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Method Development for Separation of Tall Oil Soap

Degree project within the Bachelor of Science in Chemical Engineering program

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Gothenburg, Sweden 2025
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Abstract

Tall oil soap, one of the components in black liquor that is a byproduct from the kraft process in the paper industry, is essential to be separated and recovered to maximize both efficiency and profitability for a paper industry company. This is achieved through natural separation of soap and mechanically separating through ex. Circular soap skimmer. BIM Kemi AB has additives that increase the separation rate of soap, making it rise faster, and making it more densely packed in the top layer. BIM has variations to these additives, but testing these variants proves difficult, since tall oil soap in black liquor separates naturally. Sending black liquor to BIM's laboratory won't work, since the soap will have fully separated by the time it arrives in BIM's laboratory. Thus, a solution to this problem needs to be found.

Creating artificial black liquor and developing a method around it to try BIM's additives was the goal. A simple artificial black liquor was created using a few salts and a custom tall oil. These salts are 10% Sodium Hydroxide (NAOH), 10% Sodium Sulphate (NASO4), 5% Potassium Hydroxide (KOH), and 75% Water. The custom ratio tall oil is created using 60% Rosin acids and 40% Fatty acids.

Tests comparing separation with and without additives resulted in no differences over longer periods of time. UV-Vis measurements over a large spectrum (340-1000 nanometres) showed no differences. A method called "speed test method", measuring separation time within the first minutes of mixing tall oil and the alkaline solution of salts was created. After optimizing the speed test method, some variations between each test were still present. These variations are most likely caused by chaotic flow of soap particles, variations in mixing and the artificial black liquor being too rudimentary, making soap particles separate too fast, thus not allowing the additives to impact the separation process.

Future studies should add more chemicals, especially organic to the artificial black liquor to both improve the realism of the artificial black liquor, but also slow down the separation process, so that additives can shop visible improvements to the separation of tall oil soap.

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1. Introduction

The wood industry is a large global industry that is essential in our current society. Not only does it create products humans use every day, but it is also renewable. In the wood industry, trees are cut down and processed into wood pulp. The wood pulp is then cooked in an alkaline solution, to be able to extract cellulose fibre. A byproduct of the extraction is black liquor. The black liquor consists of organic compounds such as lignin and sodium soap, and inorganic compounds, which mostly consists of diverse types of salts and silicates.
The chemicals used to cook the wood pulp can be recovered and reused. But issues arise in the evaporators and concentrators used to separate the Alkaline compounds from the black liquor. There is large scale buildup within the machineries, and the most encountered scales were of calcium and sodium. These scales are a result of the natural soap that is created, when oil in the wood mix with the alkaline solution during the cooking process. The soap creates the scale in the evaporators/concentrators if left in the black liquor. As a result, it lowers the overall efficiency of the machinery. This was an issue in the early days of the paper industry, and to combat this, several types of soap separators are now used before the recovery of the alkaline chemicals. A simple separation method is using a circular soap skimmer. Soap naturally separates by having a lower density. Therefore, letting the black liquor rest in a large tank lets the soap float up to the top. Periodically, a large rotating blade scrapes the top layer of the tank off, separating the soap from the black liquor.

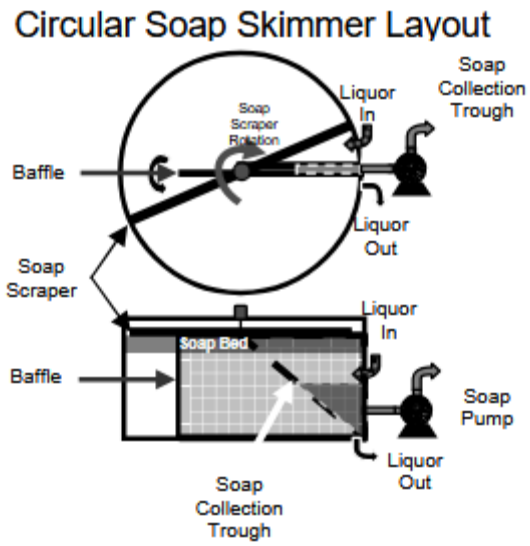

Figure 1. Example of a soap skimmer [3].

Soap is also important to recover for economical purposes. Soap is a byproduct that can be used to produce solvents within the textile and synthetic fibre production, and for detergents, textile oils, lubricants, the rubber industry, for glue and much more [1].
The soap can also be converted back into tall oil and used in biorefineries to create environmentally friendly fuel [9]. Because of the current societal pushes towards fewer emissions, converting soap into oil and selling it towards biofuel is currently the most profitable use case for the soap.
Therefore, increasing the recovery rate of black liquor soap both increases the yield from the wood industry and the total profits from either selling the soap or from creating other products from it.
BIM Kemi AB has products, as a form of additive, which increase the recovery rate of the soap from the black liquor, by increasing the separation rate of the soap. By implementing low amounts of these products into the black liquor before skimming, the total recovery rate of the soap can be increased. These products are already being used at multiple wood industry companies with varying levels of efficiency. On site lab tests with real black liquor using BIMs products have shown visibly increased efficiency of separation.
The problem is that testing new or existing additives on natural black liquor at BIMs own laboratories does not work. By the time a sample of natural black liquor arrives in the laboratories, the soap has already naturally separated. This poses the question of how products can be tested at BIM without transporting samples of black liquor.

2. Goals and directions

The goal of this project was to develop a method to evaluate BIM's soap separation products in their own labs. To achieve this, three subgoals were set to streamline the project. The first goal was to produce an artificial black liquor, to serve as the substitute to natural black liquor. The second goal was to figure out a method that shows the efficiency of BIM's additives when used on artificial black liquor, and lastly to try the newly developed method to try various products of similar functionality.
There are two general directions of evaluation for the recovery rate of soap, and these are either a visual or analytical approach. The visual approach is the simpler of the two, where tests are usually done by filling two measuring flasks with black liquor, where one of the flasks contain a product. Then, a visual comparison of the soap separation between the two flask is conducted. The analytical approach is more complicated but gives more exact results. These experiments use equipment such as GC-MS and is time consuming. Additionally, not

all labs have access to these kinds of equipment, which could be the case for some wood industry companies.

As such, the direction of the method was set to create a simple visual method that almost any laboratory can execute with the goal of making it more accessible. Having a simple method allows more opportunities to try out newly developed additives quicker or allow BIMs customers to verify the efficiency of the company's products at their own leisure.

3. Liquor

3.2 Artificial liquor

Black liquor consists of hemicellulose, lignin residues and the chemicals from the alkaline solution used in the cooking process of wood, named the *Kraft process*. Black liquor also consists of approximately 15% solids, of which two thirds are inorganic, and the remainder are organic chemicals. The organic fraction of the black liquor usually consists of around 42% soap, 40% lignin with the rest being other organic materials [9].

3.2 Tall oil composition

Tall oil is made from softwood, that is a collective name for tree types such as tall and pine. Natural tall oil consists of rosin (45%), fatty acids (42%) and unsaponifiable compounds (13%) [5].

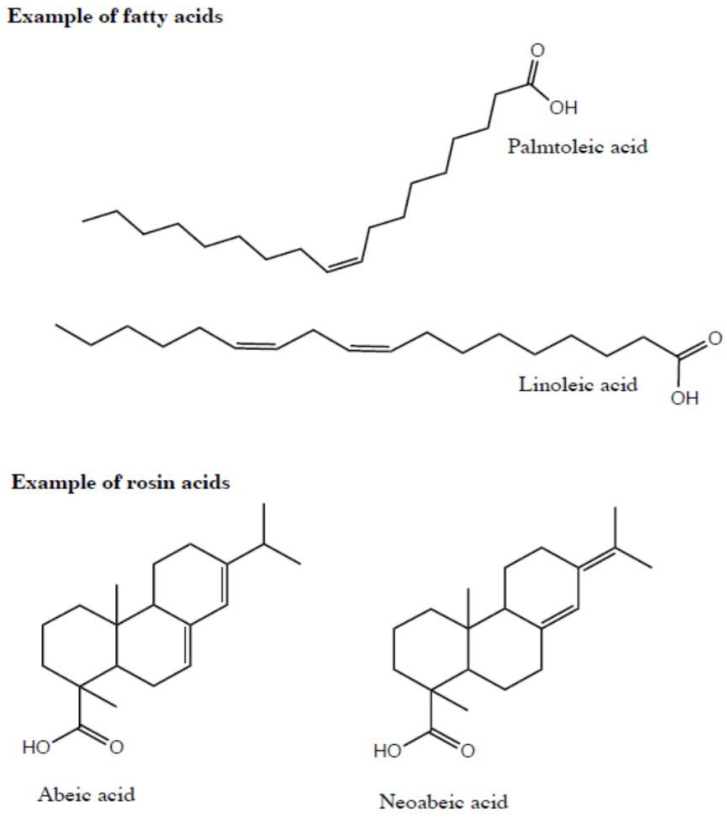

Figure 2. Examples of fatty and rosin acids [5].

The ratio between rosin and fatty acids can vary between season and tree type [3]. One of the parameters that impact the solubility of tall oil is specifically the ratio between rosin and fatty acids. Higher concentrations of fatty acids results in lower solubility since fatty acids are naturally hydrophobic [5]. On the other hand, higher concentrations of rosin acids increase the solubility of the tall oil.

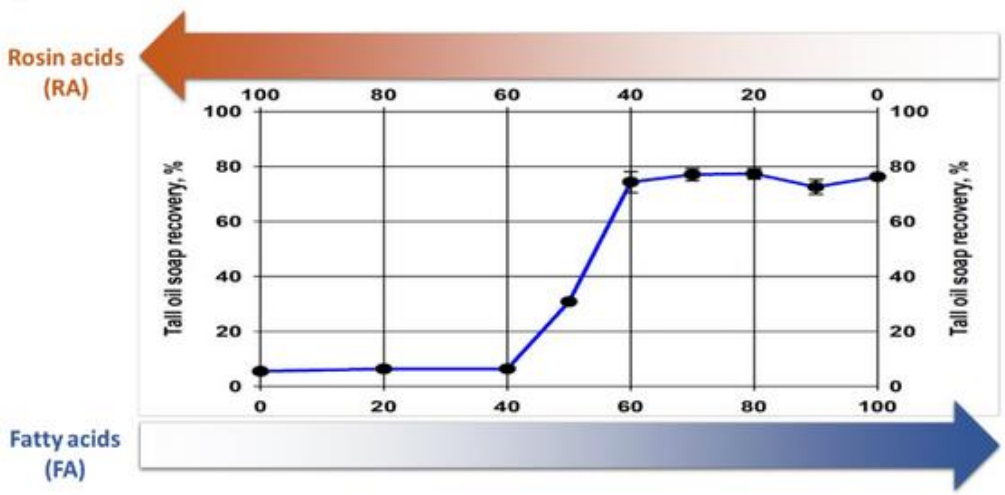

Figure 3. Plot depicting % recovery at varying ratios [5].

3.2.1 Saponification

Soap is created when fatty acids from the tall oil is mixed with an alkaline solution [5]. This process is called saponification and is a well know reaction for creating soap. The process where fatty acid esters going through hydrolysis in an alkaline solution, using hydrogen peroxide, is called Saponification.

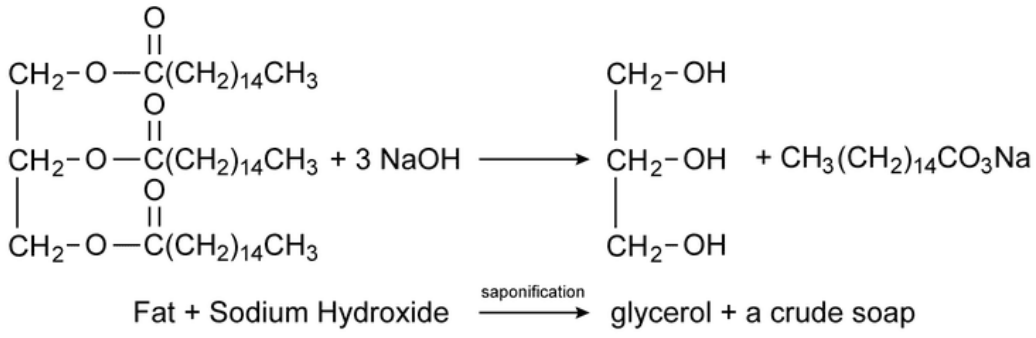

Figure 4. Example of standard fatty acid undergoing saponification.

Rosin acids also react with alkaline solutions. In fact, rosin acids undergo the exact same reaction as the fatty acids, and form rosinates, also known as rosin soaps [8].

3.3 Temperature

The temperature of the liquor impacts the solubility of tall oil. Temperature at 80°C and higher increases the solubility of tall oil [5][6][7].

To keep the method as realistic as possible, all tests were performed with a liquor temperature of 80°C or higher. Since the liquor consist of water, the temperature was kept under 100°C to prevent boiling.

3.4 Products

The product used in this project is a form of emulsion of surfactants and hydrophobic substances, which is theorized to aggregate and flocculate the soap particles, thus lowering its solubility in the black liquor. How it works in detail is not yet fully understood, but from laboratory tests on site at wood industries, and doing industrial scale tests with it, shows that it is working. The method development assumed that the product would always work. In figure 5, test using BIM's additive on natural black liquor was conducted, where separation took place for one hour. The left tube has no additives while the right has additives. Soap has separated more in the right test tube, and the soap layer is also denser. This is the optimal result for the wood industry, because when the soap layer is skimmed off, there less black liquor skimmed with the soap, increasing the efficiency of the recovery of soap.

Figure 5. Tall oil soap separation in natural black liquor. Right test tube is treated with BIM's additives.

4. Method

4.1 Liquor

A simple "liquor" composed of Sodium hydroxide (NaOH), sodium sulphate (NaSO4) and potassium hydroxide (KOH) was created for the method. These three chemicals were chosen for their availability, and similar function to the rest of their respective group of salts.

The salt ratio of the synthetic liquor was chosen to mimic that of natural black liquor. Weight percentage of every chemical substance are 10% (NAOH), 10% (NASO4), 5% (KOH), and the rest water.

In this project, organic compounds such as lignin were not included in the synthetic liquor. However, these are chemicals that should be included in future research. The reason as to why lignin and other organic compounds were not included in the liquor was because of time limitations.

4.2 Tall oil

When introducing tall oil containing 80 % fatty acids to the liquor, it results in almost no tall oil dissolving in the artificial liquor, only creating solid soap that instantly float up and shapes a layer on top of the liquor. It was deemed that if almost no tall oil can dissolve in the artificial liquor, then it will be hard to spot any differences when applying a product to help the separation process, since a large majority of the tall oil soap is instantly separated when mixed with the artificial liquor.

Therefore, tall oil consisting of less than 40 % is needed to maximize the solubility of tall oil. The theory was that if there is more tall oil present in the solution, the resolution on the difference between separation, with and without products, should increase. A ratio of around 60:40 rosin and fatty acid is created, using natural tall oil from the paper industry that has a ratio of 20:80 rosin. By adding extra rosin acids that was synthesized from natural tall oil (Sylvaros (TM) 85), the ratio is changed to a 60:40 harts to acid ratio.

Pure rosin acid has a high melting point (200°C+), and fatty acids starts boiling around the same temperature [10]. Sylvaros 85 crystallizes in ambient temperature and had to be chipped out using a screwdriver or any similar sharp objects.

Tall oil with a ratio of 80 % fatty acid was available in large quantities at the laboratory, and this tall oil was therefore used as the source for fatty acid, since it was simpler to add more rosin acids to the high percentage fatty acid tall oil, lowering the fatty acid ratio down to 40%, than to order pure fatty acid.

To create tall oil with a ratio of 60:40, the rosin acid flakes are melted together with existing 80% fatty acid tall oil on a magnetic stirrer at 150°C. It is essential that during the creation of the 60:40 tall oil that it is melted at 150°C until fully homogenized. During earlier testing, mixing was done at lower temperature, and as a result, the oil was not fully homogenized, and test results ended up varying. Time required to melt all the rosin chips depends on the size of each rosin chip.

After the oil is fully homogenized. The temperature can be lowered to below 120°C s. This is done because the pipettes used are classified to be able to handle a max temperature of 121°C Temperature should also not drop below 80°C since the viscosity of the oil increases at lower temperatures. Pipetting this oil at low temperatures becomes near impossible, because the oil gets stuck in the pipettes. Tall oil with a ratio of 40% fatty acid has a high viscosity at lower temperatures, making it very sticky below 90 degrees. The oil temperature was decreased to 110°C, to allow room for fluctuation in the temperature to not occasionally cross the 120°C barrier.

4.3 Temperature

Temperature in a real-world soap separator is around 80°C [3]. Therefore, the artificial liquor is heated to 80°C to be more realistic to a real separator environment.

4.4 Speed test

A method to evaluate the separation rate within the first few minutes of tall oil soap creation was extensively evaluated. Since temperature plays a significant role in the solubility of tall oil, this method follows a precise second by second order of operation. This method showed the most promising results and minimised variations between test results.

Equipment:

- Water bath
- Test tubes (15ml)
- Test tube rack
- magnetic heat stirrers, magnets
- Fume hood
- pipettes (1-100 µl, 10-1000 µl, 1-10 ml)
- Beakers (10-1000 ml)
- Timer
- Vortex tube mixer
- Heat resistant gloves (recommended but not mandatory)

Chemicals:

- NaOH (10% solution, from BIM's factory)
- KOH
- NaSO4
- Rosin acids, fatty acids
- Products (5% concentration)

Procedure preparation:

1. Heat the water bath to 80°C
2. Prepare Tall oil by adding sixty parts rosin acids (crystals or liquid) and forty parts fatty acids (liquid) in an appropriately sized beaker. Recommended to make at least 100 ml total oil. Mix and heat on magnetic heat stirrer at 150 degrees in a fume hood, until fully mixed/homogenized.
3. Prepare liquor by mixing with a magnetic stirrer, a solution of 10% NaOH, 10% NaSO4 and 5% KOH. Recommended at least 500ml total liquor.

4. Prepare test tubes by marking half the tubes as reference and the other half as product. Put 10ml of liquor in each test tube, and place in water bath for heating.
5. When oil is fully mixed, lower the temperature to 110 degrees Celsius.
6. Prepare a beaker with water, no more than 100 ml is necessary.

Before starting the test, make sure to have easy access to new pipette tips and a close by disposal/trashcan for pipette tips, since the tall oil viscosity drastically increases when cooled in a pipette tip, rendering it unusable after a single use. Make sure any product tube is open and ready to be sampled from. Finally, make sure to read the procedure below to minimize errors during the procedure, since time is of the essence in this method. While pipetting oil, it tends to stain the filters of pipettes, therefore it is recommended that when pulling back air into the pipette, to slowly do so to prevent drops of oil flying back into the pipette filter.

Procedure:

1. Take a test tube out of the water bath and start a timer. The time needed from taking the tube out of the water, until mixing begins needs to be the same for every test tube.
2. Open test tube lid, pipette either 60 µl water or 60 µl product, depending on if it is a reference or product test tube. Close lid and gently turn test tube up and down twice.
3. Open test tube, and gently pipette 0,5 ml oil at an angle, so that the oil only sits on top of the liquor. Place tube gently into a test tube rack.
4. Place tube gently into a test tube rack, stop the timer and take note how long it took to perform steps 1-3. Add around 10-20 seconds to the timer and set this final time as the standard time for preparation before mixing.
5. When the standard time has passed, gently turn tube upside down once, then place into vortex mixer for 20 seconds. Every four seconds, pause the mixing for one second, pausing a total of four times during mixing.
6. Quickly place test tube into a test tube rack and start a timer when the yellow/white soap layer reaches the first line from the bottom of the tube (0,1 ml). Note the time needed to reach every 1 ml increase, up to the 5 ml line. If the first line is too fast or too unclear/blurry, the starting point can be set higher on the test tube.
7. Repeat procedure steps 1-6 for the rest of the test tubes. Step 4 can be skipped after the first test tube.

Quantity of tests run only depends on the resolution of results wanted. It is recommended to have a minimum of 20 total test tubes of artificial liquor; half of which additive will be added. 20 test tubes are recommended so the resolution of the results is high enough to show patterns and tendencies.

4.5 Centrifuge

Separation using a centrifuge with 60-70 ml flasks were tested. Centrifuge tests were prepared by simply using one of the test tubes from one of the speed methods tests, carefully extract the yellow liquid without extracting any soap residue and running the centrifuge at a temperature of 80°C at 1000-3000 rpm, for a few minutes. Varying rpm of the centrifuge is tested to determine if different rpm impact the separation. Flasks are examined after centrifugation, to see if there is visibly any more separation of soap in flasks with product compared to flasks without product.

5. Results

5.1 Long period tests

Multiple tests with different volumes and concentrations were tested. Mixing liquor with tall oil and leaving it overnight yielded no visual difference between tests containing additives and those without. This experiment was performed multiple times at both 80°C and at ambient temperature, and variations were minimal and seemingly random between tests.

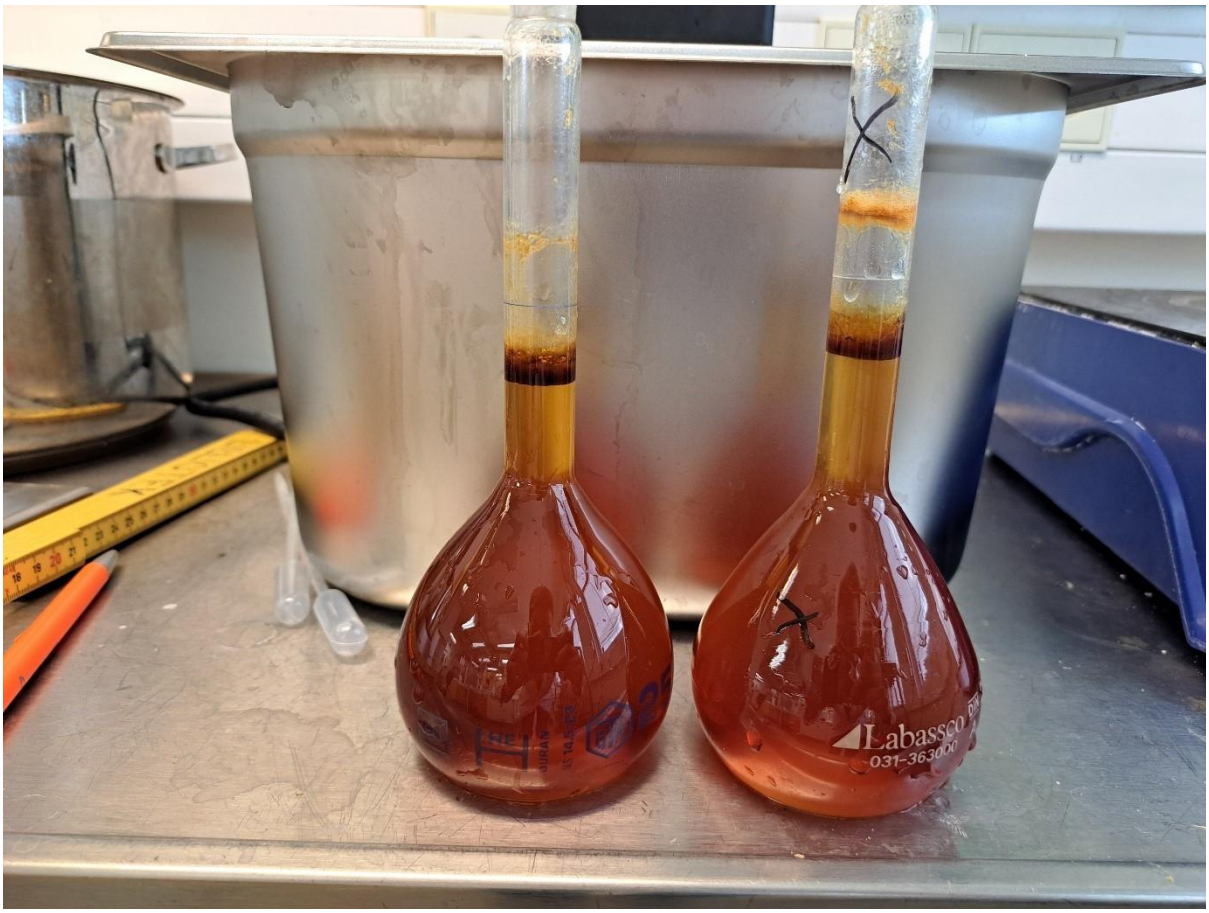

Figure 6. Early tests of soap separation, over a full day at 80°C. No difference in soap separation is visible.

5.2 UV-VIS

Multiple tests were sampled using UV-VIS, where the absorption and transmission over a large spectrum (340-1000 nm) was measured. There were minimal differences between samples with and without product, and no conclusion could be made.

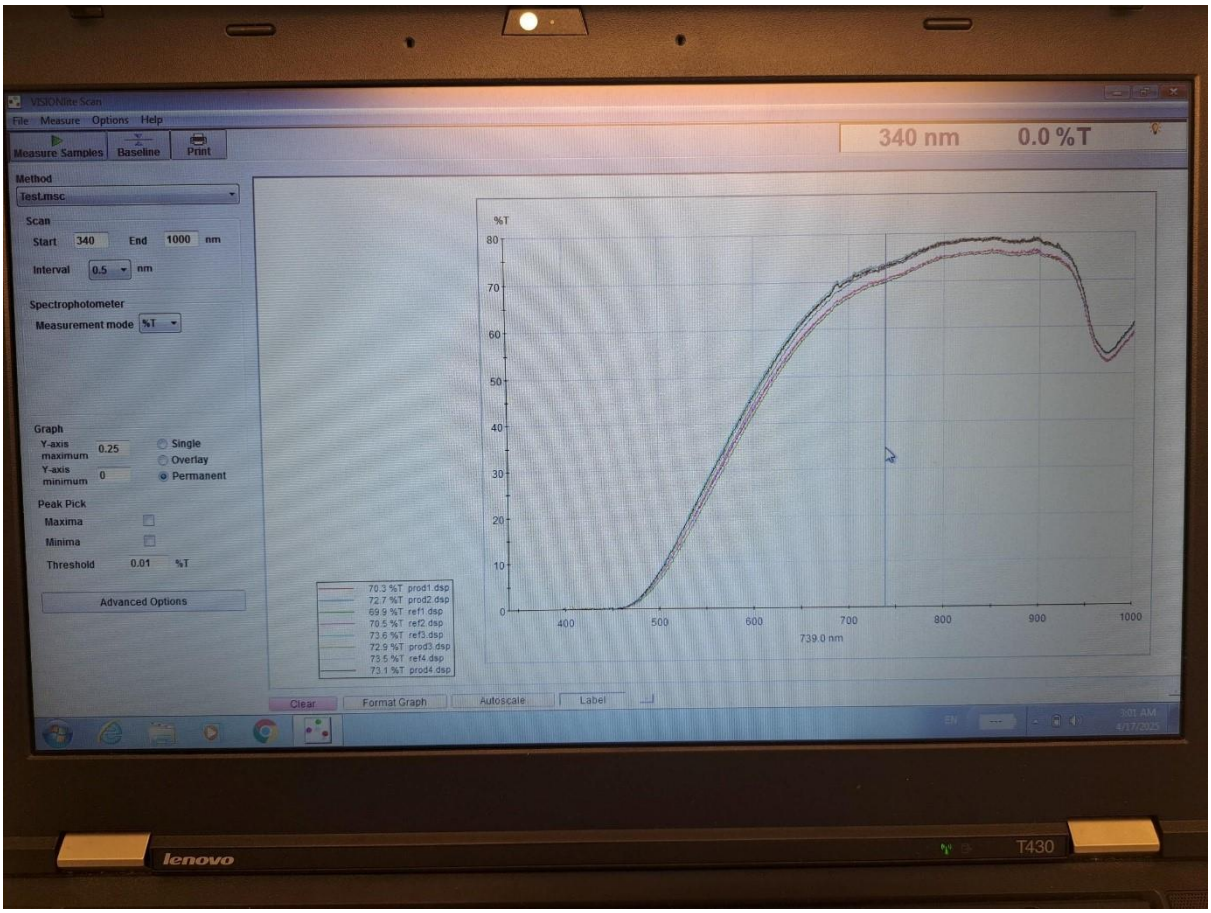

Figure 7. UV-VIS measurement of tests with and without product yielded no difference in transmittance and absorption.

5.3 Speed

Before the final version of the speed test found under section 4.4 was developed, the original version resulted in large variation in separation speed between each test tube set. Test results from the first iteration of the speed test can be found in figure 8. The original method did not take into consideration the impact of rapid cooling in room temperature, time needed to prepare test tubes before mixing, and the importance of consistent mixing. Figure 9 shows the large time decrease of separation caused by the temperature difference between test tubes with product and reference test tubes. Product test tubes had a consistently lower separation time, caused by the extra time needed to pipette additives. On the other hand, reference test tubes skipped this part, thus staying at a higher temperature before mixing.

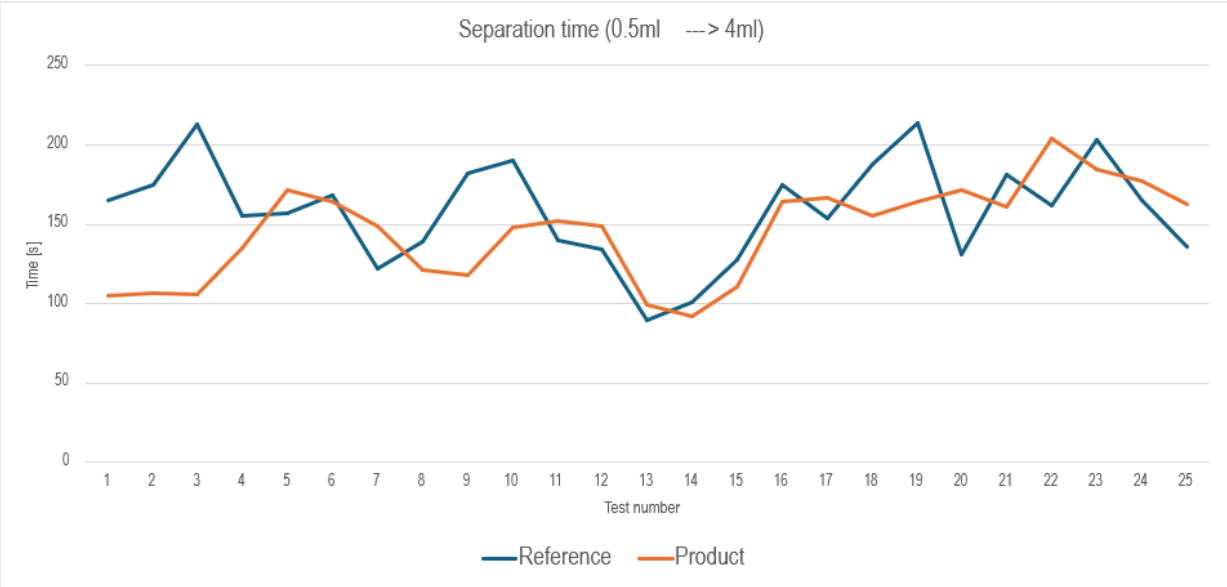

Figure 8. Results from the unoptimized speed test method.

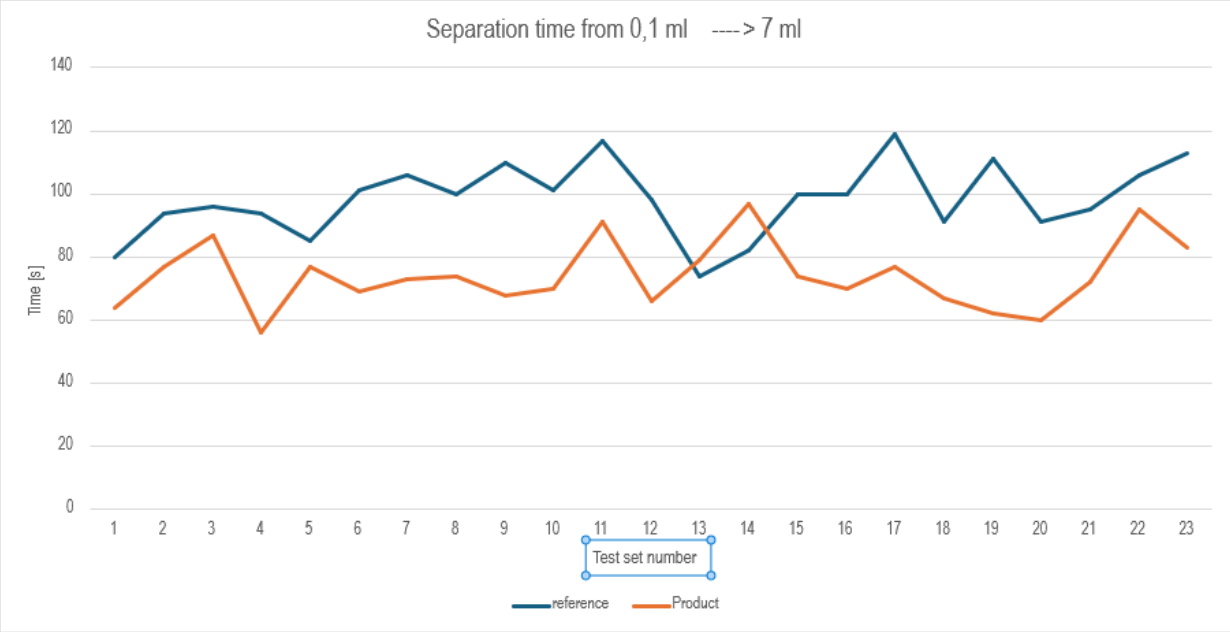

Figure 9. Test results before considering extra time needed to prepare product test tubes.

Test results of the speed method under 4.4 is shown in figure 10 and 11.

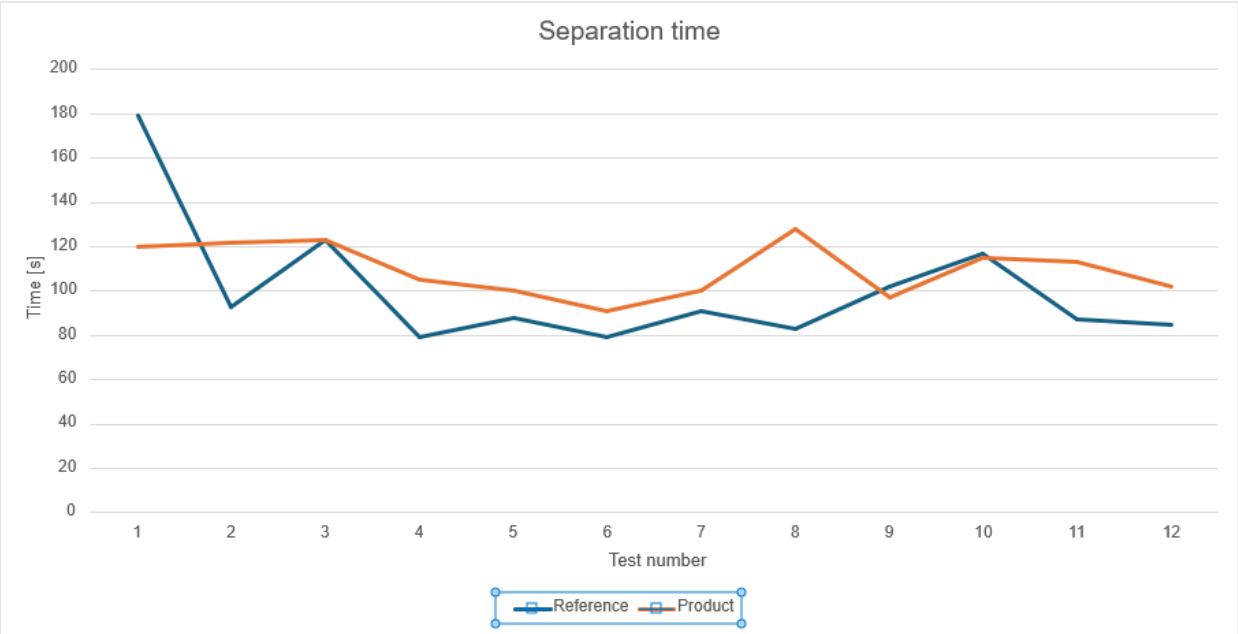

Figure 10. Results from optimized speed test method.

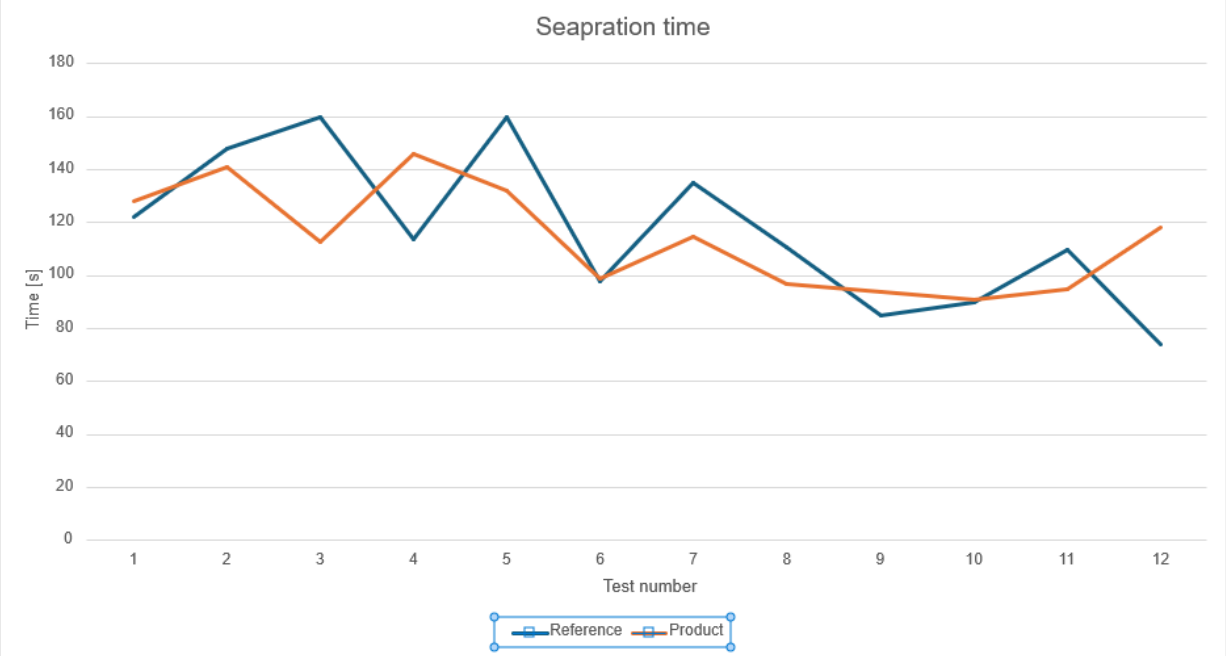

Figure 11. Results from optimized speed test method.

Results show decreased variation between each test tube set compared to figure 8, but there are still some unexplained variations.

5.4 Centrifuge

Centrifugal tests were carried out on samples from the speed test method. Variables such as time after separation, temperatures, and concentrations were extensively tested, but no noticeable variation between samples with and without product was detected.

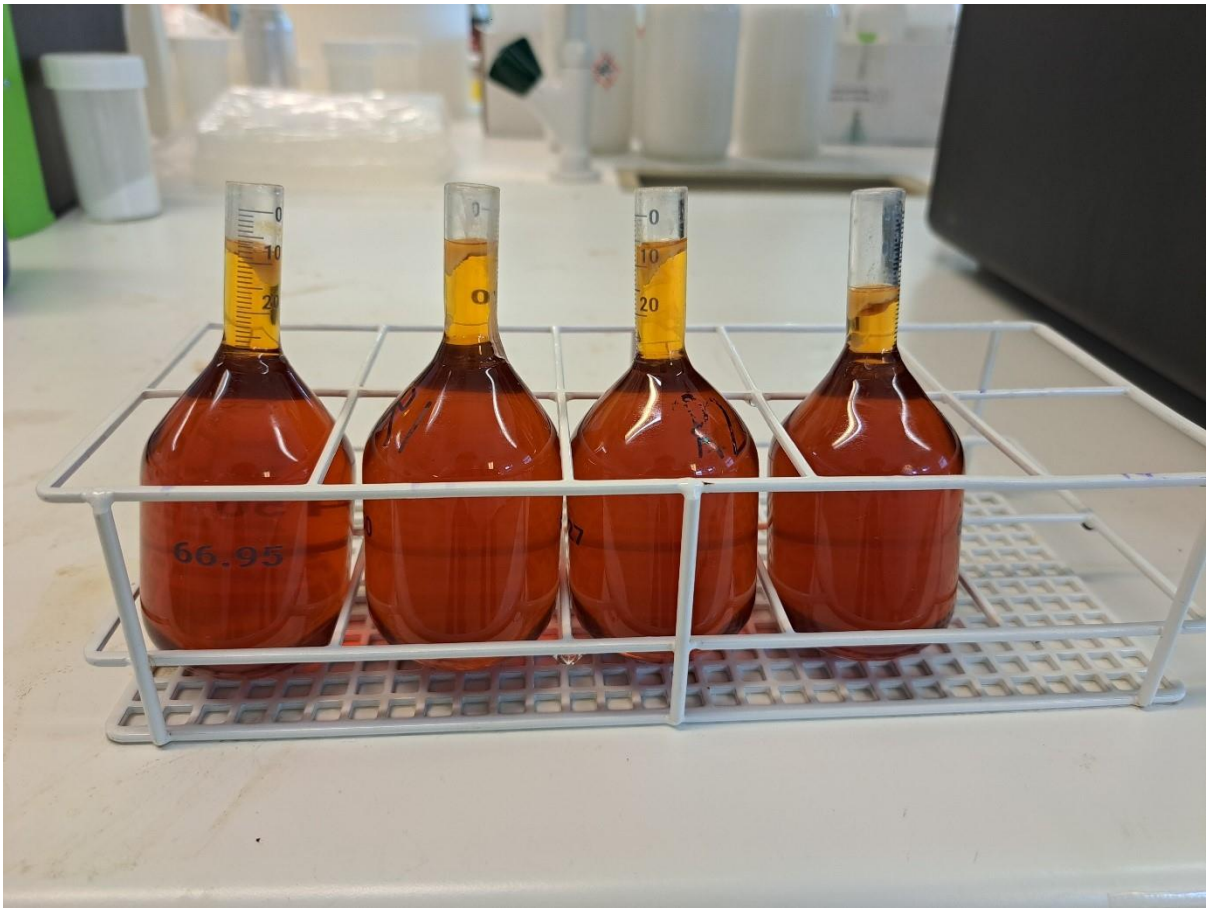

Figure 12. Centrifuge samples. Small soap layers can be seen at the top.

6. Discussion

Throughout the hundreds of tests conducted, many variables were tweaked to improve the speed test method, there are a few variables that are hard to impact.

Since the separation rate of soap in an artificial black liquor where there are a few amounts of total chemicals, the flow of the soap particles, floating upwards is chaotic. Some soap particles float upwards and downwards seemingly random in the test tubes, that potentially impact the soaps lower layers speed which it flows upwards.

Because of the artificial black liquor's contents, and the resulting separation times always being within minutes, there is a possibility that the approach of a speed test method is unviable, and the product does not have time to show any visibly improved separation rates. Tests using real black liquor usually take around an hour to show visible improvements. This test can be seen in figure 5. Real black liquor having much slower separation time can potentially be a result of having more chemicals in the solution, slowing down the float rate of soap. Having more chemicals in the solution could also impact the overall solubility of tall oil.

One thing in common within all tests performed during this project, is that the solubility of the soap is not decreased by the product. It is more likely that the product increases the speed at which the soap separates, specifically on the speed test method and the simple artificial black liquor. Another potential issue is imperfect mixing. Since the reaction speed of soap is very fast, how the tall oil mixes in exact detail with the alkaline solution might cause variations in test results as well.

7. Conclusions

Further experimentation is needed to create a method that can visually show similar results to that of using natural black liquor samples. To achieve this, more chemicals should be used in the artificial liquor, to imitate as closely as possible to real black liquor.

8. References

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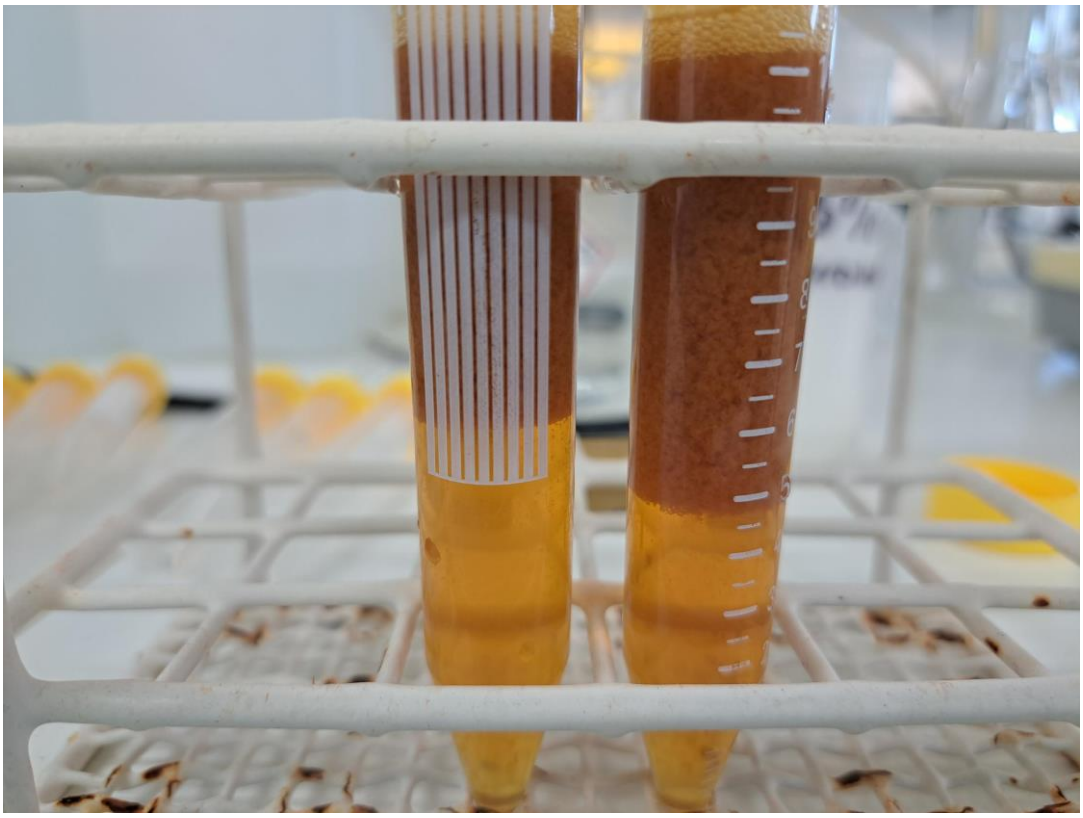
Appendix

Sylvaros 85 https://kraton.com/products/sylvaros/



Speed test method test tubes, after mixing and separation measured.

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