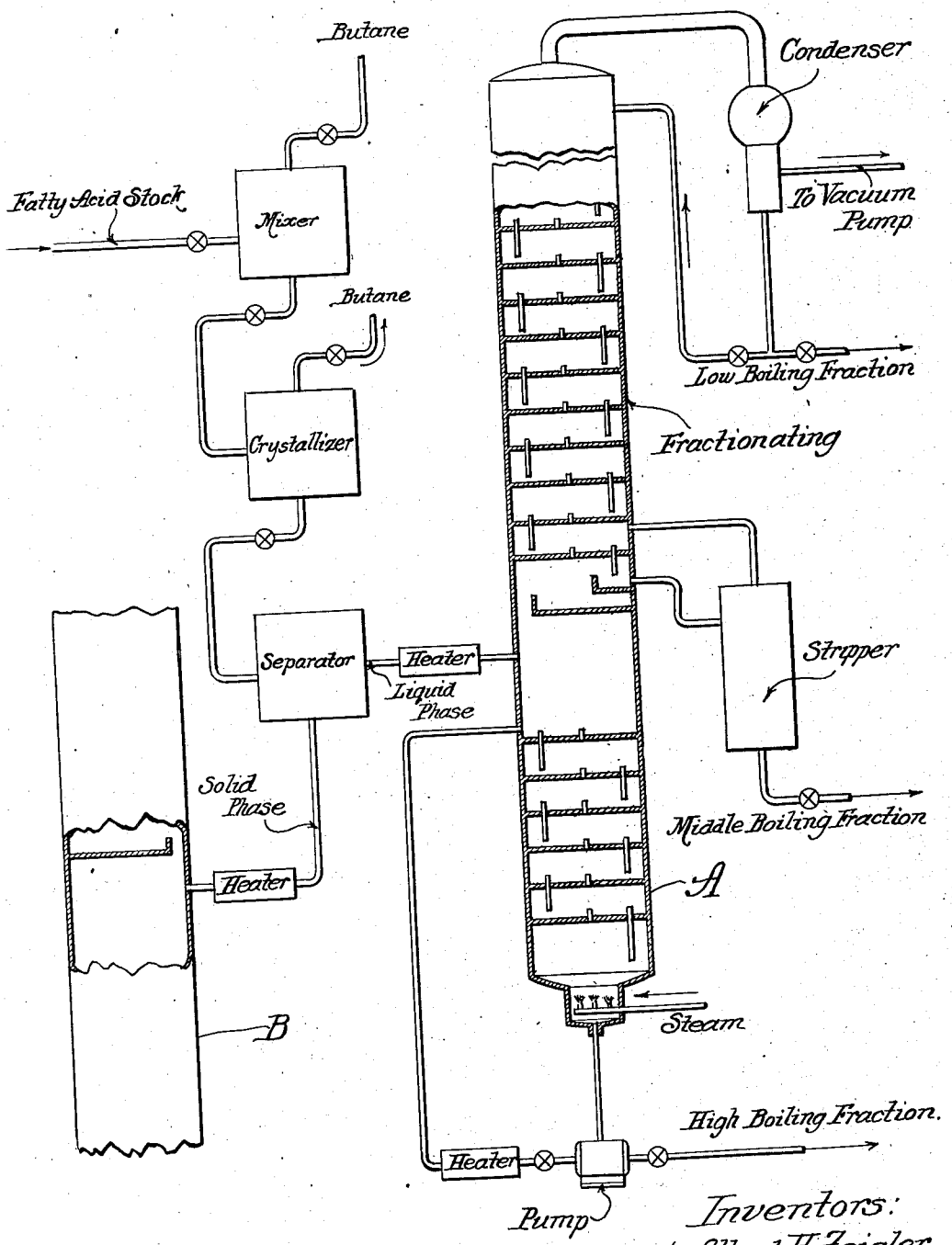
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TREATING FATTY ACIDS

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TREATING FATTY ACIDS

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In the practice heretofore employed for fractionally distilling fatty acids to effect a separation thereof substantially according to boiling point, the saturated and unsaturated fractions have been treated simultaneously. While a vacuum of 5 mm. can be maintained at the top of the fractionating tower, the pressure at the bottom of the tower, due to the large number of bubble trays by means of which the upwardly rising fatty acid vapors contact the downwardly flowing reflux liquid fatty acids, is of the order of 35 to 40 mm. mercury absolute. Because of the higher pressure in the lower portion of the tower, relatively high temperatures have to be employed such as, for example, temperatures of the order of 240° C. Furthermore, since fractional distillation involves the returning of substantial amounts of fatty acid as reflux, the heat input at the base of the tower must be from two to five times as much as that necessary for straight distillation. With such higher temperatures and with the increased required amount of heat input, unsaturated fatty acids are subject to considerable thermo-alteration. Since unsaturated fractions of fatty acids are extremely desirable for use in paints, varnishes, lacquers, baking and air drying enamels, etc., a considerable loss is encountered through the reduction in the iodine value of the unsaturated fractions recovered in the final product.

Efficiency of separation is often sacrificed by reducing the temperatures employed in the lower portion of the tower and in order to prevent an excessive thermo-alteration of the unsaturated acids.

An object of the present invention is to provide a method for separating to a substantial degree the saturated from the unsaturated acids without a thermo-alterattion of the unsaturated acids and then subsequently fractionally distilling the saturated fractions and the unsaturated fractions separately. A further object is to provide a method and means for separately fractionally distilling saturated acids with an accompanying high yield. A further object is to provide a method and means for separately fractionally distilling unsaturated acids under conditions which obviate thermo-alteration while producing a greater yield of the high iodine fraction. Still another object is to provide a method and means for effecting a substantial separation between saturated and unsaturated fatty acids without the employment of high temperatures and thus preserving unaltered the iodine value of the unsaturated fraction and then subsequently fractionally distilling the two products separately to separate the acids substantially according to chain length. Other specific objects and advantages will appear as the specification proceeds.

The invention is illustrated, in a preferred embodiment, by the accompanying drawing, in which the single figure represents, diagrammatically, the method and certain of the apparatus employed in carrying out the process.

The new method comprises the broad steps of first separating the saturated fraction from the unsaturated fraction to a fair or substantial degree by means which do not subject the unsaturated fraction to high temperatures likely to produce thermo-alteration, and then subsequently fractionally distilling the saturated fraction separately from the unsaturated fraction.

Any suitable means for separating the saturateds from the unsaturateds without the employment of such injurious high temperatures may be employed. The fatty acids may be crystallized with or without solvents or diluents and the solid fraction consisting predominantly of saturateds thus separated from the soluble or liquid fraction consisting predominantly of unsaturateds. Another method for separating the saturateds from the unsaturateds without the employment of high temperature is by selective adsorption. The mixtures of fatty acids are treated with large quantities of a surface active material which tends to adsorb the saturateds but not the unsaturateds. Other methods for producing a separation of the saturated acids from the unsaturated acids to a substantial degree will occur to those skilled in the art and may be employed so long as high temperatures deleterious to the iodine value of unsaturated fractions are avoided.

As illustrative of the process, we will describe herein specifically the method of separation wherein crystallization is the means employed. Fractional crystallization of saturated fatty acids from unsaturated fatty acids may be accomplished by simply cooling a fatty acid mixture containing preferably a relatively low amount of saturated acids, such as, for example, 10% or less, to a temperature at which partial crystallization occurs. The crystallized fraction may be separated then by filtering or other means.

We have found that a much more effective separation of the saturateds from the unsaturateds can be produced through the use of sol-

vents in conjunction with the crystallizing step and further, that solvents which differ substantially in density from the density of fatty acids increase the formation of crystals free from occluded, normally-liquid fatty acids with the result that a sharper separation of saturateds from unsaturateds is brought about. For example, low density solvents having a density not above 0.63, such as butane, propane or pentane, such density being well below that of fatty acids, are extremely effective in promoting a satisfactory crystal growth. Such crystals may be allowed to separate out by their own weight or, when placed in a centrifugal machine or in a filter, permit the liquid phase to be readily and sharply separated therefrom.

In crystallizing fatty acids, it is found that the solid phase is composed of mixed crystals of fatty acids in which the saturated fatty acids are to be found in higher concentration than in the original mixture of fatty acids. In the absence of solvents, the normally liquid unsaturated fatty acids tend to become occluded with the normally crystalline saturated fatty acids. When low density solvents of the type described are employed, we find that there is a substantially complete elimination of occluded unsaturated fatty acids from the crystalline phase.

We find that the higher the ratio of solvent to fatty acid, the freer is the crystalline phase of occluded unsaturated fatty acids.

In a specific description of the method, butane, which has a density of approximately 0.58, will be referred to as the solvent or diluent.

The mixture of fatty acids or fatty acid stock is introduced into a mixer and there brought into contact with liquid butane which is forced under pressure into the mixer from a compressor or pressure reservoir. It is important that the fatty acid mixture be completely dissolved in the solvent before allowing crystallization to proceed. The butane may be mixed with the fatty acids in the proportion of five volumes of butane to one volume of fatty acid mixture, or in any other suitable proportion. From the mixer, the material goes to the crystallizer where the temperature is reduced to a point at which crystallization occurs. The crystallization may be produced by any suitable cooling method. In the illustration given, crystallization is induced by allowing a portion of the butane to evaporate, the evaporated butane being recovered and returned to the compressor or pressure reservoir. It will be understood that the butane may also be recovered from succeeding portions of material by various recovery means not shown. Recovery stills, compressors and pressure reservoirs are well-known to those skilled in the art for such recovery purposes and need not be shown herein.

It is found that the crystals formed in this manner are crystals free from occluded normally-liquid fatty acids and tend to separate by settling out of the liquid. If desired, the liquid may be then withdrawn from the crystals and the crystallized fatty acids thus recovered from the crystallizer itself or from some other container to which the mass is passed. In this particular illustration given, the entire mass is withdrawn from the crystallizer to a separator which may be either a tank, as already described, or a centrifugal machine, filter or any other suitable mechanical means for separating the solid phase from the liquid phase.

After the solvent has been removed and recovered, the liquid phase consisting almost entirely of the unsaturated fatty acids is passed from the separator through a heater, preferably of the tubular type, to the fractionating column A. The solid phase consisting almost entirely of the saturated acids is passed through a similar heater into a similar fractionating column B. It will be understood that, if desired, a single fractionating column may be employed and the liquid phase passed through the column at one time and subsequently the solid phase treated in the fractionating tower. If two towers are employed, as illustrated, it will be found that a lesser number of bubble trays are required in tower A.

In the case of either fractionating tower A or fractionating tower B, the introduced charging stock of unsaturated fatty acids or saturated fatty acids is first passed through the tube heater, as in the usual practice, and thence into the fractionating tower. The fractionating operation is carried on by passing the vapors upwardly through the bubble trays as reflux liquid flows downwardly over the trays. A vacuum of approximately 5 mm. is preferably maintained at the top of the tower, while the pressure in the lower portion of the tower may be from 35 to 40 mm. mercury absolute but it is preferably appreciably less than 35 mm. Heat is introduced through the coils by the circulation of "Dowtherm" fluid or other suitable heating means to produce the desired vaporization. Steam is introduced preferably in the lower portion of the tower. A portion of the bottoms from the tower may be passed through a heater and recycled to the lower portion of the tower. The distilled fractions are recovered in the usual manner but in the present instance consist, in the case of tower A, almost entirely of unsaturated acids separated according to their chain length and, in the case of tower B, of saturated fatty acids separated according to chain length.

As a specific example, sardine fatty acids were separated by the process described, being first mixed with five volumes of butane to one volume of fatty acid and then refrigerated by permitting the butane to evaporate. The liquid phase was removed by withdrawing it from the settled saturated acid crystals and after the removal of all solvent remaining therein, is passed through the tube heater and thence into tower A. The distillate fraction obtained from tower A constituted 50% of the original sardine fatty acid mixture and had an iodine value of 254. The same sardine fatty acid mixture when not subjected to the crystallizing and separation operation and when fractionally distilled together gave only a 20% yield at an iodine value of 254. Since the high iodine fraction is by far the most important product recovered from the processing of the oil, the value of the preliminary step of separating the unsaturateds from the saturateds without heat treatment, thus becomes apparent.

With respect to the solid phase consisting of saturateds and sent to tower B or passed through tower A in a separate run, this resulted in a much increased yield since temperatures could be raised far beyond those formerly employed in view of the fact that there were present substantially no unsaturateds to undergo thermal change due to the high heat.

In the distillation separately of the unsaturateds, it was found that a tower equipped only with three trays might satisfactorily be employed, thus enabling a much higher vacuum and lower distillation temperatures to be used.

In connection with the foregoing fractional distillation process, it will be noted that the low density solvents already described are useful not only for separating saturateds from unsaturateds but also unsaturated fatty acids of comparatively low degree from unsaturated fatty acids possessing a high degree of unsaturation. For example, the process will result in some separation of linolic acid from oleic acid—a commercially desirable separation.

While in the foregoing description, we have referred to crystallization as an example of a method whereby separation of the saturated fatty acids from the unsaturated may be accomplished without the use of destructively high temperatures, it will be understood that other methods may be utilized for producing the same results. As already mentioned, selective adsorption may be used. It is found that certain surface active materials may be used which will select or adsorb the saturateds while not affecting substantially the unsaturateds. As a specific example, if fatty acids, preferably admixed with a solvent, are passed through a long layer of anhydrous aluminum oxide, the saturated fraction will be retained in the layer while the unsaturateds pass through the filter. Any suitable adsorbents such as alumina, charcoal, bleaching earth, gypsum, calcium carbonate, magnesium oxide, finely divided clay and other inorganic or organic materials may be used. The portion passing through the filter may be sent to tower A after the removal of the solvent while the adsorbed fraction may be recovered in the usual manner and sent to tower B.

We claim:

1. In a method for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling highly unsaturated fatty acids, to obtain a high yield of highly unsaturated fatty acids, the steps of subjecting the mixture to low temperatures to bring about crystallization of a saturated acid portion, separating the crystallized saturated portion from the uncrystallized unsaturated portion, and separately fractionally distilling said unsaturated fatty acid portion, without imparting sufficient heat to the same to produce substantial thermo-alteration of the unsaturated fatty acids, to obtain a plurality of fractions of said portion of different boiling points, including a relatively large high boiling fraction consisting predominantly of highly unsaturated fatty acids.

2. In a process for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling unsaturated fatty acids, the steps of mixing the fatty acid mixture with a solvent and reducing the temperature to bring about crystallization of a saturated fatty acid portion, separating the crystallized saturated portion from the uncrystallized unsaturated portion, and separately treating the unsaturated fatty acid portion by vaporizing portions thereof and subjecting such vapors under pressure to contact with a series of heat exchanging pools of condensed fatty acid mixtures having successively lower boiling points, the heat imparted to said vapors being insufficient to produce substantial thermo-alteration of the unsaturated fatty acids, condensing the low boiling vapors passing through the last of said pools, returning a portion of said condensed low boiling vapors to said pools as reflux liquid, and withdrawing from said pools a fraction consisting predominantly of unsaturated fatty acids of higher boiling point than said low boiling fraction.

3. In a method for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling unsaturated fatty acids, to obtain a high yield of highly unsaturated fatty acids, the steps of mixing said fatty acids with a solvent, reducing the temperature of the mixture to crystallize a saturated acid portion, separating the crystallized saturated portion from the uncrystallized unsaturated portion, and treating separately the unsaturated fatty acid portion by vaporizing portions thereof and subjecting such vapors under reduced pressure to contact with a series of heat exchanging pools of condensed fatty acid mixtures having successively lower boiling points, the pressure to which said vapors are subjected being so low that the boiling point of the fatty acids in the portion being treated at such pressures is below the temperature at which substantial thermo-alteration of the unsaturated fatty acids in such portion occurs, condensing the low boiling vapors passing through the last of said pools, returning a portion of said condensed low boiling vapors to said pools as reflux liquid, and withdrawing from said pools a fraction of fatty acid of higher boiling point than said low boiling fraction.

4. In a method for treating a mixture of saturated and unsaturated fatty acids, including relatively low boiling saturated fatty acids and relatively high boiling highly unsaturated fatty acids, to obtain a high yield of highly unsaturated fatty acids, the steps of mixing said fatty acids with a solvent, separating the mixture into two portions, one of the portions containing a predominant proportion of saturated fatty acids and the other portion containing a predominant proportion of unsaturated fatty acids, the separation being carried out at temperatures substantially below those at which thermo-alteration of the fatty acids occurs, and fractionally distilling said unsaturated fatty acid portion, without imparting sufficient heat to the same to produce substantial thermo-alteration of the unsaturated fatty acids, to obtain a plurality of fractions of said portion of different boiling points, including a relatively large high boiling fraction consisting predominantly of highly unsaturated fatty acids.

5. In a method for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling unsaturated fatty acids, to obtain a high yield of unsaturated fatty acids, the steps of mixing said fatty acids with a solvent, separating the mixture into two portions, one of the portions containing a predominant proportion of saturated fatty acids and the other portion containing a predominant proportion of unsaturated fatty acids, the separation being carried out at temperatures substantially below those at which thermo-alteration of the fatty acids occurs, and treating separately the unsaturated fatty acid portion by vaporizing portions thereof and subjecting such vapors under reduced pressure to contact with a series of heat exchanging pools of condensed fatty acid mixtures having successively lower boiling points, the heat imparted to said vapors being insufficient to produce substantial thermo-alteration of the unsaturated fatty acids, condensing the low boil-

ing vapors passing through the last of said pools, returning a portion of said condensed low boiling vapors to said pools as reflux liquid, and withdrawing from said pools a relatively large fraction consisting predominantly of unsaturated fatty acids of higher boiling points than said low boiling fraction.

6. In a method for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling highly unsaturated fatty acids, to obtain a high yield of highly unsaturated fatty acids, the steps of first separating the mixture into two portions, one of the portions containing a predominant proportion of saturated fatty acids and the other portion containing a predominant proportion of unsaturated fatty acids, the separation being carried out at temperatures substantially below those at which thermo-alteration of the fatty acids occurs, and fractionally distilling the unsaturated fatty acid portion, without imparting sufficient heat to the same to produce substantial thermo-alteration of the unsaturated fatty acids, to obtain a plurality of fractions of said portion of different boiling points, including a relatively large high boiling fraction consisting predominantly of highly unsaturated fatty acids.

7. In a method for treating a mixture of saturated and unsaturated fatty acids including relatively low boiling saturated fatty acids and relatively high boiling unsaturated fatty acids, to obtain a high yield of unsaturated fatty acids, the steps of first separating the mixture into two portions, one of the portions containing a predominant proportion of saturated fatty acids and the other portion containing a predominant proportion of unsaturated fatty acids, the separation being carried out at temperatures substantially below those at which thermo-alteration of the fatty acids occurs, and treating separately the unsaturated fatty acid portion by vaporizing portions thereof and subjecting such vapors under reduced pressure to contact with a series of heat exchanging pools of condensed fatty acid mixtures having successively lower boiling points, the pressures to which said vapors are subjected being so low that the boiling point of the fatty acids in the unsaturated portion being treated at such pressures is below the temperature at which substantial thermo-alteration of the unsaturated fatty acids occurs, condensing the low boiling vapors passing through the last of said pools, returning a portion of said condensed low boiling vapors to said pools as reflux liquid, and withdrawing from said pools a relatively large fraction consisting predominantly of unsaturated fatty acids of higher boiling point than said low boiling fraction.

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