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REVIEW

# Refining and Separation of Crude Tall-Oil Components

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## ABSTRACT

Methods for crude tall-oil refining and fractionation involving research studies of long-chain fatty and resinic acids separation are reviewed. Although several techniques have been applied since the 1940s with industrial aims, only distillation under high vacuum is economically practicable for crude tall-oil fractionation. Techniques such as adsorption and dissociation extraction seem to be the most industrially promising for implementation in the future for the separation of long-chain fatty and resinic acids fractions with a high purity level at low cost.

*Key Words*. Crude tall oil; Fatty acids; Resinic acids; Refining; Fractionation methods

## INTRODUCTION

Crude tall oil has been produced for many years, mainly in the United States and Europe, from the black liquor resulting from the production of kraft paper by the sulfate process. During digestion of pine wood, the resinous acids are converted to their salts which rise, along with the neutral components, to the surface of the cooking liquor as soap. After skimming and acidulation of the soap, the water-insoluble raw crude tall oil, from the Swedish *tallolja* meaning an oil from the pine, is separated by centrifuging. It represents the main by-product in cellulose production (1).

Characteristically, crude tall oil contains 40–50% resinic acids related to rosin or abietic acid, 30–40% fatty acids related to oleic and linoleic acids, and about 10% neutral or unsaponifiable matter of less importance in which the most important component is β-sitosterol (2, 3). The chemical composition varies with the age, pine species, and geographical location of the coniferous trees and, additionally, all operations with softwood before and during the pulping process, where most of the oxidations and isomerizations usually occur. On a dry wood basis, crude tall-oil precursors may be as high as 4%, but normally not more than about half of this amount is recovered.

Although other techniques have been suggested from time to time, fractional distillation under high vacuum remains the only practical industrial process for separating crude tall oil into good quality tall-oil fatty and resinic acids.

The end uses of tall oil fatty acids are mainly as alkyd resins, adhesives, soaps, flotating agents, protective coatings, and detergents. Resinic acids are mainly used in paper sizing agents (printability enhancers) and synthetic rubbers. The neutral fraction, which is rich in sterols, can be used in pharmacology. A good compilation by McSweeney et al. (4), entitled *Tall-Oil and Its Uses*, thoroughly examines all applications of crude tall-oil fractionated products.

Crude tall oil is dark, odorous, and inexpensive. Refining methods have generally had as their objectives the removal of the odor and color bodies and the stabilization of the resinous acidic fraction. Adopted methods have always kept in mind the low cost of crude tall oil and were developed to add as little as possible to that cost. However, distillation had been found to be the only commercially significant means of upgrading crude tall oil with the exception of acidic refining. Difficult separations which use fractional distillation under high vacuum are frequently uneconomic because they usually involve high operating costs and lead to considerable pitch formation.

Beyond recent modern chromatographic methods for analytical and research activities (5–9), several studies conducted since the 1940s have been devoted to crude tall-oil separation in pilot- and laboratory-scale plants, and these have given rise to hundreds of patents and many Ph.D. thesis dissertations. The main goal of most studies was the separation of long-chain fatty acids from resinic acids for industrial applications as well as the removal of the neutral fraction as a means of increasing crude tall-oil quality. In most of the processes described, separations were by methods other than distillation and explored the best way to utilize the main differences in physical and chemical proprieties among both classes of acids, including differential esterification rate, adducts and metal salts formation, dissociation constants, degree of unsaturation and positional double bonds, molecular structure, polarity, volatility, viscosity, density, solubility, crystallization, and diffusivity.

Although other important technological methods were studied, they showed no significant results (10–12). The main operations successfully explored physical–chemical proprieties for the refining and separation of crude tall-oil components for industrial purposes, and involved such techniques as distillation, adsorption, and solvent extraction (13–18).

## DISTILLATION

As industrially practiced (19–23), vacuum distillation of the complex crude tall-oil mixture yields five commercial products. The general average composition obtained (with a typical loss of 4%) is as follows.

Tall-oil heads (TOH: 10%), which contain mostly palmitic acid (40%), esters, alcohols, and diterpenic hydrocarbons
Tall-oil fatty acids (TOFA: 28%), which contain 2% or more resinic acids and at least 90% fatty acids (oleic and linoleic acids)
Distilled tall oil (DTO: 8%), which contains less than 90% fatty acids
Tall-oil rosin (TOR: 32%), which contains less than 5% fatty acids
Tall-oil pitch (TOP: 18%), which contains β-sitosterol as its principal component and where the yield of pitch and its composition depends not only on crude tall-oil quality but also the type of distillation equipment

Although many patents concerning vacuum distillation have appeared from time to time, a new and recent distillation technique was introduced in Austria using Swiss technology (24). This technique has now been adopted by several other plants all over the world. It includes as its main innovations thin evaporators for pitch stripping, and heat exchangers and packed towers for fractionation.

Crude tall oil may be improved in quality by chemical treatment, known as acid refining, before the distillation stage. In a batch or continuous process (25), crude tall oil is dissolved in naphtha and then treated with concentrated sulfuric acid (88–100%). Following the acidic treatment, a block of acidic sludge containing most of the coloring material and odor bodies settles to the bottom of the tank and is drawn off. The tall oil is then washed with water, washed with a very dilute alkali solution, and has the naptha stripped off. The result is the refined tall-oil product. Refining does not particularly alter the proportions of resinic and fatty acids present in the original crude.

A book written by Drew and Propst (26), entitled *Tall-Oil*, is one of the best compilations concerning fractionation and refining as well as evaluation of crude tall-oil industrial separation by the distillation technique.

## ADSORPTION

Adsorption has now become widely applicable to the separation of a wide variety of mixtures, in large part due to the development and use of various molecular sieve adsorbents and fluid-contacting schemes. The use of activated adsorbent clays or carbons for separating components or groups of components from mixtures is a very common solution in chemical processing.

Some work similar to chromatographic adsorption showed good separation when crude tall oil was hydrogenated in the conventional manner to reduce the main acidic components substantially to the stearic and abietic acids forms and then to separate them by passing an organic solution down through a column containing the adsorbent (activated carbon) (27). After the hydrogenation step, crude tall oil is fixed on the adsorbent, and abietic acid is first washed through and out of the column by additional fresh solvent, followed by the stearic acid which is preferentially adsorbed. The efficiency of such separation and the rate of throughput depends mainly on the solvent. 1-Nitropropane was shown to be the best solvent among 29 considered for removing abietic acid and not stearic acid.

Gembicki et al. (28) reported the Sorbex process in 1983. It represents a general principle that can be applied to a wide variety of specific and difficult separations. In attempting to apply Sorbex technology to any particular separation, the best adsorbent/desorbent system must be selected from a large number of adsorbents, typically crystalline alumina silicates and commonly known as molecular sieves.

Sorbex also requires a desorbent to remove the extracted components from the adsorbent, typically a liquid which is adsorbed about as strongly as the extracted feed component, which does not depress the selectivity of the adsorbent, and which has a substantially different boiling point from the feed. The last property permits both extract and raffinate components to be obtained free of desorbent by fractionation.

The separation of tall-oil fatty acids (TOFA) and distilled tall oil (DTO) was successfully demonstrated in a pilot-plant Sorbex operation. DTO and TOFA could be separated into their respective main groups of constituents at very high purities; 95% for the resinic acids fraction of DTO and 92% for oleic and linoleic acids of TOFA. The application of such methods provides a continuous liquid-phase operation process and a highly efficient use of the adsorbent bed. The preliminary process has great economic potential for those separations and can be applied to many other specific systems.

## SOLVENT EXTRACTION

Solvent extraction was extensively studied as an alternative unit operation to separate resinic acid out of fatty acids in crude tall oil by using different methodologies. At the beginning, liquid–liquid extraction was applied by using an active polar solvent with a better affinity for resinic acids, a hydrocarbon solvent which had a preference for the free fatty acids, and neutral components which are relatively immiscibility and have different specific gravities (29).

Generally, the columns used as the extraction phase comprising the polar solvent were further extracted countercurrently with additional hydrocarbon in order to obtain a raffinate rich in free fatty acids. The polar solvent mixture and nonpolar solvents were introduced at the upper and bottom ends of the column, respectively, and the crude tall oil was fed in the middle. Although such studies introduced new solvents [as, for example, furans (30)], the results obtained didn't show as good selectivities as other unit operations. It has been found that the distribution coefficients of oleic plus linoleic acids and resinic acids between two solvents with different polarity indexes showed appreciable differences in the specificity level obtained. Good pairs of solvents were *n*-heptane/methyl cellosolve containing 10% water by volume (31), naphtha/methyl or ethyl alcohol with water, naphtha/water with acetone, naphtha/glycol, and naphtha/furfural, also saturated with water.

It is a well-known fact that fatty acids may be esterified with alcohols more easily, faster, and at lower temperatures than resinic acids by using a mineral acid as catalyst because they are primary and tertiary carboxylic acids, respectively. This could be applied to make less polar fatty acid molecules with respect to the corresponding esters (32, 33). Generally, alcohols are used for the esterification of methanol, ethanol, butanol, glycerol, pentaerythritol, and sorbitol, which transform tall-oil fatty acids into products with substantially higher addict values. After the preliminary esterification and neutralization stage, several kinds of operations were tried for refining the final mixture obtained in the solvent extraction step by using a specific diluent, e.g., naphtha, gasoline, aromatic hydrocarbons, furfural, and hexane. Tall oil fatty acids esters are better solubilized in nonpolar organic solvents and resinic acids, which do not esterify easily and remain in the polar alcoholic phase. Organic layers were vacuum distilled to refine the unsaponifiable matter as well as to recover a clean organic solvent. Although some selectivity was obtained with these separation techniques, there were always problems with persistent emulsions. The data obtained did not improve on the results found for distillation.

In 1982 a pilot-scale liquid–liquid extraction apparatus was completed and placed into use in the Laboratory of Chemistry of the Technical Research Center of Finland by Oksanen (34) to separate the acidic components from the neutral fraction. These studies were made by using mixer-settler extractors to promote good performance with the increased use of hardwood as a raw material for kraft pulping which caused a decline in crude tall-oil quality (35). Results from the extraction tests showed higher acidic and saponification numbers and a low neutral yield in the final extracts by standard analysis.

Liquid water at elevated temperatures can be used to extract aromatics from hydrocarbons mixtures. Briones et al. (36) worked with temperatures and pressures between 301–312°C and 113–121 bar, respectively, to separate oleic acid, the main long-chain fatty acid, from complex crude tall-oil mixtures. This solvent extraction procedure showed a good selectivity index for the oleic acid–water system which becomes completely miscible at 317°C. The authors proposed a continuous schematic flow diagram for the fatty acid extraction process.

The Solexol process, first introduced by Hixson and Miller (37), was another solvent extraction method studied for fatty acids refining from vegetable oils. It showed a good performance for the fractionation of crude tall-oil components and involved the use of propane under a pressure between 350 and 500 psig. At the temperature used, generally 65 to 82°C, fatty acids could be removed from the top and resinic acids from the bottom of a fractionation column. Because of the quick solubility of fatty acids as promoted by the solvents, temperature control is critical. At 97°C both saturated and unsaturated fatty acids are almost completely insoluble in the solvents. The yields obtained were generally 60–87% and 63–73% for the fatty and resinic acids fractions, respectively, depending on the pressure/temperature variables used and the intended fractional purity (38).

In recent years there has also been growing interest in supercritical fluid extraction in chemical engineering processes. One commercial example is the industrial decaffeination of coffee. The word "supercritical" refers to the fact that the solvent is at a temperature above or near its vapor–liquid critical point. Thus, the solvent or fluid cannot be liquefied by increasing the pressure. Under those conditions the properties of supercritical fluids are unusual, and they have densities greater than those of gases but comparable to those of liquids. The viscosities and diffusivities are intermediate between liquids and gases.

The most commonly used supercritical fluid is carbon dioxide, although there are other supercritical solvents. The solvent power can be varied over a wide range by varying the pressure or temperature. This fluid has advantages over other supercritical solvents because it is nontoxic, nonflammable, environmentally acceptable, inexpensive, and leaves no solvent residue (39).

In 1985 Harvala et al. (40), also at the Technical Research Center of Finland, studied extraction of the neutral fraction from crude tall oil with supercritical carbon dioxide and obtained results which showed that supercritical fluid extraction can be used to improve crude tall-oil quality. When multistage supercritical extraction is used to separate neutrals from resinic and fatty acids, the selectivity seems to be good enough to recover the unsaponifiable matter, although GC analyses of extraction samples showed that among fatty acids, resinic acids, and neutral classes of compounds there were differences in the selectivities for individual compounds, especially in the neutral fraction.

The separation of fatty and resinic acids from a crude tall-oil acidic fraction by such a methodology do not show systematic changes with most important parameters: temperature, residence time, carbon dioxide density, and flow (41). A new approach for study is supercritical fluid chromatography (SFC), which has commercial application as an analytical tool. It has not been used for crude tall-oil evaluation.

Another solvent extraction process that has shown high specificity in the extraction of resinic from fatty acids in crude tall oil is dissociation extraction (42). It has been used for phenolic separation and penicillin purification (43–45). An acidic aqueous phase (pH 9.2, $T$ = 30°C) containing less than 2 g/dm$^3$ of crude tall oil to avoid micellar associations was studied using 20 different organic solvents which showed good recoveries for long-chain fatty acids other than resinic acids, resulting in high selectivity values ($2 < \beta < 6$) (46). The use of tri-*n*-octylamine in *n*-heptane as the carrier [largely used as a basic extractant in hydrometallurgy (47)] showed higher overall distribution coefficients but less selectivity than using the solvent alone. The process is supported by the dissociation extraction theory to systems having anionic and acidic dimeric species in which the pH is the most relevant parameter (48). A complete study of such a process, including a multistage bench-scale plant, will be presented soon (49). The low cost of the preliminary studies indicates great potential for crude tall-oil industrial fractionation.

## CONCLUSIONS

Separation techniques of the past 50 years for crude tall-oil fractionation have been reviewed, including the data obtained and the costs. The main methods studied all present operational difficulties.

The Sorbex process provides good separation, especially for fatty and resinic acids fractions from TOFA and DTO as well as excellent technological performance and very satisfactory yield.

Dissociation extraction may be a very good possibility as an alternative for crude tall-oil fractionation. It shows high selectivity values and low-cost operation.

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