Sodahuskommittens Rapport 2011-2 Examensarbete Tony Tran

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Soap separation efficiency at Gruvön mill

An evaluation of the process before and after a modification

Master thesis in Chemical Engineering (30hp)

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Preface

This master thesis was carried out between September 2010 and March 2011 at Billerud Gruvön mill in Grums, Sweden and concludes the Master of Science study in chemical engineering at Karlstad University.

I would first of all thank everyone at Billerud Gruvön mill in particular to the people at the Departments of technology and Liquor and Steam. Thanks to those who helped me through this thesis work and provided me with equipment and not to forget the hospitality I received.

I am especially thankful and grateful to my supervisors Eddy Sandström and Mats Lundberg for your support, enthusiasm and engagement in this project. I would also thank Professor Ulf Germgård as my mentor and supervisor and Docent Magnus Lestelius as my examiner at Karlstad University.

Finally, the help from Associate Professor Jan van Stam for contributing valuable knowledge to this project is much appreciated.

Summary

Wood consists not only of cellulose, lignin and hemicellulose but also of so called extractives which includes fats and acids and these components are separated in the mill from the black liquor. These extractives are in the mill denoted as tall oil soap. Tall oil has a large field of applications like chemicals and fuel and as it is produced to the atmosphere if it can replace oil and thus reduce the oil consumption. Tall oil soap is separated from the black liquor in a skimmer and the focus of this thesis was to examine the effect of air injection and the soap layer thickness on the soap separation efficiency in a skimmer. The work was focused on in analyzing the soap content of the inlet and outlet black liquor flow of the skimmer and to detect if an enhancement has been achieved with the two mentioned methods. The reason for the pulp mill to improve the soap separation efficiency was to decrease the risk of foaming and fouling in the evaporator but also to be able to increase the production of tall oil.

The air injection gave a 41% improvement of the soap separation efficiency and further improvements are probably possible to achieve. The air injection flow was about 7 l air /m3 liquor in the black liquor feed. The airflow lowers the density of soap, creating a greater difference in density between soap and black liquor and this improves the separation efficiency.

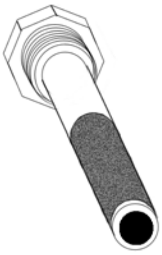

Figure i.1: A sparger used for air injection.

A thicker soap layer could increase the likelihood for soap drops to raise and reach the soap-liquor interface, because the soap drops have the tendency to bind with each other and will be separated from the liquor instead of following with the skimmed liquor outlet (fig. i.2). However, this study shows no indication of improvement with thicknesses that exceeds 0,75-3,5 m which also endanger the skimmer due to overflow from the skimmer or create a short circuit between the in- and the outlet black liquor flow.

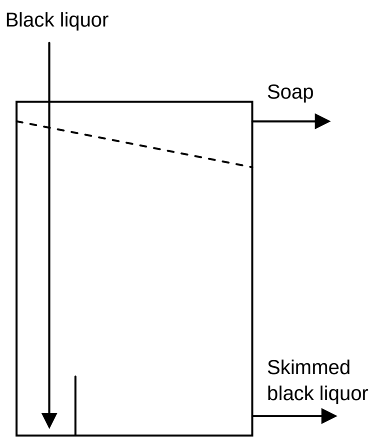

Figure i.2: A simplified drawing of the skimmer used in the study to separate tall oil soap from the black liquor.

Contents

1. Background and purpose

Wood contains extractives such as resin acids, fatty acids and neutral unsaponifiable components, but in particular softwood contains more resin acids than hardwood. During alkaline cooking, these extractives create a composition called tall oil soap in the black liquor. The tall oil soap must be separated from the black liquor in a skimmer as it otherwise will cause foaming and fouling in the evaporator plant [1]. The concentration of calcium is also 7-8 times (appendix 3) higher in soap (2 g/kg DS*) than in black liquor (60 mg/kg DS). This means that the high concentration of calcium increases the risk of creating fouling on the heating surfaces of the evaporator effects during evaporation of black liquor and an enhancement of the soap separation will therefore improve the efficiency of the evaporation plant.

Enhanced soap separation efficiency may be achieved by injection of small air bubbles in the incoming liquor to the skimmer. A certain minimum thickness of the soap layer in the skimmer may also improve the separation efficiency.

Crude tall oil is produced by acidulation of tall oil soap with sulphuric acid. The saponified components are converted into free fatty and diterpenic acids that can be separated from the water phase by gravity in a tank or in a centrifuge. The crude tall oil from the mill is delivered to a tall oil refinery where it will be distilled under vacuum to recover the products as distilled tall oil, tall-oil resin and tall-oil fatty acid.

Water repellent for paper is manufactured by tall-oil resin and is also a raw material for inks and adhesives. The main use of tall-oil fatty acid is air-drying paint binders, so called alkyds, but it is also a common raw material for producing synthetic rubber [2] [3].

Billerud Gruvön mill is located in the western part of Värmland, produces yearly about 650.000 tons of pulp and paper and 15.000 tons of tall oil.

1.1 Residue from distilled tall oil is the future of a new bio fuel

Distillation of crude tall oil creates valuable residues that can be used, for instance, as tall oil diesel for vehicles. This kind of bio fuel will replace the consumption of fossil fuel, because tall oil diesel reduces the carbon dioxide emission compared to the fossil fuel [2] [3]. Nowadays, Preem is one of the companies in Swedish market that invest in tall oil diesel, where tall oil is the primary raw material in the production [4]. This sort of second-generation renewable diesel will not compete with the food industries or cropland, which is a problem for many of today's alternative bio fuels [5].

Another byproduct from crude tall oil is pitch oil and it is used to manufacture valuable fine chemicals for the food- and pharmaceutical industries. However, at Gruvön mill this pitch oil is primarily used as fuel in the lime kiln.

The objective of this thesis study was to examine the effect of air injection and soap layer thickness on soap separation efficiency in a skimmer III at Gruvön mill.

*DS:Dry solids

2. Theory of soap skimming

2.1 Soap and its properties

In alkaline kraft pulping of softwood, the resin acids and fatty acids from the wood are converted into sodium salts. The salts and other non saponifiable compounds are dissolved in the liquor.
The reaction of extractives in contact with alkali is described below [6].

$$R-COOH + NaOH \rightarrow R-COONa + H_2O$$

The anions of these salts can be amphiphile, which means that they can be dissolved in both water and oil. This property of anions is an important component for the resin acids and fatty acids to form micelles (fig. 1). Micelles are formed depending on the concentration of soap in the black liquor, where the hydrophobic hydrogen carbon chains are collected to the interior of the micelle [2]. Micelle is an important factor for the bond between micelles and air bubbles which enhances the separation through air injection.

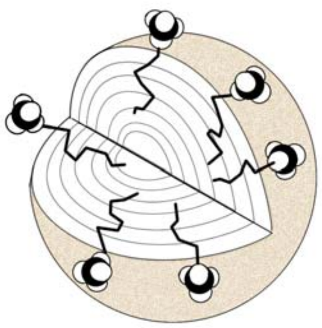

Figure 1: A spherical micelle. The picture is drawn based on [7]

When roundwood and wood chips are stored, the extractives are attacked by different processes that occur in various scopes such as hydrolysis of fats, autoxidation, metabolic oxidation and microbiological attacks [2]. Extractives in wood chips decompose faster and more extensive compared with round wood. The decomposition of extractives depends on several factors such as temperature, humidity, availability of oxygen, storage time, cf. fig. 2, of the wood and the storage time varies depending on the season [2]. The wood chips should be processed within a reasonable time after having been cut to prevent a large loss of extractives.

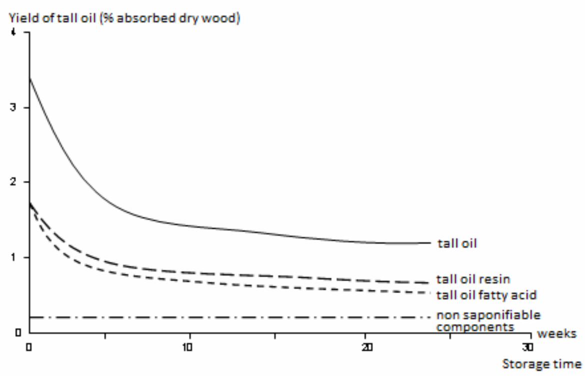

Figure 2: The effect of storage time on the yield of extractives. The plot is drawn based on [2].

Soap has a lower density compared with black liquor, which allows the soap to rise to the surface of the skimmer. It is important that the tall oil soap contains high amount of tall oil resins and tall oil fatty acids to produce good quality of crude tall oil. The soap rise rate (fig. 3) is the key element to influence the separation of soap from black liquor and can be affected by solubility of soap in the liquor, temperature, dry solids of black liquor etc. Lowering the temperature of liquor will decrease the soap solubility while increasing the rise rate, but in economical perspective it is not profitable. Increasing dry solids increases the viscosity and makes it more difficult for soap to rise to the surface, but also the density difference between liquor and soap is decreasing with increased solids concentration of liquor. [2] [8]

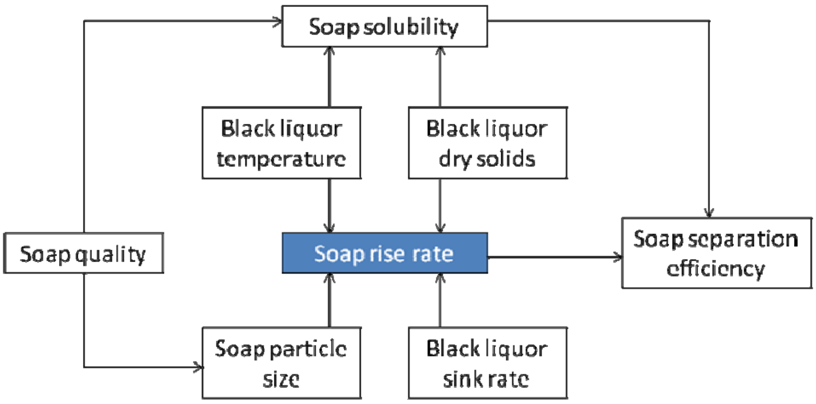

Figure 3: Different factors contributing to soap separation is presented in the picture and skimmer and process parameters are ignored. The picture is drawn based on [8].

The rate of climb for soap drops follows Stokes' law [9]:

$$U = \frac{g\Delta\rho D^2}{18\mu} \tag{1}$$

U=rate of climb (m/s), Δρ=density difference (kg/m^3), D=diameter (m), μ=viscosity (Pa*s), g =gravitational force.

Soap drops tend to bind with each other and grow larger in diameter (fig. 4). According to Stokes' law, the rate of climb can be increased with increased soap drop diameter as less soap then follows the outlet from the skimmer. An agglomeration of soap drops increases the diameter, in turn enhances the rate of climb and therefore also the soap separation efficiency [9]. Agglomeration requires several hours, where the larger particles collect the minor ones which then increase the diameter [9] [10], may not attain enough retention time in the skimmer to bind with each other effectively.

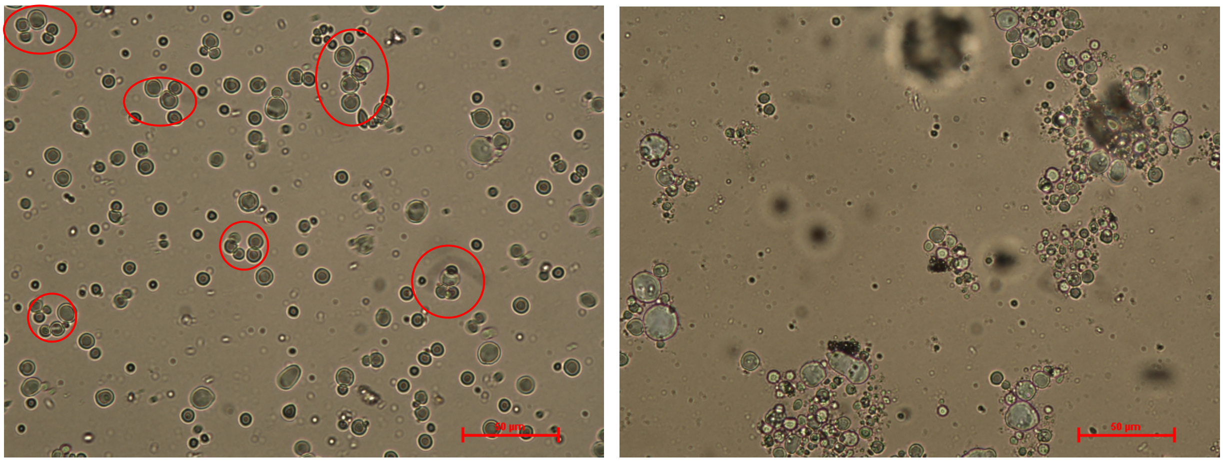

Figure 4: The two pictures show the agglomeration of soap drops. The picture on the left shows the commencing of agglomeration and the right picture shows the agglomeration after several hours. Magnified 400 times (the scale is 50 µm), has extractive content 90g/kg DS and was taken at different time.

The density of black liquor depends on the temperature and the dry solids content, and the soap concentration may affect the density because the density of pure soap is about 850 kg/m^3 while black liquor has a density around 1070 kg/m^3 [9].

2.2 Improved soap separation efficiency by air injection

Air injection has been proved to enhance soap separation in several mills and according to Uloth and Wearing [11], an enhancement of soap separation by 22% could be achieved. Flotation allows air bubbles to collect the soap drops and with a more detailed study on chemical formula of soap resembles a surfactant with a hydrophilic charged head group and a hydrophobic tail.
The hydrophilic head-group of a surfactant is faced to the aqueous media while the hydrophobic tail faces the air bubbles [12] [13]. When soap concentration increases, the surfactants become organised aggregates or micelles, where micelles can bind to the air through its centre and using the air bubbles to rise [12]. Injecting air through a nozzle creates tiny bubbles that bind to the soap drops and increase also the agglomeration (see fig. 5).

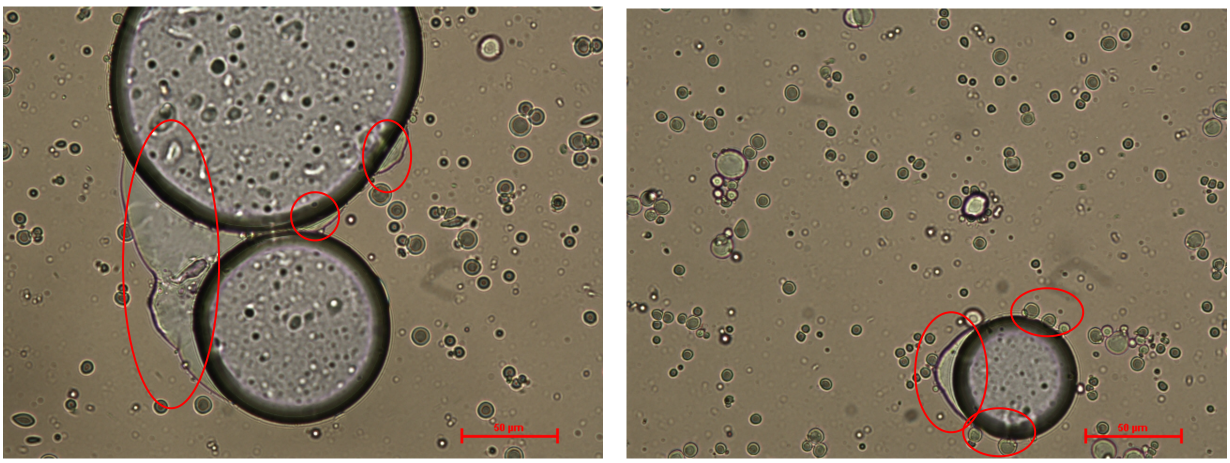

Figure 5: Microscopic picture showing how the soap drops bind to the surface of the air bubbles and simultaneously merging the soap drops together. Magnified 400 times (the scale is 50 µm) with extractive content at 90g/kg DS. Pictures were taken at different time.

3. The soap separation process at the Gruvön Mill

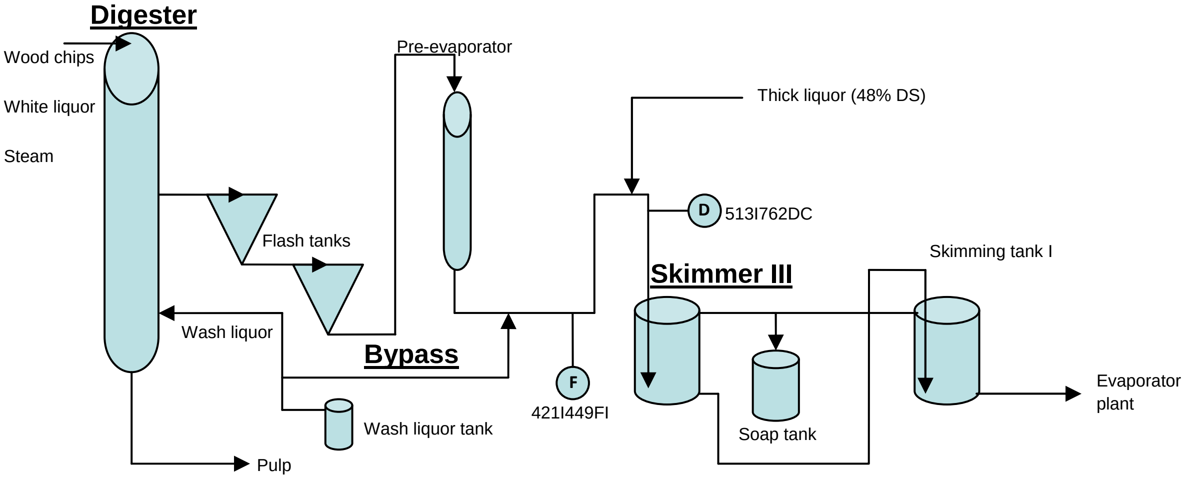

Figure 6: A mapping over the process from digester to skimmer I. D = densimeter, F = flow meter.

The cooking chemicals for the pulping process are added in a form called white liquor which contains mainly sodium hydroxide and sodium sulfide. During this process, wood chips are cooked with white liquor to break down lignin so that the fibers are released. The pulping process produces pulp and black liquor as residue, where the black liquor contains dissolved wood substances such as lignin, extractives, carbohydrates from hemicellulose etc. The black liquor that leaves the digester is transported through flash tanks that are connected in series to separate the steam and the condensate. After the flash tanks, the liquor evaporates to about 22% DS in the pre-evaporator to achieve optimal separation conditions [2] [8]. Finally, the liquor enters into skimmer III and the black liquor flow to the skimmer is about 300 m^3/h depending on pulp production and the capacity of the pre-evaporation plant. Due to the density difference between soap and liquor, where soap is lighter than black liquor, the soap is separated from the black liquor in the skimmer. The soap creates a soap layer at the top of the skimmer and by increasing the level in the skimmer the soap layer is decanted into a soap storage tank. The decanting of soap ends either when the soap tank is full or too small amount of soap is left to decant from the skimmer.
The skimmed liquor from the skimmer III enters into skimmer I, thus providing additional time for soap separation before the skimmed black liquor is sent to the evaporator plant.

3.1 Excess liquor to the digester

The maximum flow of wash liquor per ton pulp entering the digester hi-heat wash has a limit, and excess wash liquor flow bypasses the digester and enters therefore directly into the skimmer III (fig. 6). The dry solid concentration of this bypass wash liquor is only 10% dry solids i.e. much lower than dry solid concentration of the liquor fed to the skimmer. The bypass black liquor must therefore be mixed with thick liquor to achieve correct dry solid content before it enters the skimmer. A density control sensor (531I762DC) is installed at Gruvön mill to adjust the dry solid content to about 22% solids concentration.

3.2 The skimmer III

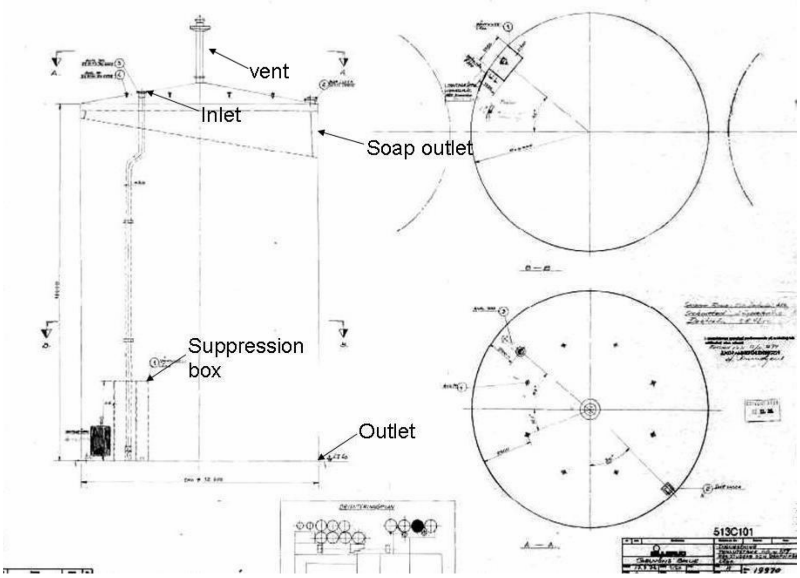

Figure 7: Layouts of the skimmer III.

The volume of the skimmer is 2000 m^3 with a height of 18 m and a diameter at 12 m. A suppression box (fig. 7) surrounds the inlet flow to decrease the velocity of the black liquor that is entering the skimmer. If the velocity is too high, it causes a stirring within the skimmer and if it's too low, the skimmer becomes vulnerable to thermal effects due to varying inlet temperature and cooling effects from the walls [9]. The theoretical retention time in the skimmer is 6-7 h, but according to a report [14], the average retention time is approximately only 15-20 minutes which indicates a short circuit in the skimmer. When bypass liquor enters the skimmer, the measurement shows an increase in retention time to more than two hours. This indicates that the bypass liquor has stirred the skimmer and altered the pattern of the flow that retains the black liquor within the skimmer.

The skimmer is not well insolated to preserve the heat, especially at the top of the skimmer where there is a vent (fig. 6) which opens when the pressure is too high in the skimmer. This causes a rapid cooling in the skimmer, which can alter the flow fields for the black liquor flow or create a short circuit between the in- and the outlet of the skimmer. These occurrences are considered as disturbances [9]. The dimension of the skimmer at Gruvön mill should preferably be wider in diameter and lower in height.

3.3 Soap layer

If decanting of soap from the skimmer is very infrequently, the soap layer at the top grows continuously thicker. As mentioned earlier, the rapid cooling from the vent at the top of the skimmer causes the soap layer to be more viscous. A thicker soap layer preserves the heat of the black liquor better which could be expected to increase the soap separation efficiency in the viscosity of the black liquor becomes lower at high temperature. This makes the soap separation efficiency more efficient. It can decrease the cooling of the black liquor near the surface of the skimmer. If the cooling of the skimmer is too great, the flow pattern alters and this creates disturbances. Literature references about this subject are limited, which makes it difficult to define a suitable soap layer thickness, whit the aim to increase of soap separation efficiency, based on already existing knowledge alone. Experimental investigations, such as the present one, is therefore of essence.

4. Material and methods

In order to evaluate both the total process from the digester to skimmer I and the process inside the skimmer III the following methods have been designed to generate data for the soap skimming efficiency:

The process components surrounding the skimmer III have an influence and must be evaluated before an optimization can be performed. Instruments like densimeter and flow meter etc. are necessary measuring devices to generate data and to detect of any unusual patterns.

An evaluation if an air injection and if a variation in the soap layer thickness may affect the efficiency of soap separation was carried out. To inject air into the liquor, a so called *sparger* was used which contains thousands of tiny pores, creating small and numerous bubbles (see fig. 9). This sparger was mounted directly into the pipeline (fig. 10) of the inlet flow. The air from the sparger is sheared by the liquor flow, resulting in fine bubbles.
The recommended air flow was about 7 l air/m^3 liquor in the black liquor feed [11].

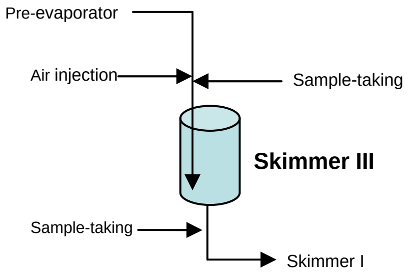

Figure 8: Mapping over the skimmer III and location of sample-taking and sparger.

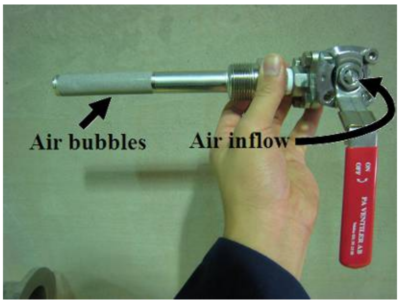

Figure 9: The sparger used for air injection in liquor.

Figure 10: Installed sparger in the pipeline.

To indicate if an improvement or a deterioration of the soap separation efficiency in the skimmer III was obtained, it was necessary to analyze (appendix 1) the soap content of the in- and outlet liquor flows of the skimmer. To maintain the same sample volume, the customized sample valves were applied to produce the same sample volumes. This technique was also necessary because the soap separated otherwise from the black liquor and this separation was not reversible. The sample volume was 30 ml.

Figure 11: Sample valve for sample-taking of inlet flow.

Figure 12: Sample valve for sample-taking of outlet flow.

To determine the thickness of the soap layer in the skimmer, a technique called *hand sounding* (fig. 13) was preformed. A vessel is lowered to a certain level in the skimmer and then filled with content. After been filled, the vessel is pulled up and then opened to verify if the content is soap (fig. 14) or liquor (fig. 15). This method is repeated until the layer between liquor and soap is confirmed.

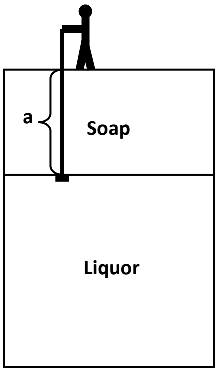

Figure 13: Illustration on how hand sounding in a skimmer is preformed.

a =thickness of soap

Figure 14: Vessel containing soap.

Figure 15: Vessel containing black liquor.

5. Work plan

1. Study the soap separation process. Find articles about air injection and soap layer and their efficiency. Discuss with people who has knowledge about the soap layer and its impact on soap separation efficiency.

2. Install the sparger for air injection in the pipeline and also install two sampling valves for in- and outlet black liquor flow of skimmer III.

3. Analyze the soap content of the in- and outlet liquor flows. Measure the height of the soap layer using hand sounding. Collect process data, calculate separation efficiency and evaluate the different methods.

4. Conclude the thesis work with analysis results and begin writing.

5. Describe problems and its consequence and provide suggestions for future improvements.

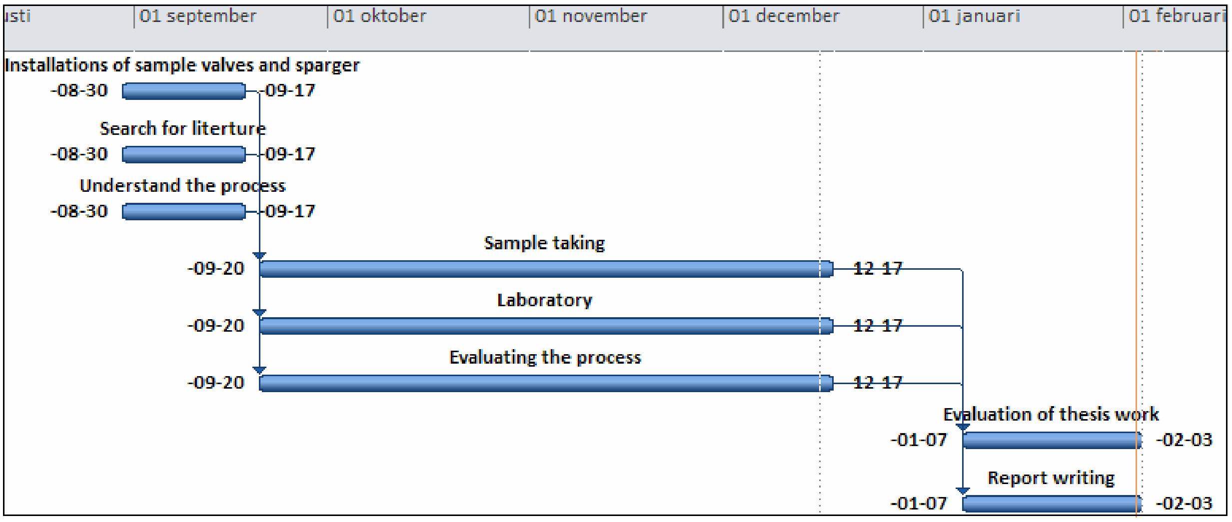

Figure 16: Work plan for this thesis work and the duration time is 20 weeks.

6. Results & Discussion

There is a potential for an increase of tall oil production at the Gruvön Mill as many disturbances and instabilities in the skimmer result in a loss of tall oil soap. Thus clarifies the scattering of the values of the analysis in the diagrams (fig. 17 and fig. 18), where measures to improve the skimmer operation efficiency will be discussed later in this chapter. The presence of soap in the black liquor also harms the process like foaming, fouling and also the capacities of both the evaporator plant [1] and the recovery boiler [15] are reduced.

A daily analysis of soap content in feed liquor stream and skimmed liquor was carried out to follow up the separation efficiency and showed a loss of 5,85% in soap separation efficiency (appendix 2) occurred during this thesis work. Soap content varies depending on the season, but under normal circumstances the soap content in the black liquor fed to skimmer is around 22-28 g/kg DS.

6.1 Thickness of soap layer

The different thicknesses of soap layer indicate no distinct improvement for the soap separation efficiency, where the values of the analysis were scattered throughout the diagrams (fig. 17 & fig. 18) and the skimmer operation efficiency was not improved by maintaining a thick soap layer. Compared to the normal soap layer of 0,75-3,5 m in the skimmer, a higher soap layer showed no improvements of the soap separation efficiency (fig. 18).

One argument for maintaining a high soap layer would be to improve the chances for the soap drops to reach the soap-liquor interface, bind to soap layer due to soap drops have the tendency to bind with each other and instead of following with the skimmed liquor outlet. However, this argument gave no improvement on the soap separation efficiency with a thicker soap layer. A high soap layer may decrease cooling effects, but there aren't any measurements of the temperature at different heights of the skimmer that can verify if there are temperature drops.

The following risks that should be considered if a high soap layer is used in the skimmer:

- The high viscous soap layer creates difficulties for the tall oil plant resulting in higher consumption of chemicals, but also other issues for the process.
- Increases the risk for a short circuit between in- and outlet black liquor flow of the skimmer when the growth of the soap layer exceeds 10m.

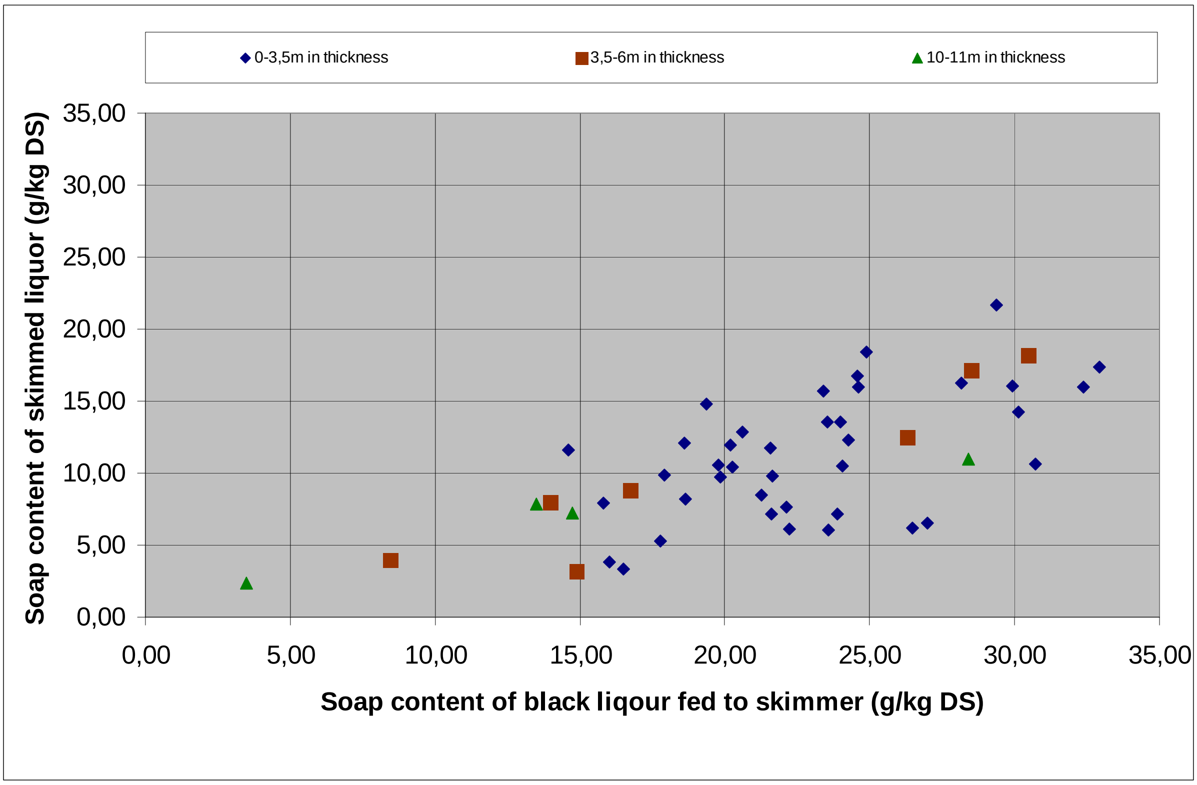

Figure 17: Effect of different thicknesses of soap layer on residual soap content of skimmed black liquor. The data is based on soap content of black liquor during normal process conditions (excluding disturbances).

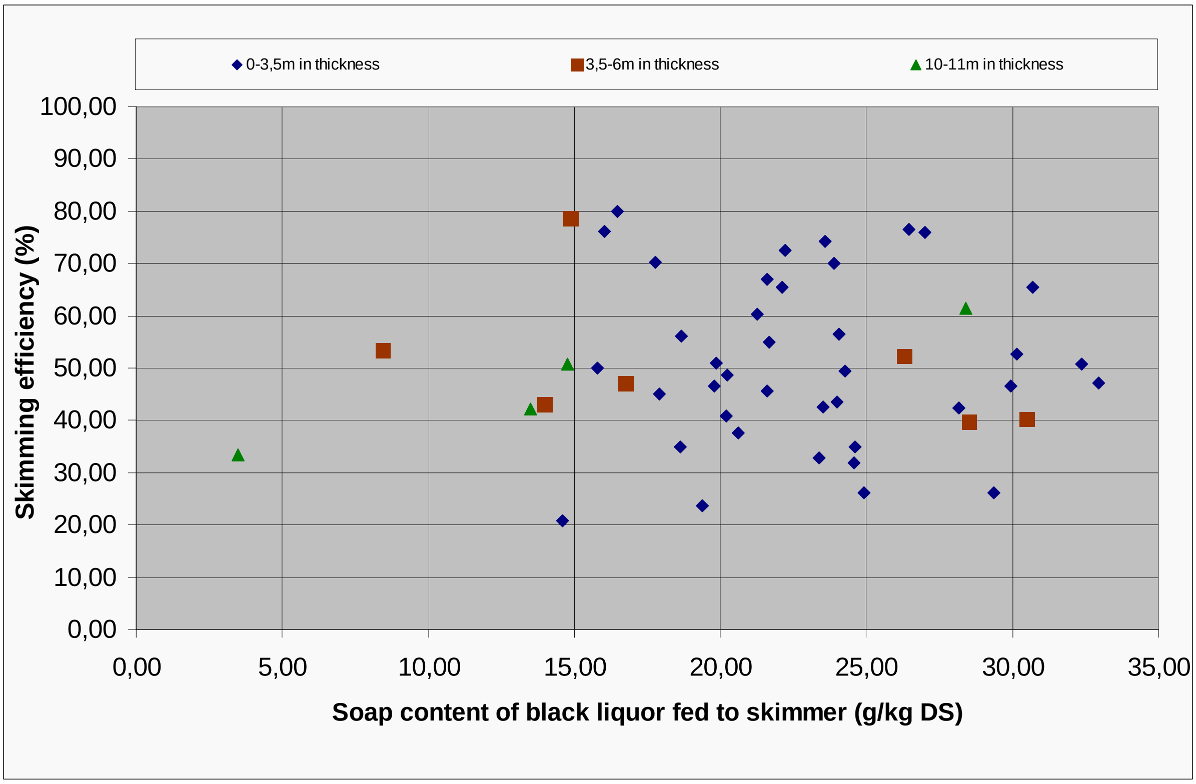

Figure 18: Effect of different thicknesses of soap layer on soap skimming efficiency. The calculation of soap skimming efficiency is based on the total soap in the liquor fed to the skimmer. The data is based on soap content of black liquor during normal process conditions (excluding disturbances).

6.2 Air injection

The mean value of soap separation efficiency for air injection was 72% (appendix 2) and compared with a case when no air was added to the feed liquor stream, in other words, the total mean value of the soap layers' separation efficiency (51%), gives a difference of additional 21% soap can be skimmed of from the black liquor (appendix 2) using air injection. The total increase of soap separation efficiency is 41%. The values of the analysis for air injection are situated in the upper right part of the fig. 19 and lower right part of fig. 20, which signify a possible improvement that can be achieved by air addition to the feed liquor stream. According to Uloth and Wearing [11], a dramatic increase of soap skimming efficiency occurs when the soap content of the feed liquor stream exceeds 25 to 30 g/kg DS, but the corresponding increase was only marginal at lower soap content. During this study a dramatic increase of skimming efficiency was noticed at 25-30 g/kg DS of the inlet flow where the separation efficiency was about 60-85% (fig. 20).

Air addition to the black liquor lowers the density of the soap drops which in turn increases the rate of climb and improves separation. By having a thick layer of soap while using air injection can increase the risk for overflow from the skimmer, so more desirable would be to maintain a thinner soap layer. The injection of air was tested with a soap layer of 10 m and because to prevent foaming that can overflow from the skimmer the air injection was preformed only at day time. This is a precaution that should be monitored and confirmed if the soap layer increases by air injection. In order to achieve the optimal efficiency from the air injection, a constant air feed (instead of discontinuous) addition of air should be applied. The air flow was adjusted manually, but a control of the air flow against the feed liquor flow should be installed to avoid excess or shortage of air to the feed liquor flow.

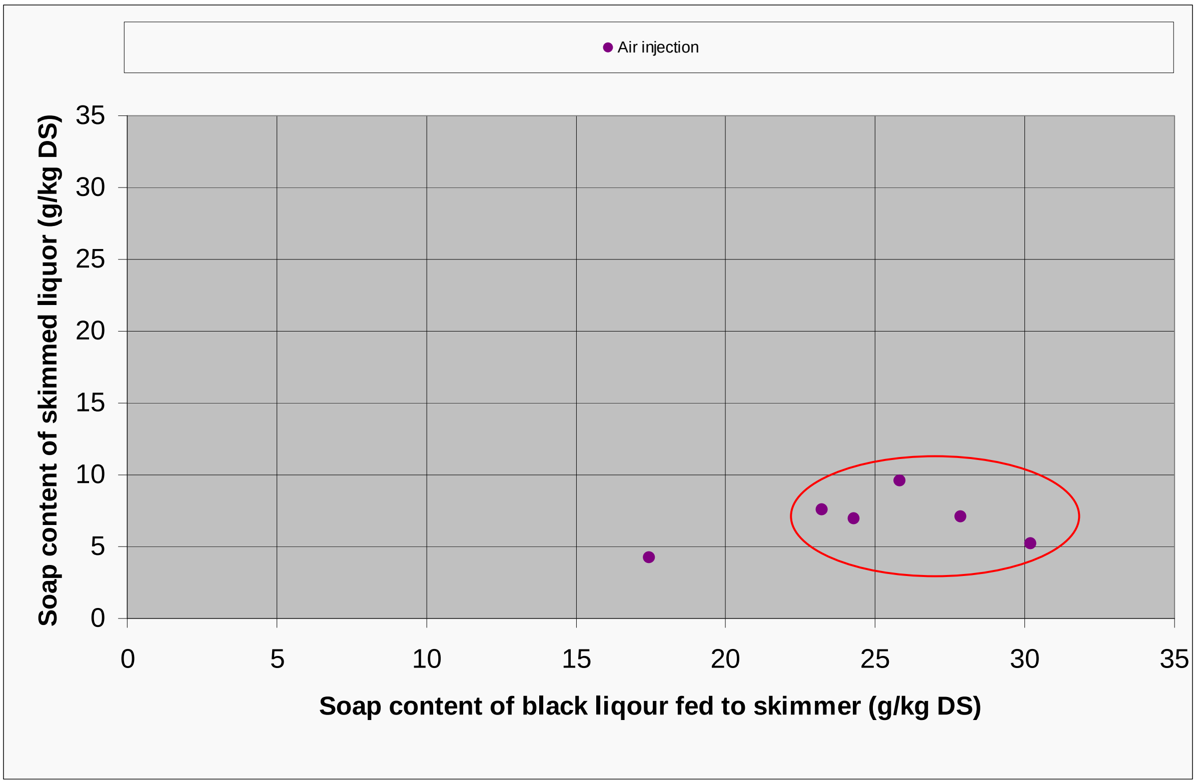

Figure 19: Effect of air injection on residual soap content of skimmed black liquor. The data is based on soap content of black liquor during normal process conditions (excluding disturbances).

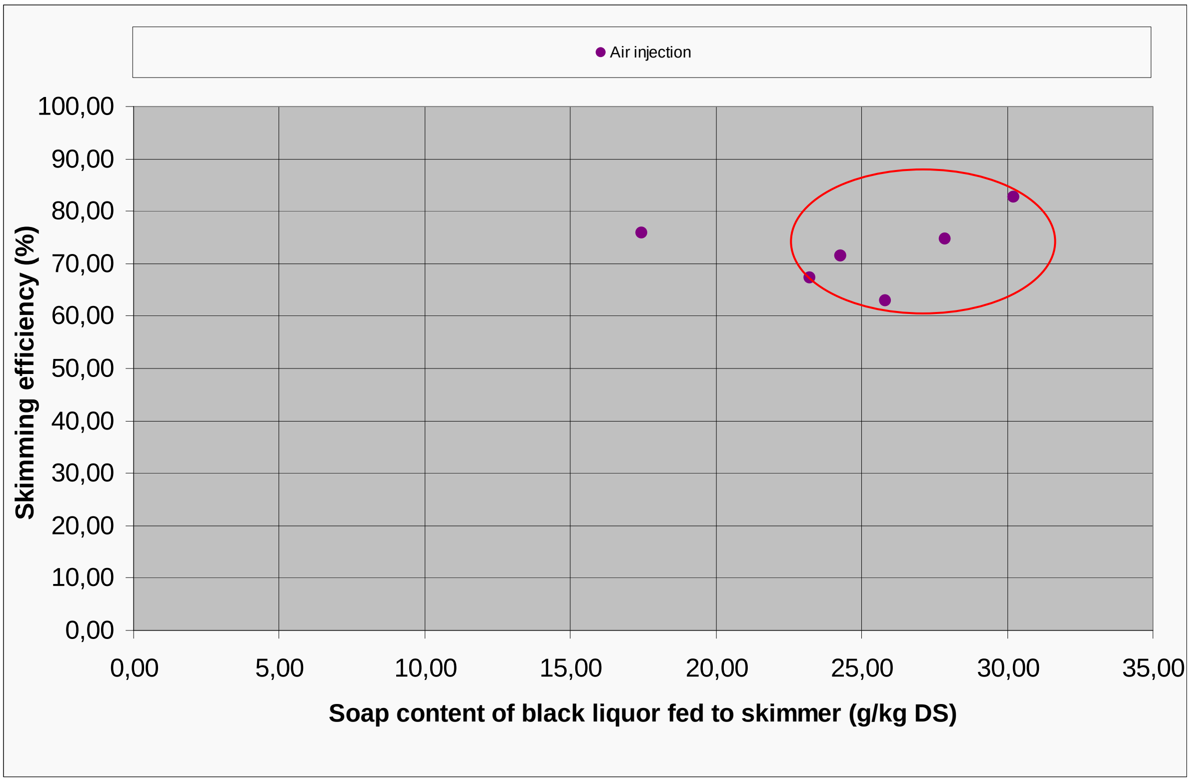

Figure 20: Effect of air addition on soap skimming efficiency. The calculation of soap skimming efficiency is based on the total soap in the liquor fed to the skimmer. The data is based on soap content of black liquor during normal process conditions (excluding disturbances).

6.3 Profitability calculations of more produced tall oil

Improved soap separation efficiency leads to an increased production of tall oil, which in turns increases the profit. Billerud Gruvön mill produces 15,000 tons of tall oil per year and an improvement of soap efficiency of 41% through air injection represents an increase of about 1,600 tons (5-6 MSEK) tall oil per year. If the soap loss could be prevented by reducing the disturbances, an additional 400 tons (1-2 MSEK) tall oil per year could be obtained. A simple calculation of profitability gives an increased total profit of about totally 6-8 MSEK, which includes operating costs, chemical costs, electricity, costs for the air compressor etc. Thus increased production of tall oil will increase the profit of the pulp mill and this is a strong argument for continued use of air injection.

Another profit that can be achieved through improved soap separation efficiency is reduced costs for the evaporator plant and increased capacity of the recovery boiler. The wash sequence is performed daily in the evaporator effects and causes a decreased capacity of the effects. However, an estimate of the profit obtained for enhanced capacity is more difficult to calculate, but should be taken into account.

6.4 Measures for improvements of the process

6.4.1 Variations in the black liquor flow from the digester

The variations of the black liquor flow (fig. 21) leaving the digester must be reduced to achieve more even flow and density (fig. 22) before entering the skimmer III, otherwise the variations will cause a stirring in the skimmer.

The scattering of the values of the analysis in the graphs (fig. 17 and fig. 18) indicates that the skimmer III is not as stable as it could be. One measure that could improve the skimmer operation efficiency is to reduce the variations of the black liquor flow leaving the digester.
The main objective of the density control is to reduce the density variations that are caused by the black liquor flow's variation. However, the density control is unable to stabilize the density variation because the black liquor flow's variations are too great.
There are numerous causes for the variations of the black liquor flow, which are reported as:

- Digester – The temperature control in the digester is difficult to manage.
- Incorrect measurement – It has been reported that the measuring devices are inaccurate resulting in incorrect values for the control.
- Liquor / wood ratio - The liquor / wood ratio variation must be reduced to reduce the variations in the outlet stream from the digester

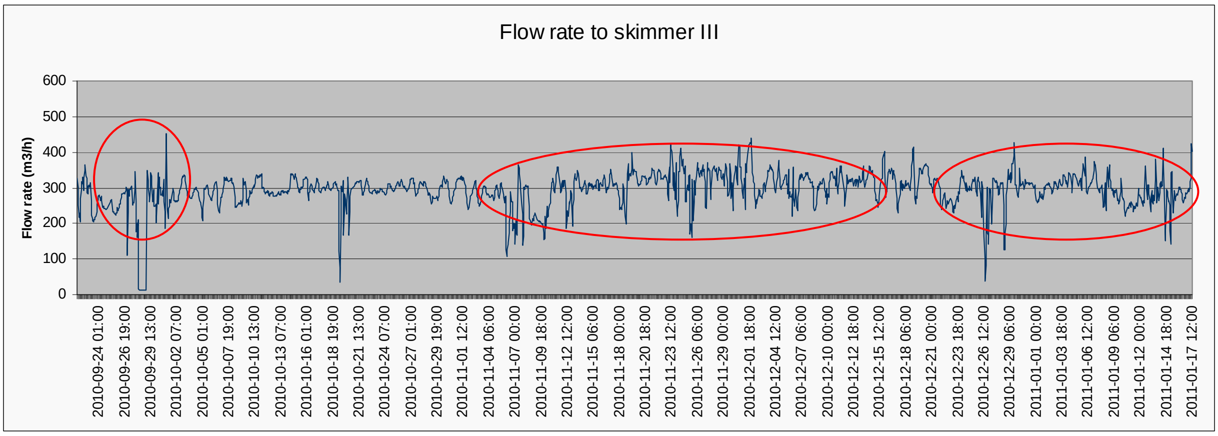

Figure 21: Flow rate recorded by flow meter 421I449FI during September to January.

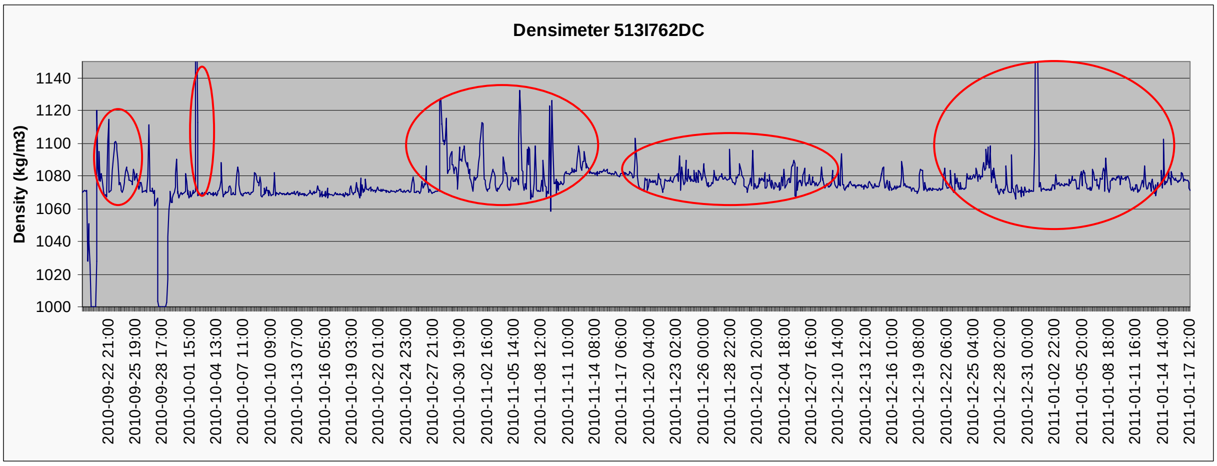

Figure 22: Density recorded by densimeter 513I762DC during September to January.

6.4.2 Bypass wash liquor

Bypass is certainly one of the major difficulties that creates disturbance within the skimmer and the density control with thick liquor to reduce the variation of density is not well improved. When a great amount of bypass wash liquor enters the skimmer III, it create disturbances that will result in an increase of soap content in the outlet black liquor flow (fig. 23), in other words, a loss of soap to the evaporator plant. There is only a density control with thick liquor if the density drops, but there exists no control to reduce the density if the density increases.

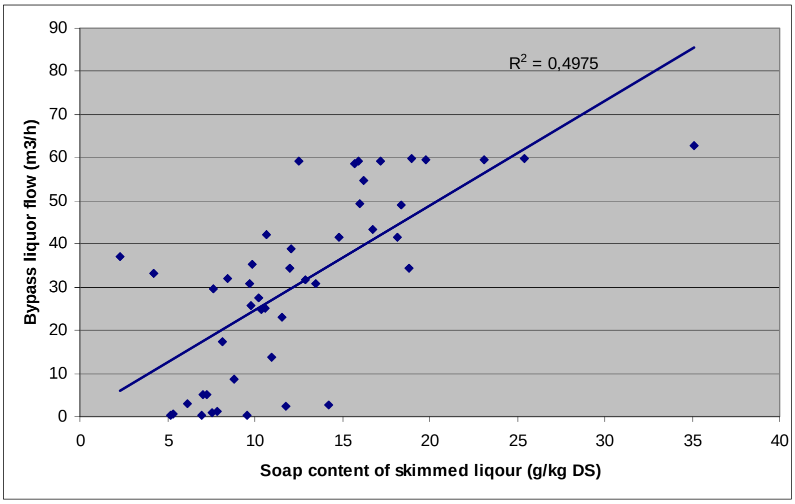

Figure 23: The effect of bypass wash liquor flow on residual soap content of skimmed liquor.

Soap content in the bypass wash liquor contains about five times more soap (appendix 4) compared with the black liquor fed to the skimmer III. However, the small amount of soap in bypass wash liquor that mixes with the black liquor flow from the digester doesn't affect the density that enters the skimmer III significantly. It is the dry solid concentration of the bypass wash liquor that affects the density dramatically.

6.4.3 A suggested solution for more stable density to the skimmer III

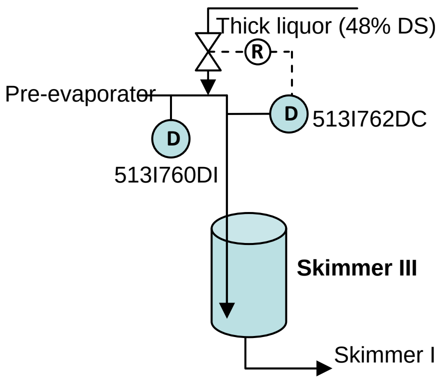

Figure 24: Mapping over a skimmer III with a density control. R = density control.

When the bypass liquor is added to the skimmer, the density control raises the density with thick liquor. The densimeter (513I762DC) is the source for this density liquor control. Calibration of this device is poor because the location of the sample valves is not convenient for the operators, but the problem is not the calibration of the device but rather the location. It is not until the bypass liquor mixed with black liquor has passed through the densimeter (513I762DC) that an action is performed by adding thick liquor into the feed stream. This gives a delay of the control adjustment. A solution to this problem would be a *feed forward control loop*. A densimeter (513I760DI) placed much earlier and closer to the pre-evaporator, discovers the density drop before it passes the thick liquor valve there improves the possibility to make an adjustment.
The density control is a PI (proportional-integral) controller, which means it eliminates residual error but performs slowly due to long dead time. The PI-controller is preferable for this process, but the variations from the digester are still too great and too rapid for the control to operate quickly, but with a feed forward control loop an improvement of the control can be gained.

7. Conclusions

Air injection in the skimmer has a potential to increase the soap separation efficiency by 41% which in turn increases the tall oil production with 1,600 tons/year corresponding to a profit increase of about 5-6 MSEK. The airflow that is recommended is 7 l air/m^3 liquor in the black liquor feed and a control sensor should be installed for permanent use to avoid excess or shortage of air to the feed liquor flow. A low soap layer would be preferred to prevent any overflow from the skimmer or short circuit in the skimmer while using the air injection.

By maintaining a thick soap layer, the chances would increase for the soap drops to reach the soap layer instead of following the skimmed liquor outlet. However, the values of the analysis are scattered throughout the diagrams likewise the separation efficiency is not improved, indicates that no additional benefit is achieved by maintaining a thick layer of soap and there are consequences with a thick soap layer that should be strongly considered and carefully prepared.

An evaluation of the digester should be done to reduce the variations of black liquor flow which then improves the stability within the skimmer. This is one of the main problems that create disturbances in the skimmer.

A modification of the black liquor density control with a feed forward control loop can probably reduce the variations of the density and improve the stability of the skimmer. The location of the densimeter (513I762DC) is a drawback and can be supported by an earlier densimeter (513I760DI) that provides an advantage for density control to make adjustments to the variations. If a more stable skimmer could be achieved then an additional profit of 1-2 MSEK can be obtained.

A continued use of air injection should be considered as more tall oil can be produced. The evaporator plant can reduce the maintenance costs by receiving better skimmed liquor that contains less soap. Thicker soap layer could theoretically increase the separation efficiency, but the risks as short circuit of the skimmer or overflow are drawbacks which should be considered.

Further studies, should verify the importance of a critical soap layer and its optimum thickness when air injection is used. Another investigation should be on how the skimmer behaves under different air flows than 7 l air/m^3 liquor in the black liquor feed.

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Appendices

Appendix 1: Lab method to determine soap content in black liquor

Trichloroethylene is used as a solvent to extract the soap content from black liquor. This laboratory method was developed by Karin Wilson [16].

Material

1. Separating funnel
2. Trichloroethylene
3. Sodium hydroxide (about 600 g/l)
4. hydrochloric acid (1 M)
5. Sample of black liquor (30 ml)

The black liquor has dry solids at 20-23% and need to be diluted down to 5-7 % DS.

$$x\ times\ diluted = \frac{22}{6} = 3{,}666... \approx 4\ times$$

The dilution is 4 times giving a total volume of 120 ml.

Pour the liquor diluted with water in a separating funnel, add 50 ml trichloroethylene and then 5 ml sodium hydroxide. Close the funnel with a lid and shake for 5 min. Wait for the layers to separate and draw off the lower layer into another funnel. Add another 50 ml trichloroethylene and do the same procedure as before. Shake for another 5 min then combine trichloroethylene with 15 ml hydrochloric acid and draw off the lower layer. Screen the trichloroethylene and pour it in round bottom flask that has been weighted.

Last step is to distil the solution. After distillation, dry the round bottom flask in drying cabinet for 5 min and let it cool for 20 min in an excicator.
Calculation of soap content:

$$soap\ weight\ (g) = e = round\ bottom\ flask\ containing\ soap\ (g) - empty\ round\ bottom\ flask\ (g)$$

$$v = total\ volume\ of\ the\ sample\ (120 ml)\ ,\ t = dry\ solid\ matter\ after\ dilution\ (\%\ DS)$$

$$soap\ content\ (g / kg\ DS) = \frac{e * 100 * 1000}{v * t}$$

Appendix 2: Experimental results of soap content in black liquor

$$Separation\ efficiency(\%) = (1 - \frac{soap\ content\ of\ outlet}{soap\ content\ of\ inlet}) * 100$$

$$Soap\ loss\ (\%) = average\ efficiency\ excl.disturbances - average\ efficiency\ incl.disturbances = 53{,}49 - 47{,}64 = 5{,}85\%$$

$$Additional\ soap\ achieved\ by\ air\ injection = air\ added(\%) - no\ air\ added(\%) = 72{,}49 - 51{,}25 = 21{,}24\%$$

The bolded values indicate that a disturbance has occurred during sample-taking.

Thickness of soap layer 0,75-3,5m

Thickness of soap layer(m)	Soap content(g/kg DS) Inlet	Outlet	Separation efficiency(%)
0,75	26,46	6,21	76,53
0,75	16,49	3,30	79,99
0,90	24,90	18,38	26,18
1,00	19,37	14,79	23,64
1,00	**14,87**	**0,11**	**99,26**
1,10	14,61	11,58	20,74
1,30	23,39	15,72	32,80
1,30	24,59	16,73	31,95
1,30	28,17	16,22	42,41
1,30	29,36	21,67	26,19
1,30	32,94	17,39	47,21
1,30	24,05	10,48	56,43
1,32	32,38	15,96	50,71
1,35	16,02	3,84	76,06
1,36	21,61	7,13	67,00
1,36	30,71	10,63	65,38
1,37	21,26	8,45	60,25
1,38	30,15	14,24	52,76
1,39	18,62	12,11	34,96
1,39	20,21	11,97	40,77

Thickness of soap layer 3,5-6m

Thickness of soap layer(m)	Soap content(g/kg DS) Inlet	Outlet	Separation efficiency(%)	
3,60	14,88	3,18	78,63	
3,90	16,75	8,85	47,16	
4,10	**21,86**	**25,38**	**-16,10**	
4,60	13,98	7,96	43,06	
5,00	30,48	18,18	40,35	
5,30	26,29	12,52	52,38	
5,40	**18,88**	**35,09**	**-85,86**	
5,50	28,50	17,17	39,75	
5,60	8,44	3,93	53,44	
Mean	value		28,09	%
Mean	value excl.	disturbances	50,68	%

Air injection

10	17,44	4,21	75,86	
10	25,83	9,59	62,87	
10	27,87	7,07	74,63	
10	23,23	7,59	67,33	
10	30,21	5,21	82,75	
10	24,29	6,93	71,47	
	Mean	value	72,49	%

Thickness of soap layer 10-12m

Thickness of soap layer(m)	Soap content(g/kg DS) Inlet	Outlet	Separation efficiency(%)
10,00	28,40	10,94	61,48
11,00	3,50	2,33	33,43
11,00	13,51	7,82	42,12
11,00	14,75	7,25	50,85
	Mean	value	46,97

1,40	20,24	10,39	48,68	
1,40	19,86	9,73	51,01	
1,50	21,59	11,75	45,58	
1,50	27,00	6,51	75,89	
1,50	23,90	7,18	69,96	
1,50	22,23	6,12	72,46	
1,50	**20,97**	**19,03**	**9,25**	
1,54	24,00	13,57	43,45	
1,55	21,65	9,77	54,88	
1,55	19,78	10,57	46,55	
1,56	23,53	13,51	42,59	
1,60	22,12	7,64	65,46	
1,60	**19,05**	**19,81**	**-3,99**	
1,70	20,60	12,87	37,52	
1,75	12,65	1,56	87,67	
1,75	22,82	2,47	89,18	
1,90	17,91	9,85	45,00	
2,10	15,80	7,89	50,06	
2,10	**18,99**	**18,85**	**0,74**	
2,25	24,60	15,99	35,00	
2,25	18,65	8,18	56,14	
2,60	24,28	12,30	49,34	
2,80	**28,19**	**26,13**	**7,31**	
2,90	23,58	6,06	74,30	
2,90	29,94	16,02	46,49	
3,25	**19,36**	**27,88**	**-44,01**	
3,30	17,76	5,30	70,16	
3,60	14,88	3,18	78,63	
Mean	value		48,26	%
Mean	value excl.	disturbances	51,78	%

Air added to feed stream	72,49	%
No air added to feed stream	51,25	%
Total mean value of separation efficiency (incl. disturbances)	47,64	%
Total mean value of separation efficiency (excl. disturbances)	53,49	%

Appendix 3: Experimental result of calcium content in soap and black liquor

Nablabs laboratories
OY LÄNNEN LABORATORIOT
WESTERN LABORATORIES INC

Elisa Sivula
Polargas Oy
Air Liquide Finland

REPORT no 4489

04.01.2005

ANALYSIS RESULTS

Sample details: Soap samples from Billerud

1. Air Liquide Finland: Barr
2. Air Liquide Finland: Löv

Sample was delivered to our laboratory on 29.12.2004

Results are calculated on "as received" basis

Analysis	Barr	Löv	Method
H_2SO_4 consumption, g H_2SO_4/kg	101,3	86,4	internal
Dry solids, %	60,1	59,4	PCTM 11
Tall oil content, %	52,0	50,7	PCTM 7
Lignin %	0,7	0,7	PCTM 8
Fiber, dirt %	0,5	0,6	PCTM 8
Ca g/kg	2,0	2,3	AAS

Sulfuric acid consumption is calculated as 100 % acid, titrated to pH 3

Lännen Laboratoriot Oy

Mari Juntunen

Mari Juntunen
Laboratory Manager

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Y-tunnus/VAT no. FI08887144

Figure A.4.1: Calcium concentration in soap is about 2,0 g/kg DS = 0,44 g/kg liquor (Dry solids 22%).

BILLERUD

Rapport

Sida 1 (2)

L0701983

1YYOGH8IPAC

Projekt

Billerud AB Gruvöns Bruk
Charlotta Sohl

Registrerad 2007-02-08
Utfärdad 2007-02-21

Box 500
664 28 Grums

Analys: V4E

Er beteckning	Mellanlut vecka 4, 2007 Gruvön			
Labnummer	U10303769			
Parameter	**Resultat**	**Enhet**	**Metod**	**Utf**
Ca*	58.3	mg/l	1	A
Fe*	18.0	mg/l	1	A
Mg*	50.9	mg/l	1	A
Na*	70100	mg/l	1	A
Si*	138	mg/l	1	A
Al*	49200	µg/l	1	A
Mn*	28800	µg/l	1	A

Er beteckning	Mellanlut vecka 5, 2007 Gruvön			
Labnummer	U10303770			
Parameter	**Resultat**	**Enhet**	**Metod**	**Utf**
Ca*	59.9	mg/l	1	A
Fe*	5.88	mg/l	1	A
Mg*	80.7	mg/l	1	A
Na*	70700	mg/l	1	A
Si*	130	mg/l	1	A
Al*	44400	µg/l	1	A
Mn*	31100	µg/l	1	A

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Figure A.4.2: Calcium concentration in black liquor is about 60 mg/l liquor = 272,73 mg/kg DS (Dry solids 22%).

Appendix 4: Experimental result of soap content in bypass wash liquor

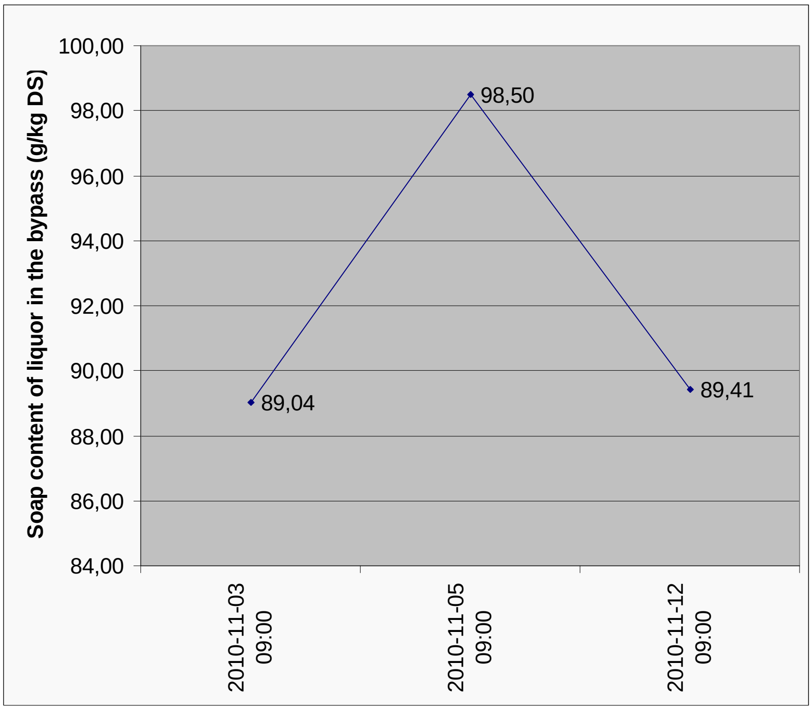

Figure A.5.1: Soap content in the bypass wash liquor.