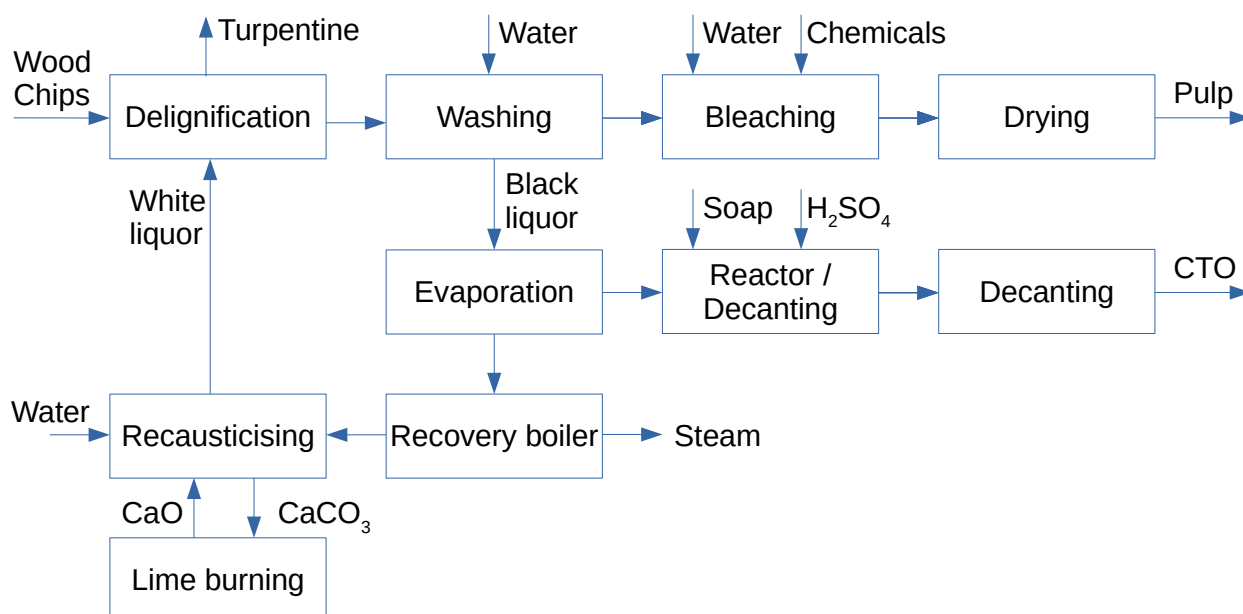


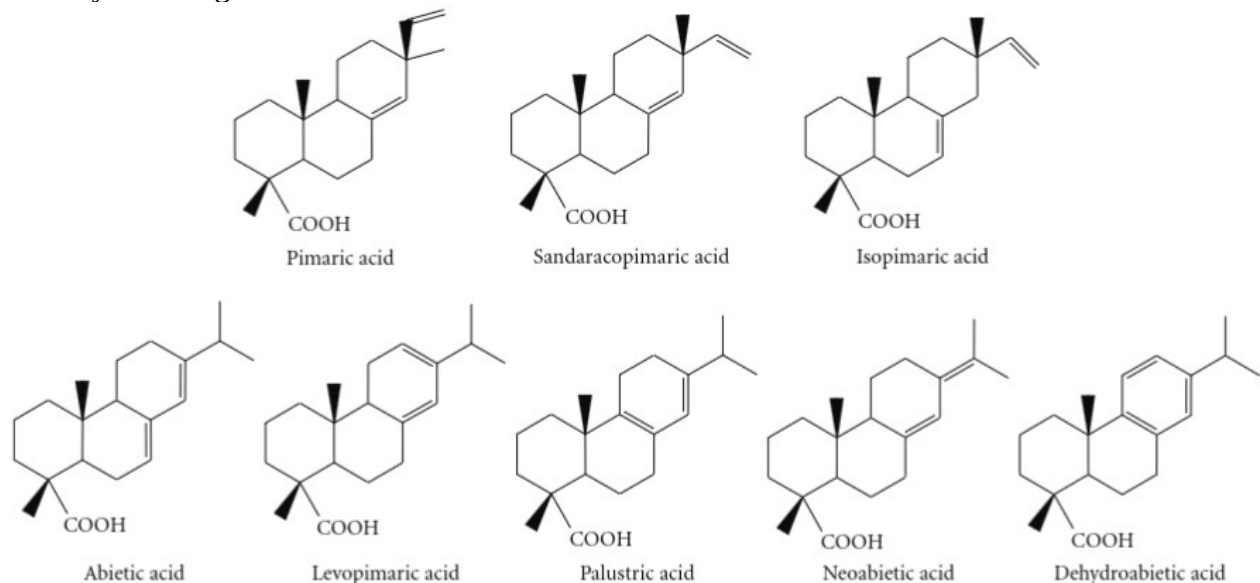
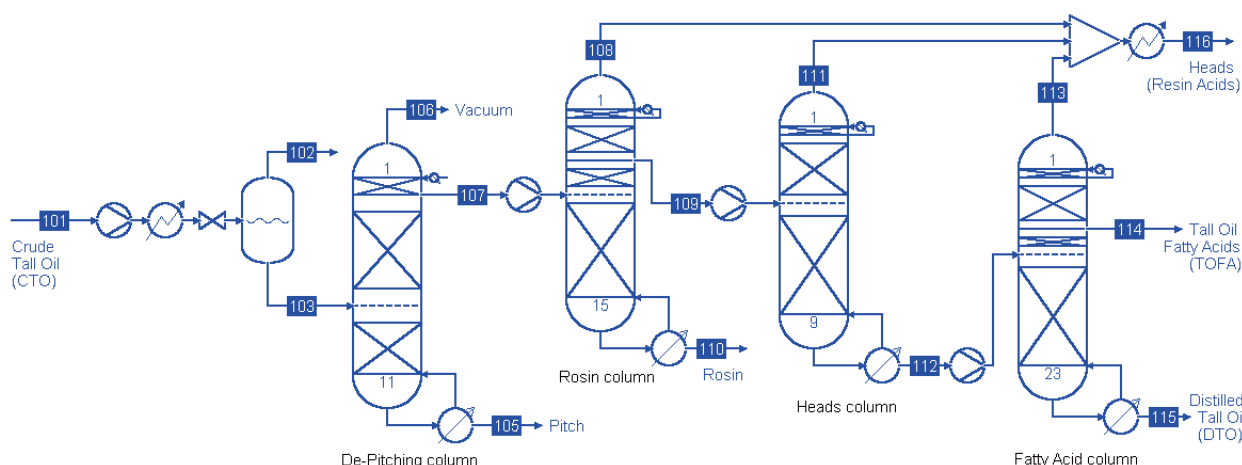
# Tall Oil Distillation

Harry Kooijman, October 2025

Crude Tall Oil (CTO) is a byproduct from the [Kraft pulping](#) or sulfate process [1,2] of coniferous trees to produce paper pulp (cellulose fibers) the main component of paper. In this process, wood chips are treated with a hot solution of caustic and sodium sulfide, called white liquor [3,4]. The caustic breaks the bonds in lignin, hemicellulose, and cellulose in the wood. The volatile part of the oleo-resinous materials is recovered by condensation, as crude sulfate Turpentine. After the pulping, the fibers are filtered for further processing. The remaining black liquor is re-concentrated via evaporation. The evaporation creates foam that contains valuable fatty and rosin acids. The foam is skimmed off and remixed with soap and sulfuric acid. After neutralization a crude tall oil can be decanted from the brine with tanks and centrifuges. The black liquor is then recausticized with lime and recycled to the pulping process as white liquor. A schematic overview is shown below.



Most pines give a soap yield between 5 to 25 kg/ton pulp but Scots pine can give yields of up to 50 kg/ton. Globally about 2 million ton/year of CTO is refined. It is first dehydrated and subsequently vacuum distilled into five products: Pitch, Heads, Resin Acids (known as Rosin), Tall Oil Fatty Acids (TOFA), and Distilled Tall Oil (DTO). Vacuum distillation is used to minimize the exposure to elevated temperatures of the Tall Oil components, many of which are heat sensitive. Originally this separation made use of steam distillation. However, the low vapor pressure of these fatty acids required a large amount of steam. In the 1980s, dry distillation system of Tall Oil were developed that took advantage of the low pressure drop characteristics of structured packing [5]. The higher efficiency of this type of packing resulted in lower column bottom temperatures, which increased the relative volatility between the fatty acids and the rosin acids, enhancing their separation.

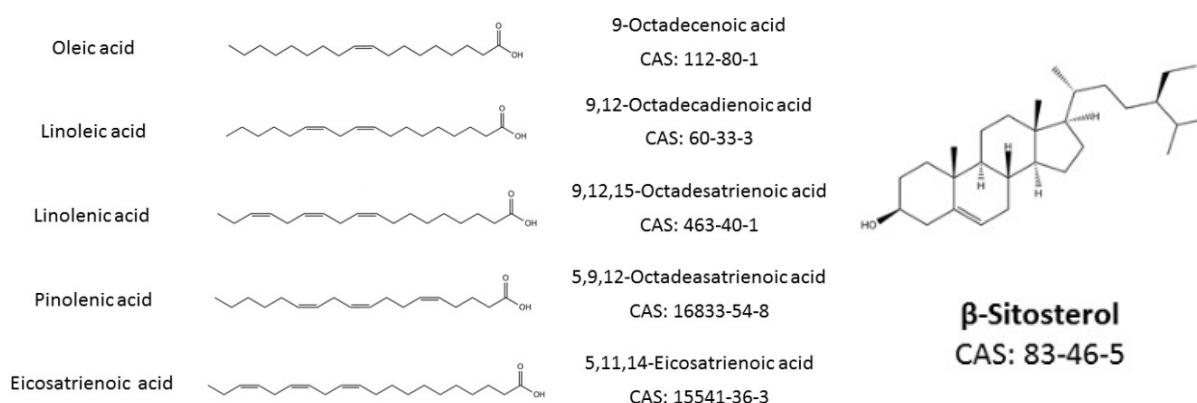


Note that the condensers are implemented as circulating reflux sections that condense the heads. This allows operation at the lowest pressure drop [9]. Here we follow the simulation [6], where the vapor overheads were combined to one common condenser. However, it may be advantageous to condense the vapor heads separately, using the respective circulating reflux sections, and to combine the heads only as liquid products. By recycling the heavier head of the fatty acid column back to Rosin column a thermally coupled distillation arrangement is obtained. The heavier compounds can enhance the condensing power of the circulating reflux sections.

Also note that the Rosin product is taken directly from the reboiler here. This has a disadvantage in that it can contain colored bodies, especially when there are upsets. Alternative line-ups [10] use liquid side draws just above the reboiler to prevent colored bodies in the Rosin. Similarly, products can be taken as vapor side-streams from the column to prevent heavy tails and colored bodies.

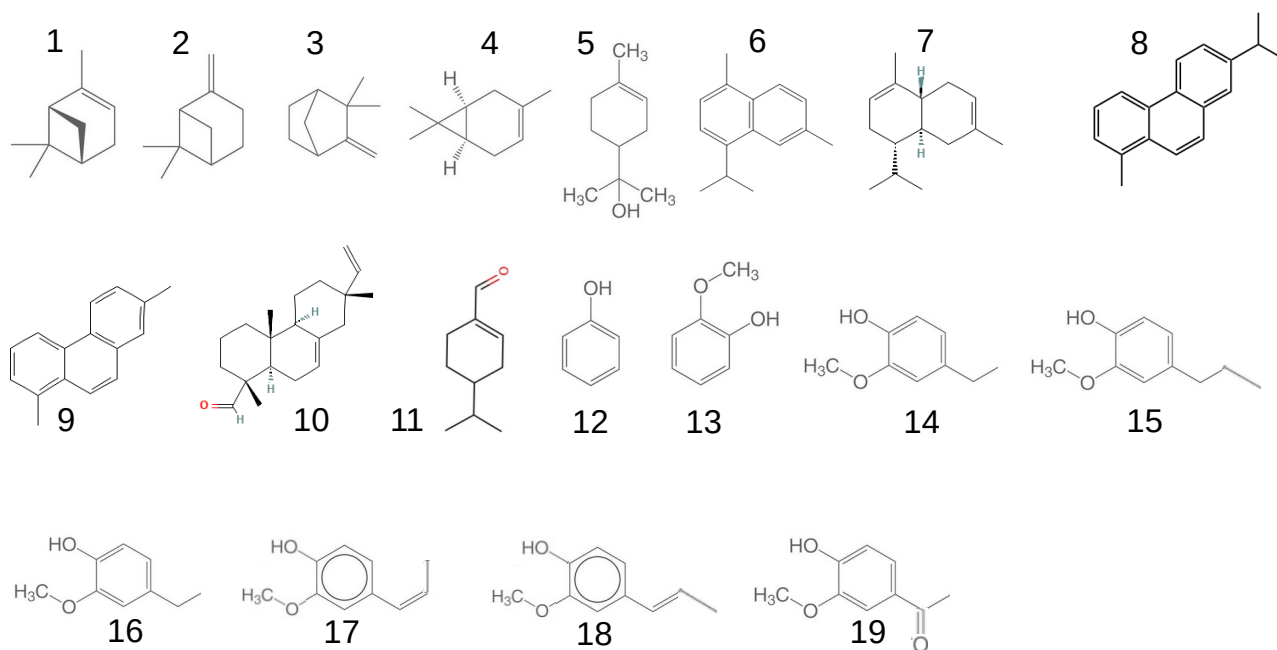
Besides purities, all tall oil products have specifications on ash/solid/metal content, flash point, specific gravity, cloud and softening point, acid and iodine number, diene value, moisture and color. It must be realized that exposing Abietic acid to heat causes it to partially isomerize into the lighter boiling Palustric and Neoabietic acid. This happens in a matter of hours. Furthermore, hot spots in the reboiler ( $T > 400^{\circ}\text{C}$ ) must be avoided as the acids can polymerize under such conditions. Care must also be taken to limit any air ingress during the vacuum distillation as oxidation of the resin acids can occur which creates colored bodies that can make the products off-spec in color.

The chemical structures of the unsaturated fatty acids and the  $\beta$ -Sitosterol are shown below.



Tall Oil Heads (TOH) is actually a mixture of fatty acids and unsaponifiable compounds. The main fatty acids are  $\text{C}_{16}$  and  $\text{C}_{18}$  (saturated Palmitic and Stearic, unsaturated Palmitoleic, Oleic, and Linoleic), as well as small amounts of lighter fatty acids: 2-3% Myristic ( $\text{C}_{14}$ ), 1% Lauric ( $\text{C}_{12}$ ), and 2-3% of lighter  $\text{C}_7$  through  $\text{C}_{11}$ .

The non-acidic compounds are terpenic, phenolic, and neutral in nature. The chemical structures are shown below. Terpenic components are mainly precursors of Retene (8) and Pimanthrene (9), but also smaller amounts of  $\alpha$ - and  $\beta$ -Pinene (1, 2), Camphene (3), 3-Carene (4),  $\alpha$ -Terpinol (5), Cadalene (6),  $\beta$ -Cadinene (7), Isopimaral (10), and Phellandral (11). The main phenolic substance is cis-Isoeuganol (17). The heads also contain smaller amounts of Phenol (12), Guaiacol (13), Ethylguaiacol (14), Hydroeuganol (15), Euganol (16), trans-Isoeuganol (18), and Acetoguaiacol (19). These are complemented with neutral components:  $\text{C}_{22}$ - $\text{C}_{26}$  linear hydrocarbons, Disulfides, and Mercaptanes.



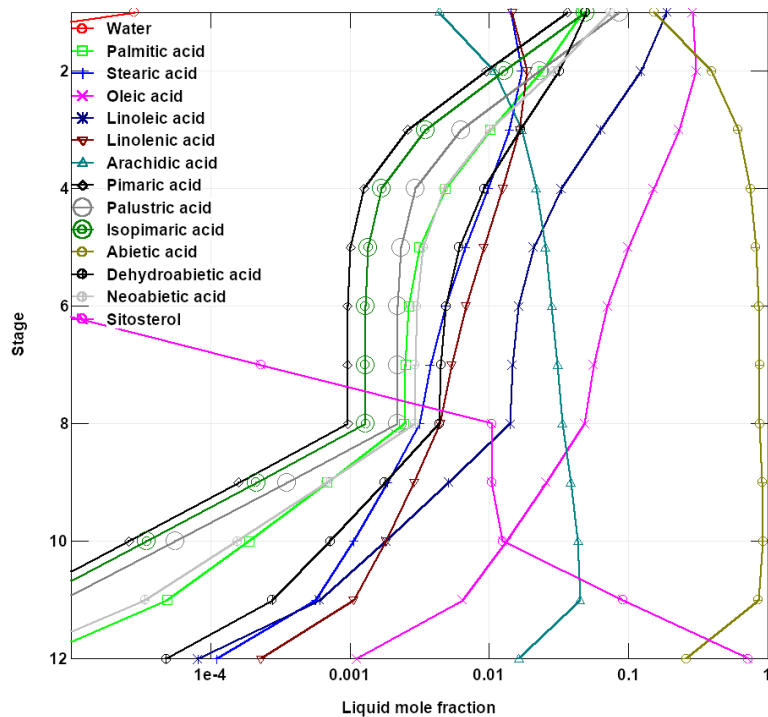
## Simulation and Specifications

Here the vacuum distillation process simulation follows the component selection and cuts as per [6]. The COCO simulator [11] was used and ChemSep LITE [12] for the thermodynamics and columns. DECHEMA K-model is used which assumes ideal gas for the vapor phase. The UNIFAC group contribution method is used for the liquid activity coefficients. The Antoine temperature correlations are used for the vapor pressures (see the appendix). Full heat balances are included, the enthalpies are computed from the ideal gas heat capacities, heat of vaporization, and the Excess enthalpies from the UNIFAC model.

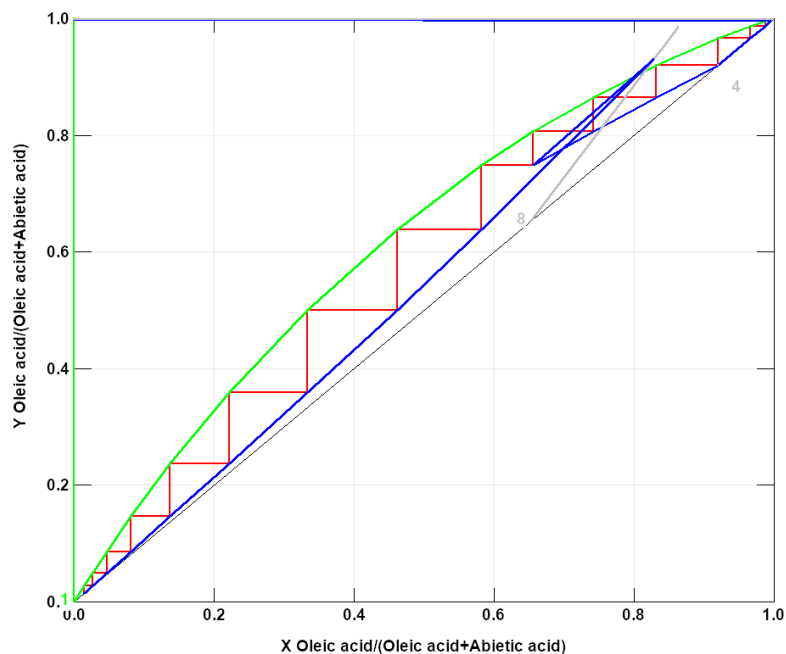
The Crude Tall Oil is first heated to **84.4°C** and flashed at **20 mbar** abs. This evaporating most (97% wt) of the water. The liquid is fed to the de-pitching column where it is further dehydrated.

The operation of the de-pitching column is determined by the degradation temperature of the Tall Oil. The column has **12** stages with the feed on stage **8** and uses a falling film reboiler to minimize the exposure time to the high temperature surfaces. The reboiler temperature is specified as **263°C** with a bottom operating pressure of **10 mbar** abs. The column top operates at **4 mbar** and is equipped with a condensing circulating reflux (CR) section: a pump-around that circulates **55 t/h** of liquid over stage **1** which is cooled with a duty of **13.7 MW**. This results in a top vapor temperature of 163°C and less than 1% loss in Palmitic acid via the overhead water vapor. The top product liquid side-draw rate is set to **19 t/h**, roughly 85% of the feed. The resulting side-draw product temperature is 189°C. The bottoms flow rate is determined by the column mass balance. Since the heavies (represented by  $\beta$ -Sitosterol) only make up 11% on mass, this implies there is an inherent loss in Abietic acid (Rosin) of 18% via the Pitch.

The profiles of the various acids in de-pitching column is below shows that because of the limit in reboiler temperature, the Abietic acid becomes a non-key component, in that it distributes over both the top and bottom products. Arachidic acid distributes also, but to a lesser extent. The losses in  $C_{18}$  acids however are minimized, with Oleic acid having a low 0.1% concentration in the bottoms.

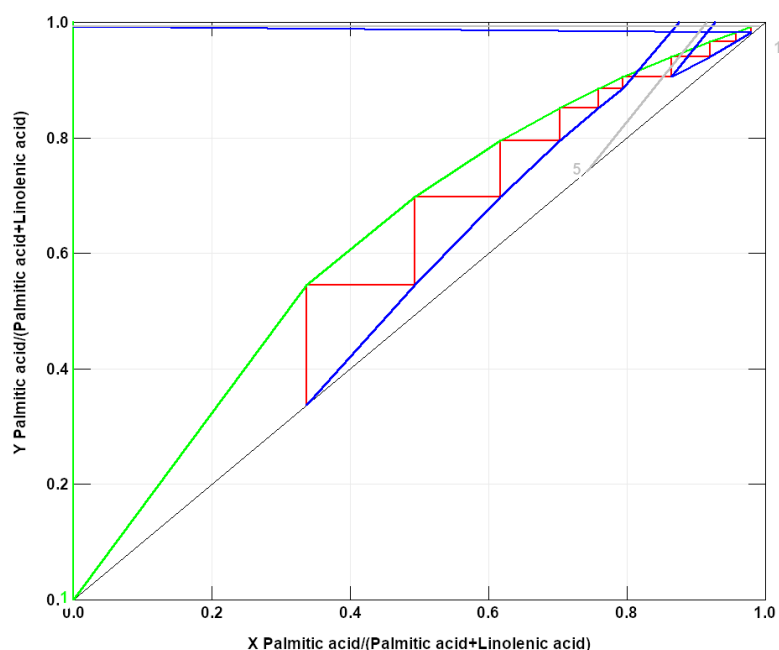


The Rosin column requires a high boil-up ratio to obtain a high-purity Rosin. The column has **16** stages with the feed on stage **8**. The Abietic acid purity is specified at **99.2%** resulting in a boil-up ratio of 13.2. The actual column control can be done e.g. on the reboiler temperature that is 248°C. The top of the column operates at **4 mbar** using a condensing CR section on stage **1** circulating **21 t/h** of liquid which is cooled with a duty of **2.8 MW**. The resulting vapor top temperature is 178°C. The bottom operates at **12 mbar**. The liquid side product flow is taken from stage **4** and is set to **13.9 t/h**, which brings the bottoms flow rate on mass balance to 2.6 t/h. This results in a Rosin recovery in the column just shy of 80%, approximately 73% of the total Rosin present in the CTO feed. A good separation is obtained between the Abietic acid in the bottoms and the lighter Linoleic acid:

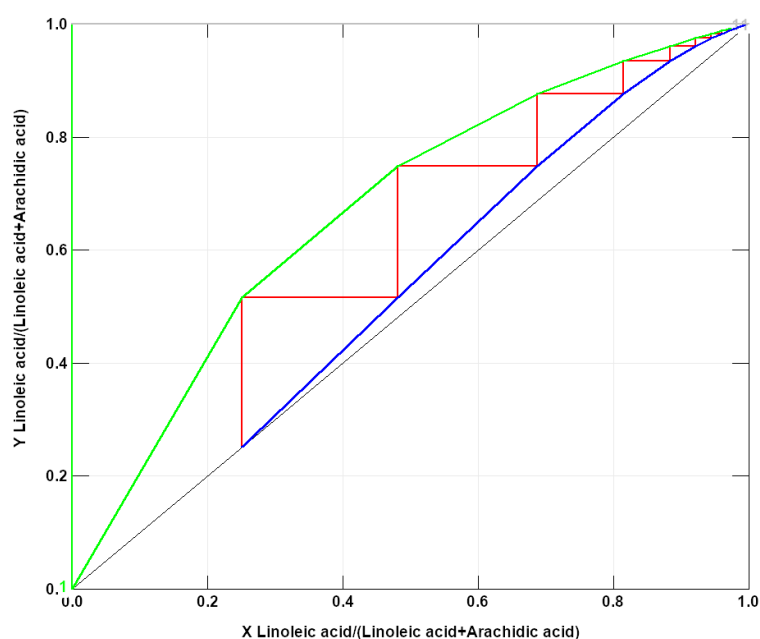


The Heads column has **10** stages with the feed at stage **5**. The top operates at **6 mbar** using a condensing CR section circulating **31 t/h** over stage **1** with a specified cooling duty of **1.53 MW**, resulting into a mere 3% loss of Palmitic acid via the vapor overhead that has a temperature of 195°C. The bottoms flow is feed-forward controlled to **60%** of the feed. This results in a 58% loss

of fatty acids to the vapor heads. Note that the actual acids losses are lower, as the heads contain a good 30-50% unsaponifiable compounds that were lumped as fatty acids. The reboiler operates at **11 mbar** and has a boil-up ratio of 2.89. A good separation is obtained between the Palmitic acid in the heads and the C<sub>18</sub> fatty acids (among which Stearic acid) that transfer via the bottom.



The Fatty Acids column has **24** stages with the feed on stage **11**. The top of the column operates at **6 mbar** and 195°C and has a condensing CR section circulating **10.2 t/h** of liquid over stage **1** which is cooled with a duty of **0.8 MW**, resulting in a 4% loss of the Stearic acid in the overheads. The TOFA draw is taken as liquid from stage **8** at a temperature of 218°C and set to **6.73 t/h** or 80% of the feed. It recovers 73% of the Stearic acid and 85% Oleic, 90% Linoleic, and 65% Linolenic acids in the feed, respectively. The bottom operates at **18 mbar** and 235°C. The bottoms flow is feed-forward controlled to **15%** of the feed. The resulting boil-up ratio of 7.35 provides a good separation between the unsaturated C<sub>18</sub> Linolenic in the TOFA side product and the saturated C<sub>20</sub> Arachidic acid in the DTO:



## Usage of Tall Oil Products

The Tall Oil Pitch (TOP) is used as a binder in cement and for ceramics (e.g. for carbon electrodes), rubber modifier, adhesive, emulsifier for asphalt, and in mineral flotation & processing. However, the majority of TOP is used as Nr. 6 Fuel for the CTO distillation process itself.

The unsaponifiable components in TOH dictate its odor and color. Derivatives of the heads (as well as that of the other distilled Tall Oil compounds) find application as lubricants, corrosion inhibitors, ore flotation (frothing) reagents, surfactants, and emulsifiers.

Rosin finds a major use as a sizing agent in paper making. Rosin soap and Alum are precipitated on paper fibers to coat them with Aluminum resinate, forming a uniform hydrophobic layer that retards water take-up, preventing ink from blotting. To inhibit the Rosin from crystallizing before reacting it is either isomerized by a heat treatment or stabilized. Stabilization can involve dimerization, or a treatment with formaldehyde, or a “fortification” through Diels-Alder addition of Maleic anhydride or Fumaric acid. Both isomerization and stabilization remove the conjugated bond that causes yellowing from oxidation.

Rosin salts are used in soaps and detergents. When esterified (e.g. with EG, DEG, Glycerol, Pentaerythritol) it is used as plasticizers of lacquers, coatings, adhesives, and chewing gum. Alkoxylated (e.g. with EO) it finds use in surfactants and polyurethane foams. Rosin derivatives with ammonia are used as lubricant and fuel additives (that protect engine wear). When fully hydrogenated to alcohols it is used in protective coatings, adhesives, wetting agents, and plasticizing agents. Decarboxylated Rosin gives products with good electric insulation properties (which also find use in printing inks and lubricants). Diels-Alder addition of Rosin with acrylic acid or paraformaldehyde is used in the making of polyurethane and polyester films and also as paper sizing agents. Polymerization creates dimers and longer chains which get used in inks and adhesives.

The main use of Tall Oil Fatty Acids is in poly-amide (PA) synthesis. First the unsaturated bonds in the acids are dimerized via Diels-Alder using acid activated clay/zeolites. The dimers are then polymerized with diamines into poly-amide. PA has a good water resistance, and the amide groups provide good adhesion onto difficult substrates like PVC. Tall Oil fatty acids can also be used as a low-cost alternative for tallow fatty acids in the production of soaps and lubricants. TOFA esters with higher alcohols are used as plasticizers and stabilizers for plastics, as synthetic lubricants, vinyl ester (co)polymers, or as waxes for cosmetics. Esters with polyols are used as protective coatings. Esters with Pentaerythritol, are used as adhesives and oil-based varnishes. Complete hydrogenolysis of Fatty Acids Methyl Esters (FAME) gives fatty alcohols that are alkoxylated to make surfactants and emulsifiers. However, the  $C_{18}$  fatty alcohols are less in demand than the  $C_{12}$ - $C_{16}$  from tallow and fat are esterified more easily than TOFA. Amine oxides are used in detergents, cosmetics, and pharmaceuticals. Diamines are used as cationic surfactants and polyurethanes. Decarboxylation of TOFA leads to ketones.

DTO contains a significant amount of Rosin but is heavier; it has uses similar to those of Rosin but in applications that need a heavier, less volatile cut, such as adhesives. It is also used for making alkyd resins, which improve the hardness, drying time, and water resistance of paints and varnishes.

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- [11] COCO Simulator, free software from <https://www.cocosimulator.org/>
- [12] ChemSep LITE, free software from <http://chemsep.org/>

## Appendix

Antoine parameters  $\ln(P^*) = A - B/(T + C)$ , with vapor pressure in Pascal and temperatures in K

| Component           | CAS Nr.   | A     | B       | C       |
|---------------------|-----------|-------|---------|---------|
| Water               | 7732-18-5 | 23.4  | 3987.3  | -37.16  |
| Palmitic acid       | 57-10-3   | 22.13 | 5092.85 | -142.1  |
| Stearic acid        | 57-11-4   | 21.86 | 5035.96 | -157.77 |
| Oleic acid          | 112-80-1  | 25.7  | 7856.05 | -73.88  |
| Linoleic acid       | 60-33-3   | 23.63 | 6401.46 | -99.18  |
| Linolenic acid      | 463-40-1  | 25.57 | 7915.2  | -72.39  |
| Arachidic acid      | 506-30-9  | 21.92 | 5399.29 | -150.78 |
| Pimaric acid        | 127-27-5  | 21.97 | 5326.57 | -113.08 |
| Palustric acid      | 1945-53-5 | 22.36 | 5376.33 | -119.49 |
| Isopimaric acid     | 1945-53-5 | 21.95 | 5296.72 | -114.63 |
| Abietic acid        | 5635-26-7 | 21.15 | 4261.88 | -207.02 |
| Dehydroabietic acid | 1740-19-8 | 22.14 | 5956.67 | -98.86  |
| Neoabietic acid     | 471-77-2  | 22.19 | 5462.55 | -118.67 |
| Sitosterol          | 83-46-5   | 22.99 | 7467.53 | -127.68 |