiling constituents of the fatty acid vapors are condensed by the reflux and the material on each succeeding higher tray is of a lower boiling point. The fractionating column reaches the state of equilibrium in which the composition of the material on each plate remains substantially constant and the boiling point of the material on each higher tray is lower than the liquid on the next lower tray. The vapors pass upwardly through a series of pools of liquid having the different constituents of the vapors in varying amounts, and having progressively lower boiling points.

From the upper bubble plate of the fractionating column the vapors, consisting principally of steam and low boiling acids, pass through line 37 into a condenser 38 which reduces the temperature of the vaporized material to about 150° F., thereby liquefying the fatty acids. As the entire system is maintained under a high vacuum the steam does not liquefy at this temperature, but passes onwardly leaving the condensed fatty acids behind. If desired to recover from the steam the entrained fatty acids which it contains, it may be introduced into apparatus such as the tank 40 through the line 39. The vapor line 39 extends downwardly in the tank 40 and terminates at an intermediate point therein so that the steam is caused to change its direction sharply thereby sweeping the entrained materials downwardly into the liquid pool at the lower portion of tank 40. The steam passing upwardly within tank 40 may be caused to proceed through a bubble plate indicated at 45 and through baffle plates 49 and 50 and through line 51 to vacuum apparatus indicated at 52. The apparatus 52 may include a barometric condenser connected to suitable vacuum pumps not shown.

The temperature of the liquid within tank 40 may be maintained at about 150° F. by the closed steam coil 44. This liquid may be withdrawn

from the tank 40 by the line 53 and returned in part to the column 24 by means of the pump 54 and lines 55 and 56. Also a part of this liquid may be returned through pipe 47 to the bubble plate 45 and a part withdrawn through line 57 as an overhead product.

Preferably at least 80 percent of the vapors withdrawn from the column should be returned as condensed liquid to serve as a reflux material. For example where about 3000 pounds of vaporous fatty acids are withdrawn and condensed, about 2500 pounds of condensed acids may be returned as reflux. The amount of reflux returned is a quantity which will vary somewhat according to the type of raw stock being treated.

A second fraction may be taken from the column at any desired point depending upon the character of the product required. For example, liquid may be withdrawn from the selected tray through line 58 and passed into a stripper 59 which contains a series of bubble plates 60. Steam may be introduced into the bottom of the stripper 59 through the line 61. The stripped portion of the material entering the stripper through line 58 is returned to the fractionating column through the outlet line 62. The higher boiling portion of the material within stripper 59 is withdrawn through line 63 and cooled in the cooler 64. Thereafter the product material may be disposed of as desired.

In the fractionation of fatty acids, the column should be operated within rather narrow vacuum limits, and it has been found satisfactory to maintain the upper portion of the column at a pressure of about 5 mm. of mercury, or as low as can practicably be maintained. The pressure at the vapor inlet will be substantially higher than that maintained at the top of the column, and with a pressure of 5 mm. at the top of the column the pressure at the feed stock inlet may be, for example, about 43 mm. We have found that there is a limit to the pressure which can be permitted at the inlet, and if the pressure at this point is allowed to exceed about 50 mm. of mercury, there will usually be polymerization and poor operation to the detriment of the products obtained.

It is now apparent that when a greater number of trays are introduced into the fractionating column and the differential between the pressure at the top and inlet portions of the column thereby increased, that no possible vacuum at the top of the column would be sufficient to maintain the vapor portion at a pressure below the minimum required.

However, by the solution given by this invention in the reduction of the amount of steam introduced into the fractionating zones, the number of trays need not be increased, the pressure differential between the top and inlet portions of the column may remain the same yet the sharpness of fractionation is found to be greatly improved. By reducing the amount of steam to a substantial extent and supplying the necessary heating for reboiling reflux by other means than the steam introduced, we are able to produce greater separation and less overlapping of the high and low boiling fractions along the height of the fractionating tower. To accomplish this purpose we have found that the total amount of steam introduced into the zones of fractionation must be less than one-half and preferably less than one fourth of the amount of the feed stock treated. This total amount includes the steam introduced through line 28 at the bottom of the

column, the amount introduced through line 26 at the tube heater, and the steam introduced through line 61 in the stripper 59. There may be also other strippers besides 59, and the total amount of steam is intended to include the steam supplied at these or from any other source to the fractionating zones. We have found that the amount of steam introduced at the bottom of the fractionating column may advantageously be less than 20 percent of the feed stock. For example, assuming that 3000 pounds of feed stock are treated per hour, 500 pounds of steam per hour may be introduced into the bottom of the column, 300 pounds per hour in the tube heater, and 250 pounds per hour into each of two side strippers, making a total of 1300 pounds per hour. To take a further specific example, we have found that under conditions where 3000 pounds of feed stock per hour was treated extremely efficient operation was obtained where only 300 pounds of steam per hour was introduced into the bottom of the column and 100 pounds of steam per hour in each of two side strippers, and with no steam introduced into the tube heater.

Referring more particularly to Figure 2 of the drawings, there is here shown a second type of means for indirectly supplying to the column the necessary heat for reboiling reflux liquid. As here shown the glycerides at the bottom of the column are withdrawn through line 25 and a part is passed through the secondary heater 70 where its temperature is raised, and from this heater it is introduced back into the column. The point of introduction back into the column may be at any suitable point below the feed stock inlet. Heater 70 may be of the same type as heater 14, having the inlet 71 and outlet 72 for the mixture of diphenyl and diphenyl oxide. In the drawings the material is shown as being withdrawn from the bottom of the column, reheated, and introduced through line 73 on the third tray from the bottom, but the material may be withdrawn from other desired zones in the lower portion of the column and introduced at other zones including the zone from which it was withdrawn. In principle this means of supplying heat is substantially the same as that shown in Figure 1, except that here the glycerides by means of which the heat is added, are recirculated independently of the fatty acid feed stock. It will be understood that the glyceride materials cause less trouble in reheating than do the fatty acids themselves. The heated glyceride materials re-introduced within the lower portion of the column provide heat for the reboiling of the reflux liquid descending within the column.

Still another means of indirectly supplying heat for reboiling reflux is illustrated in Figure 3 of the drawings. Here the tray heaters 74 which may contain electrical elements, pass heat directly to the glycerides on the trays in the lower portion of the column, and these in turn serve as the means for supplying heat to the zones throughout the tower for reboiling the descending reflux liquid. The heaters 74 may be spaced along the tower's height and though only two are here shown, as many may be used as desired.

The foregoing detailed description, and the illustrations given are intended for explanation only, and it will be recognized that many changes may be made in the process and apparatus for carrying it out without departing from the scope of the invention as defined in the appended claims.

We claim:

1. A process for the fractional distillation of fatty acids comprising heating a feed stock containing fatty acids of different boiling points to produce a vaporized fatty acid mixture, passing said vaporized mixture upwardly through zones of condensed fatty acid mixtures having progressively lower boiling temperatures against a countercurrent of reflux liquid, passing steam upwardly through said zones with said fatty acids, the total amount of said steam being less than one-half the amount of said feed stock, and indirectly heating the fatty acids within said zones to supply the heat which is necessary in addition to the heat supplied by said steam for reboiling said reflux liquid.

2. A process for the fractional distillation of fatty acids comprising heating a feed stock containing fatty acids of different boiling points to produce a vaporized fatty acid mixture, passing said vaporous mixture upwardly through zones of condensed fatty acid mixtures of progressively lower boiling points, condensing fatty acid vapors from an upper of said zones, returning at least 80 percent of the condensate to said zones as reflux liquid, passing steam upwardly through said zones with said fatty acids, the total amount of said steam being less than one-half the amount of said feed stock, and indirectly heating the fatty acids within said zones to supply the heat which is necessary in addition to the heat supplied by said steam for reboiling said reflux liquid.

3. A process for fractionally distilling fatty acids comprising heating a feed stock material containing glycerides and fatty acids to produce a vaporous fatty acid mixture and a glyceride portion; passing said mixture upwardly in a fractionation enclosure through zones of condensed fatty acid mixtures having progressively lower boiling points against a countercurrent of reflux liquid, passing said glyceride portion downwardly in said enclosure through successive zones in which entrained volatile matter is separated from the glycerides, passing steam upwardly through said zones containing glycerides and fatty acid mixtures whereby to effect the separation of volatile matter from said glycerides and to reduce the fatty acid vapor pressure, the total amount of said steam being less than one-half the amount of said feed stock, and indirectly heating said glycerides within said enclosure to supply the heat which is necessary in addition to the heat supplied by said steam for reboiling said reflux liquid.

4. A process as set forth in claim 3 wherein said glycerides are withdrawn from said enclosure, reheated, and returned to said enclosure for supplying heat to reboil said reflux liquid.

5. A process for the fractional distillation of fatty acids comprising heating a feed stock containing fatty acids of different boiling points to produce a vaporized fatty acid mixture, passing said vaporized mixture upwardly through zones of condensed fatty acid mixtures having progressively lower boiling temperatures against a countercurrent of reflux liquid, and passing steam upwardly through said zones with said fatty acids, the total amount of said steam being less than one-half the amount of said feed stock, a part of said steam being introduced into said zones through said heater with said feed stock, and indirectly heating the fatty acids within said zones to supply the heat which is necessary in

addition to the heat supplied by said steam for reboiling said reflux liquid.

- 5 6. A process for fractionally distilling fatty acids comprising heating a feed stock containing glycerides and fatty acids to produce a vaporous fatty acid mixture and a portion containing glycerides, passing said mixture upwardly within a fractionating enclosure through zones of condensed fatty acid mixtures having progressively 10 lower boiling points against a countercurrent of reflux liquid, passing said portion containing glycerides downwardly within said enclosure through a series of stripping zones, passing steam upwardly through said stripping zones and 15 said zones of condensed fatty acid mixtures, the amount of said steam being less than 20 percent of said feed stock, and indirectly heating the fatty acids within said zones to supply the heat which is necessary in addition to the heat sup-

plied by said steam for reboiling said reflux liquid.

7. A process for the fractional distillation of fatty acids comprising heating a feed stock containing fatty acids of different boiling points to produce a vaporized fatty acid mixture, passing 5 said vaporized mixture upwardly through zones of condensed fatty acid mixtures having progressively lower boiling temperatures against a countercurrent of reflux liquid, passing steam up- 10 wardly through said zones with said fatty acids, the total amount of said steam being less than 25 percent the amount of said feed stock, and indirectly heating the fatty acids within said zones to supply the heat which is necessary in 15 addition to the heat supplied by said steam for reboiling said reflux liquid.

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