Solvent Extraction of Fatty Acids from Natural Oils with Liquid Water at Elevated Temperatures and Pressures

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The use of liquid water at elevated temperatures and pressures as an extractive solvent for separating mixtures of compounds which occur in natural oils has been studied. A southern pine tall oil and a distillate from the deodorization of soybean oil were extracted with liquid water at temperatures from 298 to 312°C and pressures between 103 and 121 bar. Results indicate that water can be used to extract fatty and resin acids from crude tall oil to obtain a product with a high acid content that produces less pitch during distillation. The process can also be used to extract fatty acids from vegetable oil deodorizer distillate.

KEY WORDS: Deodorizer distillate, extraction, fatty acids, phase equilibria, solubility, sterols, tall oil, tocopherols.

For over twenty years, researchers in the petroleum industry have known that liquid water at elevated temperatures can be used to extract aromatics from hydrocarbon mixtures. Arnold and Coghlan (1) recovered toluene from reformed naphtha with liquid water at 274 and 302°C. Connolly (2) determined that benzene and toluene become completely miscible with liquid water at 300 and 320°C, respectively, but that nonaromatic hydrocarbons such as heptane are essentially insoluble at these temperatures. O'Grady (3) extended Connolly's work to mixtures and discovered that liquid water could be used to recover benzene from a mixture of benzene and heptane at approximately 300°C. More recent work has shown that two-ring aromatics can also become completely miscible in water (4,5). Aromatics are highly soluble in liquid water at elevated temperatures for two reasons—the extent of hydrogen bonding between water molecules at 300°C is reduced by about 50% compared to ambient temperatures (6), and intermolecular attraction occurs between the hydrogen atoms of water and the aromatic π bonds (7).

Previous studies of the solubilities of the components of natural oils in liquid water at elevated temperatures are scarce. Over forty years ago, researchers determined that fatty acids derived from coconut oil and tallow become completely miscible in liquid water at 290 and 320°C, respectively (8). More recently, we have measured mutual liquid solubilities for oleic acid-water mixtures (9). The system was found to exhibit complete miscibility above 317°C. However, to our knowledge no measurements of water's ability to fractionate such substances have been made.

Clearly, previous work has established that the properties of liquid water become dramatically different at elevated temperatures. Substances which are essentially insoluble in water at ambient conditions but which contain polar substituent (e.g., carboxyl) or other interacting (e.g., aromatic) groups can become highly soluble at elevated temperatures. Therefore, the objective of this study is to investigate the ability of liquid water at elevated temperatures to fractionate the components of natural oils. Since these compounds frequently have different types of substituent groups, we would expect them to have different solubilities in liquid water at elevated temperatures.

We chose to investigate two mixtures of natural compounds in order to evaluate the potential of water as an extractive solvent—crude tall oil and deodorizer distillate. Crude tall oil is a by-product of the Kraft pulping process for the manufacture of wood pulp. The main components of tall oil are fatty acids, resin acids and non-acidic components known as neutrals, which include diterpenes, sterols, wax alcohols, stilbenes, and other minor constituents (10). β-Sitosterol is the largest single component in the neutrals fraction and comprises up to a third of the neutrals present. The fatty acid fraction contains mainly oleic and linoleic acid. Typical resin acids include dehydroabietic and abietic acid. The composition of tall oil is dependent on the species of trees used in the pulping process. For example, a typical southern U.S. crude tall oil, derived mainly from pine trees, contains 52% by weight fatty acids, 40% resin acids and 8% neutrals(11). On the other hand, tall oil from Canada and Scandinavia, where spruce and hardwood trees are used along with pine, can contain from 22 to 49% resin acids and up to 28% neutrals (11,12).

The conventional process for fractionating crude tall oil is by vacuum distillation at elevated temperatures of 200-285°C (13). Relatively pure fatty acids and resin acids are recovered as products. However, the process has drawbacks—a high percentage of the sterols react with the acids to form pitch, reducing potential product yields by as much as 20% (11). Unreacted sterols cannot be separated by distillation and end up as impurities in the resin acids. In recent years, the use of sterol-rich hardwoods in the Kraft pulping process has increased, resulting in even higher losses.

The classic method of reducing acid losses is to convert the tall oil to its soap form, if not already present as such, and to remove the neutrals by solvent extraction. This method has been practiced commercially in Finland since 1977 (14,15). An acetone-water mixture and hexane are used as the solvents. No other commercial processes for reducing acid losses are known. In general, tall oil producers would prefer a process in which the tall oil would not have to be present as a soap. Clearly, the investigation of a new process for fractionating tall oil is warranted.

The other mixture which we chose to investigate is the distillate obtained from the deodorization of vegetable oils, especially soybean oil. A typical deodorizer distillate contains 30-60% by weight free fatty acids, 10-35% sterols and esters, 10-30% hydrocarbons, 10-20% glyce-

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rides, 1-20% tocopherols, and minor amounts of other materials (16). Deodorizer distillate is treated to recover the tocopherols, which are commonly known as Vitamin E. Although the technology is proprietary, existing processes are known to involve extraction with solvents which are coming under increasing scrutiny. In these days of increasing environmental regulation, a process which used water as its extractive solvent would certainly be an attractive alternative.

EXPERIMENTAL PROCEDURES

Apparatus. The success of a solvent extraction process is largely dependent upon the equilibrium phase behavior exhibited by the systems of interest. Liquid-liquid equilibrium compositions were therefore measured for the tall oil-water and the deodorizer distillate-water systems at elevated temperatures and pressures. An equilibrium flow apparatus (9) was used to measure the desired phase compositions. This apparatus is designed to minimize the residence times of the components of interest at elevated temperatures, which is an important consideration for thermally sensitive substances such as natural oils. A schematic of the apparatus is shown in Figure 1. Unless otherwise noted, all fluid transfer lines are 316 stainless steel with an o.d. of 1.59 and an i.d. of 0.762 mm. For an experimental run, the oil of interest (either tall oil or deodorizer distillate) and water are delivered as compressed liquids by separate high pressure feed pumps (Milton Roy Minipump, model no. 396, Milton Roy Co., Rochester, NY; and Isco Syringe Pump, model no. LC 5000, Isco, Inc., Lincoln, NE; respectively). The combined constant flow rate from the two pumps ranges from 375 to 500 mL/hr. A 150-mL gas sample cyclinder serves as a surge tank and dampens pressure fluctuations caused by the Milton Roy pump. The pump feed reservoir for the oil is maintained at 60-70°C to reduce the viscosity of the oil for easier pumping, and to ensure that all compounds are in solution. A nitrogen blanket is maintained over the contents of the feed reservoir so that no oxidation reactions occur.

After leaving the pumps, the two liquids enter the equilibrium coil, which is used for heating the two-phase mixture to the desired operating temperature. The temperature of this mixture was always within 1°C of the contents of the view cell. After exiting the coil, the equilibrated, two-phase mixture enters the view cell,

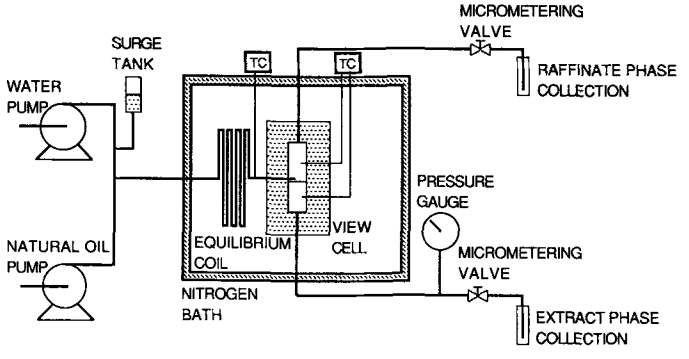


FIG. 1. Schematic diagram of equilibrium flow apparatus.

which functions as a phase separator. The raffinate phase, which is richer in organics, exits the top of the cell and is expanded to atmospheric pressure across a micrometering valve (Autoclave Engineers, Inc., Erie, PA model no. 60VRMM). The extract phase, which is richer in water, exits the bottom of the cell and is similarly expanded through a micrometering valve. The micrometering valves and sample collection lines are heated to 50-70°C to reduce sample viscosity and prevent the precipitation of solids in the lines. Five consecutive 10-15 g samples of each phase are collected to ensure representative samples and smooth out scatter due to phase separation in the lines.

Temperatures of the feed mixture and of each phase in the cell are measured with Type K differential thermocouples referenced to an aluminum block located inside the constant temperature bath. The absolute temperature of the aluminum block is measured with a secondary standard RTD (Burns Engineering, Inc., Minnetonka, MN). Operating pressures are measured with a Bourdon-tube type, Heise gauge (model CM, 0-5000 psi range) which had been calibrated against a Budenberg dead weight gauge (model 380 H). Additional details of the experimental apparatus are described elsewhere (9,17).

Sample analysis. The water content in the samples was determined by Karl Fischer titration. The collected samples from the organic-rich raffinate phase were first homogenized by the addition of 30-40 mL of toluene and 40-50 mL of anhydrous methanol. Samples of the water-rich extract phase were homogenized by the addition of 50-60 mL of methanol and 10-15 mL of toluene. Portions of the homogeneous solution (0.5-2 mL) were analyzed for water using a Metrohm automatic titrator (model no. E547) and buret (model no. E535) from Brinkmann Instruments, Inc. (Karlsruhe, Germany). The percent deviation in the measurements of a given sample were always less than $\pm$ 1%.

Samples were also analyzed by gas chromatography (GC) to quantify the acids, sterols and/or tocopherols present. Samples were analyzed on a Hewlett-Packard 5980A gas chromatograph (Hewlett-Packard, Norwalk, CT) equipped with a flame ionization detector and a 0.53 μm i.d. $\times$ 15 m long $\times$ 0.15μm film methyl silicone column (DB-1, J&W Scientific, Folsom, CA).

For the experiments with tall oil, the samples were diluted and injected into the GC without derivatization. The percentage of sterols in the samples was determined by comparing the resulting GC area ratio of acids to sterols with previously prepared calibration mixtures of oleic acid and β-sitosterol. The response of fatty acids, resin acids, and light neutrals was assumed to be the same as the oleic acid. The response factor of β-sitosterol was used for the sterol fraction and dehydrated sterol by-products. The total amount of neutrals present in the samples was determined by first dissolving a sample in diethyl ether. The acids were then extracted with a 2-5% aqueous KOH solution. The neutrals were determined gravimetrically after evaporating the diethyl ether phase. The acid number was determined using ASTM D803-65.

For experiments with deodorizer distillate the tocopherol and sterol contents of the samples were determined by a silylation technique. Marks (18) demonstrated that samples of deodorizer distillate could be derivatized by silylation and analyzed by GC without

requiring previous saponification or separation of the neutral and acid fractions. However, unlike Marks' samples, ours contained substantial amounts of water. Since most of the silylation reagents react with water, silylation is generally avoided in aqueous solutions. Valdez *et al.* (19) developed a method for silylation of fatty acids in aqueous solutions. Using the results of these two workers, we have developed a method for the silylation for aqueous solutions containing deodorizer distillate, eliminating the need for tedious saponification, extraction or dehydration steps. Valdez's (19) method was modified and used for the analysis. The samples were derivatized by placing three drops of the previously homogenized sample into a 2-mL vial followed by 200 μL of acetonitrile and 800 μL of the silylation reagent. The reagent used was *bis*-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethyl-chlorosilane (TMCS). Additional details on the use of silylation for aqueous solutions containing fatty acids and neutrals such as sterols are discussed elsewhere (17). β-Sitosterol was used to establish the response factor for the sterols and tocopherols, and oleic acid was used to obtain the response factor for the acids.

Materials. Soybean oil deodorizer distillate was supplied by Cargill, Inc. (Fayetteville, NC). A southern pine crude tall oil was obtained from an industrial source, and had been previously extracted with hexane to remove lignin and solid matter. Distilled and deionized water was used for all experiments. BSTFA + 1% TMCS was obtained from Regis Chemical Co. (Morton Grove, IL). High performance liquid chromatography (HPLC) grade Acetonitrile, Karl Fischer grade Methanol and ACS grade Toluene were obtained from Fisher Scientific (Fairlawn, NJ). β-Sitosterol with a purity of 90% was supplied by Dérivés Résiniques et Terpéniques (Dax, France). Oleic acid with a purity of 99% was supplied by Chemical Dynamics Corporation (South Plainfield, NJ).

RESULTS AND DISCUSSION

Crude tall oil extraction. Crude tall oil was extracted with liquid water at three temperatures—301, 306 and 312°C. Pressures were maintained several bar above the vapor pressure of water at all times to keep water in the liquid state and ranged from 113 to 121 bar. The flow rate of the tall oil pump was 100mL/hr and of the water pump was 400mL/hr.

Liquid-liquid equilibrium compositions are shown on a temperature vs composition diagram in Figure 2. The extract phase contains the components of tall oil which have been extracted into the water, and the raffinate phase contains the unextracted portion of the tall oil. For comparison, we have also plotted our results for the oleic acid-water binary system, which have been reported elsewhere (9). As shown in Figure 2, the amount of tall oil in the extract phase ranged from 3 wt % at 299°C to about 6 wt % at 312°C with the remainder being water. Note that the raffinate phase, which contains the unextracted tall oil, also contains substantial amounts of water (e.g., about 30 wt % at 312°C). Although the oleic acid-water system becomes completely miscible at 317°C, the tall oil-water system still splits into two phases at this temperature. This phenomenon is caused by the presence of neutrals in the tall oil, many of which are essentially insoluble in water at these temperatures.

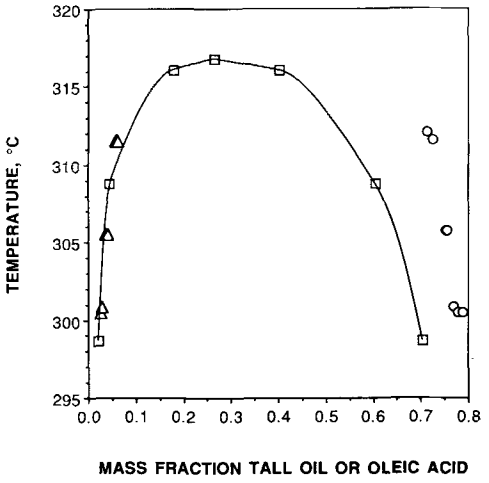


FIG. 2. Liquid-liquid equilibrium compositions for the tall oil-water and oleic acid-water systems. (△) Tall oil extract, (○) tall oil raffinate, and (□) oleic acid-water.

The tall oil in each phase was analyzed for both β-sitosterol and total neutrals content. Results of these analyses are shown in Table 1 for the three experimental runs. The given weight percents are on a water-free basis. Acid numbers of the tall oil feed and of the two product streams are also given in Table 1.

Two parameters which are important for evaluating liquid-liquid extraction processes are the selectivity β and the distribution coefficient k_D (20). The selectivity of water for the acids over the neutrals is defined as:

$$\beta = \frac{\left[\dfrac{\text{weight fraction acids}}{\text{weight fraction neutrals}}\right]_{\text{in extract phase}}}{\left[\dfrac{\text{weight fraction acids}}{\text{weight fraction neutrals}}\right]_{\text{in raffinate phase}}}$$

TABLE 1

Extraction of Tall Oil with Liquid Water

	wt % β-Sitosterol (neutrals) in		
Temperature, °C	Feed	Extract phase	Raffinate phase
301	5.6 (11.3)	0.7 (3.8)	5.5 (13.5)
306	5.6 (11.3)	0.7 (5.5)	9.3 (13.7)
312	5.6 (11.3)	1.6 (4.7)	10.5 (17.0)
	Acid Number in		
Temperature, °C	Feed	Extract phase	Raffinate phase
301	158.3	176.2	157.9
306	158.3	174.5	155.7
312	158.3	173.4	151.6

The distribution coefficient of the acids is defined as:

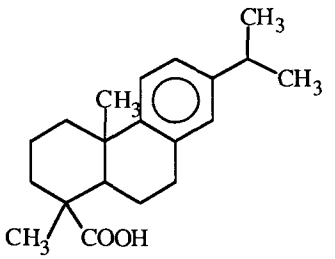
$$k_D = \frac{\text{weight fraction acids in extract phase}}{\text{weight fraction acids in raffinate phase}}$$

These parameters can be readily calculated from the data given in Figure 1 and Table 1, and are shown in Table 2. As is required for a useful extraction process (20), the selectivities are greater than one. Although larger distribution coefficients and selectivities would be desirable, our results are comparable to those obtained in conventional liquid-liquid extraction processes (20).

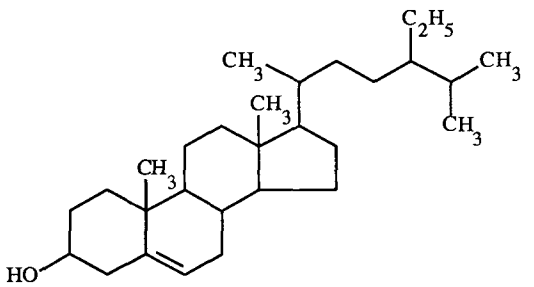
TABLE 2

Selectivities and Distribution Coefficients for the Extraction of Tall Oil with Liquid Water

Temperature, °C	β	k_D
301	4.0	0.035
306	2.7	0.052
312	4.2	0.083



(A)



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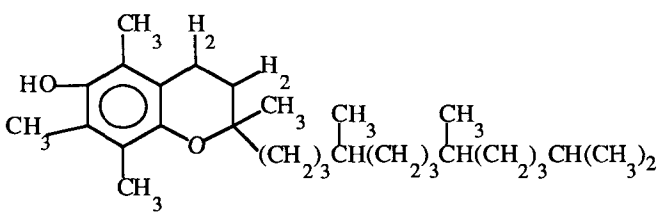

(C)

FIG. 3. Structures of natural oil compounds. (A) Dehydroabietic acid, (B) β-sitosterol, and (c) α-tocopherol.

The above data clearly indicate that the fatty and resin acids are being selectively extracted into the extract phase, and the unextracted neutrals are being concentrated in the raffinate phase. These results can be qualitatively explained in terms of our understanding of the behavior of the components of tall oil in water at elevated temperatures (Fig. 3). The fatty and resin acids, with their polar carboxyl groups, have significantly higher solubilities in the aqueous extract phase than neutrals such as β-sitosterol, which has a less polar substituent group and a higher molecular weight.

GC analysis indicates that only about 20% of the sterols in the feed tall oil either reacted with acids to form pitch or underwent dehydration (i.e., loss of their alcohol group); recall that in vacuum distillation most of the sterols react with the acids to form pitch. The presence of water in the raffinate phase appears to inhibit the pitch formation reaction, which involves the formation of water. Approximately 5% of the resin acids underwent decarboxylation. The extracted tall oil was subsequently fractionated by vacuum distillation; pitch production was about 50% less than was obtained when the feed tall oil was similarly distilled.

We should emphasize that the above results were obtained with an equilibrium flow apparatus, which is equivalent to one equilbrium stage. Solvent extraction is typically carried out in a multistage extraction column (20). Extraction with water in such a column would yield a higher recovery of acids and a higher concentration of neutrals in the raffinate phase than was obtained with one stage.

Deodorizer distillate extraction. A sample of deodorizer distillate of soybean oil was extracted with liquid water at 298 and 307°C. Pressures were maintained about 6 bar above the vapor pressure of water. Feed pump flow rates were 150 mL/hr for the water and 225 mL/hr for the deodorizer distillate.

Liquid-liquid equilibrium compositions are shown in Table 3. Note that the weight percents of deodorizer distillate in the extract and raffinate phases, with the remainder being water, are similar to those obtained for tall oil extraction (Fig. 2). A comparison of the

TABLE 3

Liquid-Liquid Equilibrium Compositions for the Deodorizer Distillate-Water System

	wt % Deodorizer distillate	
Temperature, °C	Extract phase	Raffinate phase
298	2.2	85.2
307	2.3	82.0

TABLE 4

Extraction of Soybean Oil Deodorizer Distillate with Liquid Water

	Mass ratio fatty acids/sterols in		
Temperature, °C	Feed	Extract phase	Raffinate phase
298	2.5	27.8	2.6
307	2.5	37.3	2.5
	Mass ratio fatty acids/tocopherols in		
Temperature, °C	Feed	Extract phase	Raffinate phase
298	2.1	31.1	2.3
307	2.1	18.9	2.2

TABLE 5

Selectivities and Distribution Coefficients for the Extraction of Soybean Oil Deodorizer Distillate with Liquid Water

Temperature, °C	$\beta\left(\frac{\text{acids}}{\text{sterols}}\right)$	$\beta\left(\frac{\text{acids}}{\text{tocopherols}}\right)$	k_D
298	10.7	13.5	0.026
307	14.9	8.6	0.028

fatty acid, sterol and tocopherol levels in the feed, extract and raffinate phases on a water-free basis is shown in Table 4. Since we did not determine the amount of glycerides in the samples, results are not reported in terms of weight percent, but as the mass ratio of fatty acids to sterols and of fatty acids to tocopherols. GC area ratios were converted to mass ratios from previously prepared calibration curves. Selectivities of water for the acids over the sterols and tocopherols, and the distribution coefficients for the acids are shown in Table 5. Significant amounts of glycerol were detected by GC in the extract, which indicates that glyceride splitting and the resulting formation of fatty acids is occurring during the extraction process. As a result of this reaction, the mass ratio of fatty acids to either sterols or tocopherols was found to be slightly higher in the raffinate than in the feed.

These results dramatically indicate that water selectively extracts fatty acids over tocopherols. Like the sterols, the tocopherols are significantly less soluble in the extract phase than the fatty acids. Surprisingly, no noticeable decomposition of the tocopherols was observed at the elevated temperatures of operation.

Proposed extraction process. From the experimental results obtained in this investigation, we propose an extraction process to fractionate a natural oil such as tall oil or vegetable oil deodorizer distillate (Fig. 4). Liquid water would be compressed, heated and fed countercurrently to the oil feed in a liquid extraction column. The operating temperature would depend on the type of natural oil being extracted; for tall oil and deodorizer distillate it would be expected to be 290-330°C. Operating pressures would be just a few bar above the vapor pressure of water to maintain it as a liquid. The organic acids (fatty and/or resin) would be extracted into the aqueous phase and exit the bottom of the column. The raffinate phase would consist mainly of neutrals, such as sterols or tocopherols, and would exit the top of the column. A minor amount of water would be present in this phase and would help prevent dehydration reactions. During the fractionation of deodorizer distillate, the splitting of glycerides to fatty acids and glycerols would go to completion in the first stages of the column; the raffinate phase exiting the top of the column would thus be depleted of fatty acids.

After exiting the column, the temperature of the extract phase is reduced to below 200°C. The acids now are insoluble in the water, and a pure water and a pure acid phase are recovered. The acid phase can now be fractionated by vacuum distillation if desired, for example, if it consists of a fatty acids-resin acids mixture. The raffinate phase is similarly cooled, pure water condenses out, and a neutrals phase is recovered. This phase can be further purified by methods such as crystallization to recover sterols or tocopherols.

In conclusion, liquid water at elevated temperatures and pressures can be used to extract fatty and/or resin acids from natural oils. The process has been tested on crude tall oil and could be used to recover high purity acids. A sterol-rich neutrals fraction may also be recoverable. The greatest potential for indus-

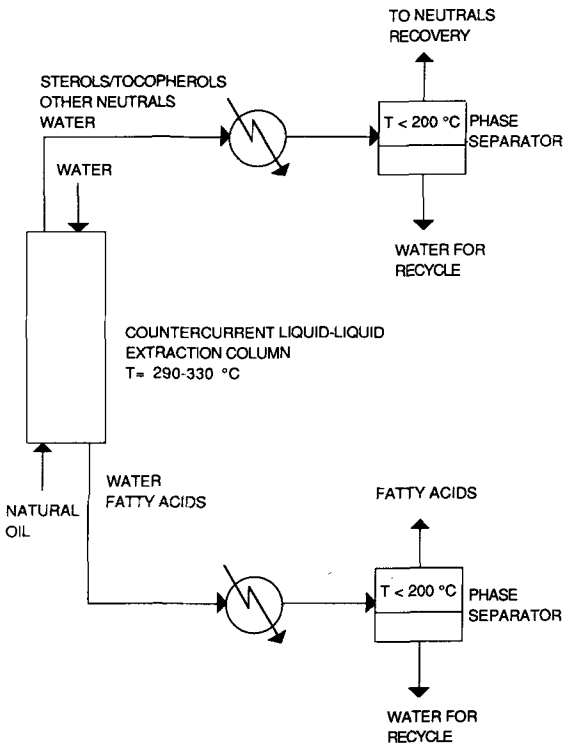

FIG. 4. Proposed fatty acids extraction process.

trial application of this process would be on crude tall oils with a high neutrals content, such as those derived from hardwoods and spruce. Results also indicate that water can be used to remove the fatty acids and glycerol from deodorizer distillate, which could be used to facilitate the recovery of tocopherols. Finally, a unique advantage of the proposed process is that the most abundant and environmentally acceptable solvent, water, is used for fractionation.

ACKNOWLEDGMENTS

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