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TALL OIL

Tall oil [8002-26-4] is a by-product of kraft pulping of pine wood. *Tall* is the Swedish word for pine, *kraft* the German word for strength. Crude tall oil (CTO), formed by acidifying black liquor soap skimmings with sulfuric acid, is a dark oily liquid with 26–42% resin acids or rosin, 36–48% fatty acids, and 10–38% neutrals. CTO is an excellent source of oleic/linoleic fatty acids and resin acids or rosin (1, 2). Extensive fractional distillation is required, not only to separate these desirable products but also to remove the neutrals. The bulk of these neutrals, largely esters of fatty acids, sterols, resin and wax alcohols, and hydrocarbons, boil at either lower or higher temperatures than the boiling range of the fatty and resin acids. The wax alcohols and related components with boiling points in the rosin range are notable exceptions, but they are minor constituents.

Considering their heat sensitivity, the separation of fatty acids and rosin with minimal degradation by fractional distillation under vacuum and/or in the presence of steam is surprisingly good (3). Tall oil rosin (TOR) contains about 2% fatty acid and small amounts of neutrals. Tall oil fatty acid (TOFA) contains as little as 1.2% rosin and 1.7% neutrals. In typical U.S. TOFA, 49% of the fatty acids is oleic, 45% linoleic, and 3% palmitic, stearic, and eicosatrienoic acid. TOR and TOFA are upgraded to resins and chemicals for the manufacture of inks (qv), adhesives (qv), coatings (qv), and lubricants (see Lubrication and lubricants).

The 1995 annual global CTO production was about 1.7 million metric tons. About half of that output was in the United States and one quarter in Europe outside the CIS. U.S. CTO production climbed 4.2% per year from 0.45 million metric tons in 1963 to 0.68 in 1973. After that the average annual increase slowed to 1%. The five U.S. CTO processors are listed in Table 1.

CTO prices are closely tied to the cycles of the U.S. economy and the paper industry. They vary between $120 and $220 per metric ton. In 1995 they were close to $200/t (4). With 50% of pine wood being converted to linerboard valued at $400–$600 per ton, pulp manufacturers do not focus on optimum black liquor soap recovery, which only amounts of 60–70 kg/t of southern pine pulp. This soap is converted to 30–35 kg of CTO, worth $6–$7 or less than a little over 1% of the pulp value (5). This recovery is only 45% of the CTO available in the pine tree. With more care and higher CTO prices, 10–15 kg of additional CTO could be obtained per ton of pulp (6).

1. Composition and Properties

Variations found in CTO composition result primarily from the species of wood pulped and the location and climate where the trees are grown. Pulping process variations further affect CTO composition. The best CTO is produced from pine wood. However, many U.S. mills mix hardwood with pine to reduce fiber costs, or mix hardwood black liquor with pine black liquor. This lowers the rosin content. The composition of CTO produced in the southeastern United States and of typical Canadian and Scandinavian CTOs are shown in Table 2.

Table 1. U.S. Tall Oil Processors

Company	Capacity[a], 10^3 t/yr
Arizona Chemical	360
Georgia Pacific	70
Hercules	170
Union Camp	125
Westvaco	210
Total	*935*

[a] 1995 estimated U.S. fractionation.

Table 2. Typical Tall Oil Compositions

Component, wt %	Southeastern United States	Canadian	Scandinavian
	Principal fatty acids		
palmitic and lower	2.5	1.6	1.2
oleic	16.3	9.1	9.2
linoleic	13.6	10.9	14.4
conjugated linoleic and linolenic	6.9	13.1	15.9
stearic	0.7	0.3	0.3
eicosatrienoic and eicosadienoic	6.0	3.0	2.0
Total fatty acids	46.0	38.0	43.0
	Principal rosin acids		
pimaric type	8.2	4.7	4.8
abietic type	19.2	11.1	12.3
dihydroabietic	4.4	4.3	3.6
neoabietic	5.4	1.9	3.7
other resin acids	2.8	6.0	4.6
Total rosin acids	40.0	28.0	2.09
	Other		
neutral components[a]	14.0	34.0	28.0
acid number	167.0	128.0	138.0

[a] Unsaponifiables and esters.

2. Tall Oil Recovery and Processing

2.1. Process Sequence

The process sequence consists of recovery of tall oil soap from the pulping black liquor, acidulation, ie, conversion of the soap into CTO with sulfuric acid, fractional distillation to separate rosin, and fatty acids and purification of the fatty acid fraction.

The kraft pulping process yields strong cellulose fibers by digesting pinewood chips for about two hours with an aqueous mixture of sodium hydroxide and sodium sulfide at 165–175°C under pressure. During pulping, the 2–3% resin and fatty acids that naturally occur in resinous wood are saponified. After filtration of the fibers, pulping black liquor is concentrated by multistage evaporation prior to feeding to a furnace for the recovery of the sodium salts and energy values.

2.2. Black Liquor Soap Recovery

Black liquor soap consists of the sodium salts of the resin and fatty acids with small amounts of unsaponifiables. The soap is most easily separated from the black liquor by skimming at an intermediate stage, when the black liquor is evaporated to 25% solids (7). At this solids level, the soap rises in the skimmer at a rate of 0.76 m/h. At higher solids concentrations, the tall oil soap is less soluble, but higher viscosity lowers the soap rise rate and increases the necessary residence times in the soap skimmer beyond 3–4 hours. The time required for soap recovery can be reduced by installing baffles, by the use of chemical flocculants (8, 9), and by air injection into the suction side of the soap skimmer feed pump. Soap density is controlled by the rate of air injection. Optimum results (70% skimmer efficiency) are obtained at a soap density of 0.84 kg/L (7 lb/gal). This soap has a minimum residual black liquor content of 15% (10–12).

Proper soap removal increases the pulp mill's evaporator capacity by 5%. Therefore, soap is often recovered as well at other places in the pulp mill, such as the weak black liquor storage tanks and the heavy black liquor oxidation system (13, 14).

Only approximately 45% of CTO available in the pine tree is recovered. The rest is lost during woodyard operations (20%), pulping (15%), black liquor recovery (15%), and acidulation (5%). Several processing changes have been proposed to improve this yield. For instance, woodyard operations have become more efficient, with a turnover of one week, as opposed to two months, when these numbers were recorded. This has compensated for CTO losses that resulted from an increased use of hardwood. CTO losses due to soap adsorption on the pulp can be reduced, too. In a 1400 t/d pulp mill, about 25 t/d of soap is left on the pulp. Much of this soap can be recovered by adding *N,N*-dimethyl amides of tall oil fatty acids to the wash water of the rotary drum vacuum filter in the third and final pulp washer stage. Also, the addition of 6–7 grams of propyl stearic amide to the wash system per ton of pulp has been reported to increase tall oil soap yields significantly (15, 16).

2.3. Black Liquor Soap Acidulation

Only two-thirds of a typical black liquor soap consists of the sodium salts of fatty acids and resin acids (rosin). These acids are layered in a liquid crystal fashion. In between these layers is black liquor at the concentration of the soap skimmer, with various impurities, such as sodium carbonate, sodium sulfide, sodium sulfate, sodium hydroxide, sodium lignate, and calcium salts. This makes up the remaining one-third of the soap. Crude tall oil is generated by acidifying the black liquor soap with 30% sulfuric acid to a pH of 3. This is usually done in a vessel at 95°C with 20–30 minutes of vigorous agitation. Caution should be taken to scrub the hydrogen sulfide from the exhaust gas.

The long reaction time needed for this apparently simple neutralization is on account of the phase inversion that takes place, namely, upon dilution, the soap liquid crystals are dispersed as micelles. Neutralization of the sodium ions with sulfuric acid then reverses the micelles. The reverse micelles have a polar interior and a hydrophobic exterior. They coalesce into oil droplets.

When the acidified soap solution is allowed to stand, it separates into four different and fairly distinct phases. The uppermost layer is CTO. The second layer is a rag layer containing a mixture of CTO, lignates, and other solids. Next is a 15% sodium sulfate brine, commonly called spent acid. At the bottom precipitated calcium sulfate can be found. CTO can be recovered by gravity separation or centrifugation. The CTO phase separation rate can be accelerated 10-fold by the addition of a small amount (0.5% based on the gross weight of soap) of dispersants, such as certain commercial lignosulfonates (17). Dispersants also raise the acid number of the recovered CTO by as much as 12 points in the case of the addition of 0.42% Lignosol SFX. This indicates that the dispersant promotes the coalescence of the reverse micelles of fatty and resin acids, which are formed upon neutralization of the sodium salts.

The typical CTO yield from early batch acidulation systems was 75–80% of the total available in the skimmed soap. Direct steam injection was used for both soap heating and agitation. With improved reactor vessel design and mechanical agitation, CTO yield has been raised to 80–85%. High losses of CTO trapped in the lignin layer and the excessive amount of sulfuric acid required to speed up processing are the main disadvantages of the batch recovery system. Incorporation of self-cleaning centrifuges into a continuous acidulation process improved CTO recovery to 90%. The internal bowl of these centrifuges collects interfacial solids. These solids are ejected by a self-opening through a slot once every five minutes (18).

Even centrifuged CTO contains 2–3 wt % of water captured by the fatty and resin acids in reverse micelle structures. The water content can be reduced to the standard 1.5% by gravity settling at 80°C in a large tank. The remaining water is removed in a vacuum dehydrator before the CTO distillation. It is desirable to filter or centrifuge the CTO after dehydration. This removes residual lignin, estimated at 0.9%, which was finely dispersed in CTO, together with sodium sulfate crystals, estimated at 0.3–0.4% (19, 20). This solids removal step prevents fouling of the distillation column and the power boiler in which tall oil pitch is burned. The residual sodium salts can also be removed by washing of CTO with pH-adjusted water.

2.4. Distillation

Separation of rosin from fatty acids is an essential step in utilizing CTO. The basic patent for tall oil distillation was granted in 1911 and the first commercial plant was constructed in Kotka in 1913 (21), making Finland the birth place of the tall oil industry. In the United States, CTO distillation started in the early 1930s (22). The first continuous large-scale fractionation plant began operations in 1949. It was built by the Badger Company of Boston, Massachusetts, adapting vacuum fractionation techniques from the petroleum industry to heat-sensitive CTO. Steam was injected to further reduce the partial pressure of the components. The plant was operated by Arizona Chemical Company. During the 1950s a number of large CTO fractionation plants were constructed (23).

The first step in CTO distillation is depitching. A relatively small distillation column is used as a pitch stripper. The vapor from the pitch stripper is fed directly into the rosin column, where rosin and fatty acids are separated. Rosin is taken from the bottoms of the column and fatty acids as a sidestream near the top. Palmitic acid and light neutrals are removed in the rosin column as heads. The operation is designed to minimize holdup and product decomposition. Care is taken to prevent carryover of some of the heavier neutrals, such as the sterols, from the depitcher to the rosin column (24).

The crude tall oil fatty acids obtained from the rosin column usually contain about 5% rosin because the boiling points of the heavier fatty acids and the lighter resin acids overlap. By adding the intermediate fraction to the fatty acid, rosin does not have to be redistilled.

The rosin column split is controlled by the fatty acid content specified for rosin. This is usually set at 2% fatty acids. At the high temperature near the bottom of the column and the reboiler, rosin dimerizes to some extent. By taking rosin from the column as a sidestream above the bottom, its rosin dimer content is minimized. Because of its high purity, sidestream rosin product is prone to crystallization.

Higher grade fatty acids with less than 2% rosin are obtained by further distillation. Union Camp uses two columns to achieve this. The first column is used to separate light ends and the second column to separate a mixture of rosin and higher boiling fatty acids. This mixture with about 40% rosin is sold as Distilled Tall Oil (DTO). Standard specifications for TOFA grades have been established by ASTM (25) as shown in Table 3. Also, the Pulp Chemicals Association provides specifications on TOFA having either more or less than 2% rosin.

The older tall oil distillation columns used bubble cap trays. In new columns, structured packing is preferred. Because of the low pressure drop of structured packing, steam injection is no longer necessary. The low liquid holdup of this packing minimizes the reactions of the fatty and resin acids. A specific distillation sequence for vacuum columns using structured packing of Sulzer has been described (26). Depitching is carried out at a vacuum of 0.26–1 kPa (2–8 mm Hg) and a temperature of 220–270°C. The rosin column is operated at 0.4–1.2 kPa (3–9 mm Hg), a temperature of 204–260°C, and a reflux ratio of 2–3. These conditions give a bottoms rosin with a softening point of 80°C and an acid number of 178–180, as well as a crude fatty acid stream with 3% rosin.

Table 3. Grades I–III of Tall Oil Fatty Acids

Specification	ASTM method	Values III	 II	 I
acid number	D1980	190–194	192–197	197–198
rosin acid, wt %	D1240	4.5–6.0	0.9–2.0	0.5–1.0
unsaponifiables, wt %	D1965	2.7–4.0	1.3–2.0	0.7–1.0
fatty acids, wt %	D1983	90.0–92.8	96.0–97.8	98.0–98.8
Gardner color	D1544	5–7	3–4	2–3
iodine value	D1959	131	130	130

2.5. Environmental Considerations

All CTO processing plants have environmental safeguards (27, 28). CTO contains small amounts of volatile odor compounds that are exhausted by the vacuum systems of the distillation columns. They are captured, along with the more volatile fatty acids, in the cooling water of the barometric condensers. This oily water is recycled from the receivers or hot wells to the barometric condensers through heat exchangers, where it is cooled indirectly with water from the cooling towers. The oily water purge stream is skimmed and passed to the wastewater treatment system. The organic phase, consisting mostly of neutrals, palmitic acid, and organosulfur compounds, is usually sent to the heads storage tank.

All vapors, including hotwell odors, are captured in a header system linked with the incineration air of a steam boiler or hot oil vaporizer. Drain seals avoid escape of odors from the sewer lines. This completely eliminates total reduced sulfur (TRS) emissions. The SO_2 emissions are subject to local regulations.

3. Uses of Tall Oil Products

3.1. Tall Oil Rosin

U.S. production of tall oil rosin (TOR) in the 1990s is about 255,000 metric tons per year. It was introduced in the 1950s as a low cost substitute for gum and wood rosin, particularly for paper size. In 1960, 122,000 tons was used in this application in the United States. The introduction of the more economical dispersed rosin size (requiring only 0.25 and 0.75% alum based on printing paper weight) and the inroad of alkaline size have led to a decrease in this use to 50,000 t/yr (29). Substitution of rosin by alkaline size has been accelerated by the use of precipitated calcium carbonate filler in printing and writing papers. Waste-paper mills, finding large quantities of calcium carbonate in their furnish, are also switching to alkaline size. More than 80% of the printing and writing paper in the mid-1990s is alkaline-sized. Europe leads in this endeavor. The largest U.S. TOR uses for oligomeric resins in printing inks are 85,000 metric tons, and in adhesives, 60,000 metric tons (30). Another use of rosin is as an emulsifier in the manufacture of synthetic rubber, eg, styrene–butadiene rubber (SBR), by emulsion polymerization.

3.2. Tall Oil Fatty Acids

U.S. TOFA production in the mid-1990s is about 210,000 t/yr (see Carboxylic acids, fatty acids from tall oil). TOFA can replace fatty acid mixtures from vegetable oil sources in industrial applications, such as the manufacture of drying alkyd resins (qv) (31). At least one-third of TOFA is turned into dimer acids (qv) with a yield of about 60%, or 42,000 t/yr of dimer acids. They, in turn, by reaction with diamines, are converted to noncrystalline polyamides with low softening points and low transition temperatures. These polyamides find application in hot-melt adhesives, printing ink resins, and epoxy curing agents.

3.3. Distillation By-Products

Of the CTO distillation by-products, ie, pitch, heads, and Distilled Tall Oil (DTO), only the last, a unique mixture of rosin and fatty acids, has significant commercial value. Pitch and heads are used as fuel; the former has a fuel value of 41,800 kJ/kg. Tall oil heads have outstanding solvent properties, but also have a bad odor, which is hard to remove. They contain a relatively high fraction of palmitic acid which can be recovered by crystallization.

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