

SUOMEN SOODAKATTILAYHDISTYS FINNISH RECOVERY BOILER COMMITTEE

Suomen Soodakattilayhdistys ry

Mechanisms and rate of soap separation **KCL Reports 2875**

Kurt Sirén, KCL

Raportti 11/2007

Mechanisms and rate of soap separation

8 August 2007, KCL Reports 2875

Confidential, available for the financing parties within Metsäliitto Group, Myllykoski Corporation, Stora Enso Oyj, UPM-Kymmene Oyj, and Finnish Recovery Boiler Committee Confidential, available for the financing parties within Metsäliitto Group, Myllykoski Corporation, Stora Enso Oyj, UPM-Kymmene Oyj and Finnish Recovery Boiler Committee. Confidential, available for the financing parties within Metsäliitto Group, Myllykoski Corporation, Stora Enso Oyj, UPM-Kymmene Oyj Finnish Recovery Boiler Committee

MECHANISMS AND RATE OF SOAP SEPARATION

Kurt Sirén

8 August 2007

Project: Calcium carbonate scaling and soap separation	Research Theme: Operational efficiency
Project Group: Kurt Sirén, Klaus Niemelä, Elina Pajula.	Research Project: 1098-1110
Contact Group: Timo-Pekka Veijonen (Chairman), Seppo Martikainen, Keijo Salmenoja, Vesa Mikkonen, Sanna Siltala, Björn Åkerlund, Petri Lundén	KCL Reports no: 2875
Keywords: soap, black liquor, kraft pulping, particle size distribution, measurement technique	The results contribute to the following Business Areas: Chemical pulp

CONTENTS

1	INTRODUCTION11					
2	OBJECTIVE11					
3	BACKGROUND11					
4	METHODS					
5	5 OBSERVATIONS ON MECHANISMS					
	5.1		Images from the mills	13		
	5.2		Various observations			
		5.2.1	Merging			
		5.2.2	Different phases			
		5.2.3	Interaction with fibers			
	5.3		Summary of observations			
6		PART	TICLE SIZE DISTRIBUTION			
	6.1		Microscopy and image treatment			
	6.2		Number and volume distributions			
	6.3		Particle size distributions	40		
	6.4		Volume distributions	44		
	6.5		Largest particles			
7		RISE	RATE			
	7.1		Size distribution changes with time			
	7.2		Calculation of rise rate	53		
	7.3		Comparison with simulations			
8		CONCLUSIONS63				
RE	REFERENCES					

MECHANISMS AND RATE OF SOAP SEPARATION

EXECUTIVE SUMMARY

The rising of soap in black liquor was studied with respect to mechanisms, rise rate and particle size distribution. These issues are essential in optimizing the yield of tall oil and avoiding process disturbances. The value of tall oil is increasing, as fossil fuels are being replaced by biofuels, and it can serve as a raw material for production of for example Diesel fuel. The mechanisms of soap separation were found to be more complicated than the commonly adopted idea of spheres moving upward. A method was developed for measurement of the particle size distribution, and the rise rate was determined as a function of particle size for a number of cases.

Value to customers: Increased understanding of factors influencing the yield of tall oil

Tall oil has found a growing place in bio-based fuel production, and there is a growing interest in optimizing the yield. A part of the soap is normally "lost" with the liquor due to incomplete separation, and ends up in the recovery boiler.

Technical objectives:

The objective of this study was to clarify factors that influence the rise rate and, if possible, to measure the rise rate of soap as a function of particle size. The aim was also to develop a method, based on microscopy, to measure the particle size distribution.

Main technical and scientific results: New light on phenomena that contribute to the rising of soap and tools for studying the process in mills.

- Particle size was found to be greatly influenced by two opposite factors: Pumping shatters the particles to smaller peaces, and the particles merge when the liquor stands in the tanks.
- The fusion process requires hours.
- Small particles are extremely slow-moving and do not rise to the surface during the retention time in the tanks.
- Small particles are collected by larger ones rising up, which enhances their separation.
- A method was developed for measurement of the particle size distribution, based on microscopy.

- There is a large variation in the degree of agglomeration of particles both between mills and between tanks in the same mill.
- In the intermediate liquor tank the soap is mainly in the form of agglomerates.
- The rise rate of soap was determined in cases where the particles occur predominantly as free spheres.

Contributions to industrial business areas: Chemical pulping: Aid in production of tall oil

The method of particles size distribution measurement can be used in studies aiming at optimizing the yield and trouble-shooting in the soap separation. It can also be used in further studies of the fundamental mechanisms that operate in soap separation.

Technical details:

The rate by which soap gathers to the surface in the liquor tanks is of interest for several reasons: The surface load, i.e. the area of the tank relative to the flow through it, must be sufficient. This is frequently not the case, since mills are often running at a greater production rate than they are designed for. Occasionally the soap does not rise in an expected way. The yield of soap and thus the production of tall oil depends on how much soap remains in the liquor after the intermediate liquor tank, i.e. how large fraction is "lost" and proceeds to the recovery boiler. The value of the oil is, however, not entirely lost, because it is correspondingly used to produce electricity and heat. This is, though, a less profitable way to use it than to produce bio-fuel. Sometimes the recovery boiler is a bottle neck, and there is therefore a desire to minimize extra load on it.

The process of rising of soap to the surface of black liquor in the tanks is often imagined as small spheres that migrate upwards driven by a difference of density relative to the surrounding liquid. The rate of migration is determined mainly by the density difference and the viscosity of the liquid. Such a process is normally described by Stokes' law. Attempts to calculate the rise rate have been reported in the literature, but the results vary widely depending on the input values. Due to low difference of density, the system is sensitive to the input values.

A mill study was performed in six mills, in which the liquors were examined in a microscope and photographed. The study showed that the model of rising spheres is too simplified. There are no objections to the validity of Stokes' law in the case itself, but there are other factors influencing. The model does not give a sufficient base for a calculation of how rapidly soap gathers on the surface of the liquor. Even if a correct value of the rise rate can be determined, it will not enable us to make such calculations.

The results showed that pumping in evaporator effects and transfer lines shatters the soap into smaller particles. These particles can either remain as free individual spheres, or they can agglomerate. It was found that the degree of agglomeration varies very widely. In some mills the particles remain separate all the way through the evaporator

train until the intermediate liquor tank is passed. In other mills the soap is almost completely agglomerated already when the liquor is received from the cooking area.

On standing in the feed liquor tank, the agglomerates are slowly transformed to bigger particles, i.e. they merge. This process is, however, slow, and takes several hours. The fusion of the particles improves the buoyancy, which enhances separation.

Small particles were found to move so slowly that they have no chance of reaching the surface during normal liquor retention times. They may, however, be collected by larger particles as these rise through the liquor. They may also simply merge with other particles.

A method of measuring the particle size distribution of soap was developed, based on microscopy. A preparate of a liquor droplet is prepared and photographed, and at the same occasion a microscopic scale is photographed. The particle size is then measured by means of the image and the scale. The particle size measurement also opened an opportunity to measure the rise rate, as it changes when the liquor is left to stand at controlled temperature for a desired time period. The rise rate measurement is, however, confined to spherical particles, because it is difficult to determine the size of irregular agglomerates.





Fig. 1. Rise rate of spherical particles in the feed land thin liquor in one mill.

Other reports and publications of the project

Niemelä, K. Sulphate soap separation and acidulation, Literature review on process improvements, KCL Reports 2720, STFI report CHEM 96, 2003.

Niemelä, K. Sulfate soap separation and acidulation, Part 2. Composition of the soaps, KCL Reports 2874, 2007.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, KCL Reports 2824, 2006.

Pajula, E., Sirén, K. Calcium carbonate scaling in black liquor evaporation, Part 2. Multivariate analysis of mill data, KCL Reports 2876, 2007.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, paper at the ABTCP-PI conference, Sao Paulo, Brazil, Oct. 17 - 20, 2005.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, paper at the International Chemical Recovery Conference, Quebec, Canada, May 29 - June 1, 2007.

MECHANISMS AND RATE OF SOAP SEPARATION

EXECUTIVE SUMMARY

Suovan nousu mustalipeässä tutkittiin mekanismeja, nousunopeutta ja hiukkaskokojakaumaa silmälläpitäen. Nämä seikat ovat olennaisia pyrittäessä optimoimaan mäntyöljyn saantoa ja minimoimaan prosessihäiriöitä. Mäntyöljyn arvo on nousussa fossiilisia polttoaineita korvattaessa biopolttoaineilla, jolloin se voi toimia lähtöaineena esim. dieselöljyä valmistettaessa. Todettiin, että suovan erottumisen mekanismit ovat monimutkaisempia kuin miten ne tavallisesti kuvitellaan, eli siten, että pallomaiset hiukkaset yksinkertaisesti nousevat lipeän läpi. Kehitettiin menetelmä hiukkaskokojakauman mittaamiseksi, ja nousunopeus määritettiin hiukkaskoon funktiona muutamille tapauksille.

Tutkimuksen arvo asiakkaille: Suovan ja mäntyöljyn saantoon vaikuttavien tekijöiden ymmärtämyksen parantuminen

Mäntyöljy on löytänyt kasvavan paikan biopohjaisten polttoaineiden tuotannossa, ja saannon optimointi on saanut yhä suuremman kiinnostuksen osakseen. Osa suovasta tavallisesti "karkaa" lipeän mukana soodakattilaan epätäydellisen erotuksen seurauksena.

Tekniset tavoitteet:

Tämän tutkimuksen tavoitteena oli selvittää nousunopeuteen vaikuttavia tekijöitä ja, jos mahdollista, määrittää nousunopeus hiukkaskoon funktiona. Tavoitteena oli myös kehittää mikroskopointiin perustuva menetelmä hiukkaskokojakauman määritykseen.

Tärkeimmät teknis-tieteelliset tulokset: Uutta tietoa ilmiöistä, jotka vaikuttavat suovan nousuun, ja työkaluja prosessin tutkimisen tehtaissa

- Hiukkaskoko todettiin riippuvan voimakkaasti kahdesta vastakkaisesta tekijästä: Pumppaaminen hajottaa suopahiukkaset pienemmiksi osiksi, ja hiukkaset yhdistyvät, kun lipeä seisoo säiliöissä.
- Yhdistymisprosessi vaatii tunteja.
- Pienet hiukkaset ovat erittäin hidasliikkeisiä, eivätkä nouse pinnalle säiliöiden viipymäaikojen puitteissa.
- Isot hiukkaset keräävät pienempiä noustessaan lipeän läpi ylös, mikä parantaa pienten erottumista.
- Kehitettiin mikroskopiaan perustuva menetelmä hiukkaskoon mittaamiseen.
- Hiukkasten agglomeroitumisaste vaihtelee suuresti tehtaiden välillä ja saman tehtaan säiliöiden välillä.

- Välilipeäsäiliössä hiukkaset ovat pääasiassa agglomeroituneina.
- Nousunopeus määritettiin tapauksissa, joissa hiukkaset esiintyvät pääasiassa vapaina palloina.

Analyysi vaikutuksista teollisuuden liiketoiminta-alueisiin: Sellu: Apu mäntyöljyn tuottamisessa

Hiukkaskokojakauman määritysmenetelmää voidaan käyttää tutkimuksissa, joissa pyritään optimoimaan saantoa ja selvittää suovan erotuksen ongelmatilanteita. Sitä voidaan myös käyttää perusmekanismien tutkimiseen.

Tarkemmat tekniset tiedot:

Nopeus, jolla suopa kertyy lipeäsäiliöiden pinnalle, on tärkeä useista syistä: Pintakuorman, eli säiliön pinta-ala suhteessa läpivirtaukseen, on oltava riittävä. Tämä usein ei ole tapaus, sillä tehtaita ajetaan usein suuremmassa tuotannossa kuin mihin ne on suunniteltu. Ajoittain suopa ei nouse odotetulla tavalla. Suovan saanto ja siten mäntyöljyn tuotanto riippuu siitä, miten paljon suopaa jää jäljelle lipeään välilipeäsäiliön jälkeen, eli miten suuri osa siitä kulkee eteenpäin soodakattilaan. Suopa ei tosin mene kokonaan hukkaan, sillä siellä se hyödynnetään sähkön ja lämmön tuotantoon. Tämä on kuitenkin vähemmän taloudellinen tapa käyttää suopaa kuin biopolttoaineiden tuotanto. Joskus soodakattila on pullonkaula, jolloin pyritään minimoimaan ylimääräinen kuorma.

Suovan nousutapahtumaa lipeän pinnalle ajatellaan usein siten, että pallomaiset hiukkaset liikkuvat ylöspäin tiheyseron vaikutuksesta ympäröivään lipeään nähden. Nousunopeuden määrää pääasiallisesti tiheysero ja nesteen viskositeetti. Sellaisen prosessin kuvaamiseen käytetään normaalisti Stokes:in lakia. Kirjallisuudessa on raportoitu laskelmia nousunopeudesta, mutta tulokset vaihtelevat suuresti syöttöarvojen mukaan. Koska tiheysero on pieni, laskelmat ovat herkkiä lähtöarvoille.

Tehtiin tehdastutkimus kuudessa tehtaassa, jossa lipeät tutkittiin mikroskoopilla ja valokuvattiin. Tutkimus osoitti, että malli, jossa pallomaiset hiukkaset nousevat ylöspäin, on liian yksinkertaistettu. Sinänsä Stokes:in laki kyllä soveltuu, mutta asiaan vaikuttavat myös muut tekijät. Malli ei anna riittävää perustaa suovan pinnalle kertymisen nopeuden laskemiseen. Vaikka oikea nousunopeuden arvo löydetäänkin, se ei riitä sellaisten laskelmien tekemiseen.

Tulokset osoittivat, että haihduttimissa ja siirtolinjoissa tapahtuva pumppaaminen hajottaa suovan pienemmiksi hiukkasiksi. Nämä hiukkaset voivat joko pysyä vapaina hiukkasina tai agglomeroitua. Todettiin, että agglomeroitumisaste vaihtelee suuresti. Joissakin tehtaissa hiukkaset pysyvät vapaina koko matkan haihduttamon läpi kunnes välilipeäsäiliö on ohitettu. Toisissa tehtaissa hiukkaset ovat melkein täydellisesti agglomeroituneet jo, kun lipeä tulee keittämöltä.

Lipeän seistessä syöttölipeäsäiliössä, agglomeraatit muuttuvat vähitellen isoiksi hiukkasissa, ts. hiukkaset yhdistyvät. Tämä prosessi on kuitenkin hidas, ja vaatii tunteja. Hiukkasten yhdistyminen parantaa niiden kelluvuutta, mikä parantaa erottumista. Pienten hiukkasten todettiin liikkuvan niin hitaasti, ettei niillä juurikaan ole mahdollisuutta nousta pinnalle tavanomaisten viipymäaikojen puitteissa. Ne voivat kuitenkin tarttua isompiin hiukkasiin näiden liikkuessa ylöspäin lipeän läpi. Ne voivat myös yksinkertaisesti yhdistyä muiden hiukkasten kanssa.

Kehitettiin mikroskopointiin perustuva menetelmä, jolla hiukkaskokojakauma voidaan mitata. Valmistetaan ohut lipeäpreparaatti, joka kuvataan. Samalla kuvataan myös mikroskooppinen skaala. Hiukkasten koko mitataan tämän jälkeen kuvasta skaalan avulla. Hiukkaskokojakauman mittaus antoi myös mahdollisuuden nousunopeuden mittaamiseen sen muuttuessa, kun annetaan lipeän seistä halutussa lämpötilassa tietyn ajan. Nousunopeuden mittaus rajoittuu kuitenkin pallomaisiin hiukkasiin, sillä epäsäännöllisten agglomeraattien koon määrittäminen on vaikeaa.

Projektin muut raportit tai julkaisut:

Niemelä, K. Sulphate soap separation and acidulation, Literature review on process improvements, KCL Reports 2720, STFI report CHEM 96, 2003.

Niemelä, K. Sulfate soap separation and acidulation, Part 2. Composition of the soaps, KCL Reports 2874, 2007.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, KCL Reports 2824, 2006.

Pajula, E., Sirén, K. Calcium carbonate scaling in black liquor evaporation, Part 2. Multivariate analysis of mill data, KCL Reports 2876, 2007.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, paper at the ABTCP-PI conference, Sao Paulo, Brazil, Oct. 17 - 20, 2005.

Sirén, K. Calcium carbonate scaling in black liquor evaporation, paper at the International Chemical Recovery Conference, Quebec, Canada, May 29 - June 1, 2007.

1 INTRODUCTION

Pulp mills have an interest in optimizing the yield of tall oil from the kraft process, because of economic values, but occasionally also in order to reduce the load in the recovery boiler. In the era of biofuels, the value of tall oil is increasing, as it can replace fossil oil in the production of motor and other fuels.

The yield of tall oil depends on both soap separation efficiency in the liquor tanks and acidulation efficiency. This study is focused on the former one. One factor that strongly influences the yield is the rate of rising to the surface in the feed liquor and intermediate liquor tanks. This rate depends on the size of the particles. Obviously, the yield is also strongly affected by technical factors, such as the retention time in the tanks, density fluctuations, possible short circuiting in the tanks, and other features. In spite of a large number of earlier studies, there still seems to be work to be done to improve the understanding of mechanisms in the process of soap separation.

2 OBJECTIVE

The objective of this study was to clarify factors that influence the rise rate and, if possible, to measure the rise rate of soap as a function of particle size. The aim was also to develop a method, based on microscopy, to measure the particle size distribution.

3 BACKGROUND

The process of rising of soap to the surface of black liquor in the tanks is often imagined as small spheres that migrate upwards, driven by a difference of density relative to the surrounding liquid. The rate of migration is determined mainly by the density difference and the viscosity of the liquid. Such a process is normally described by Stokes' law. Stokes' law was developed for settling particles, i.e. particles having a higher density than the liquid, but it can as well be applied reversely to particles rising due to lower density. Stokes's law is:

$$v = \frac{2ga2(d1 - d2)}{9\eta}$$
 (1)

where a is the radius of a spherical particle, d1 and d2 the densities of the particle and the surrounding medium respectively, and η the coefficient of viscosity.

Attempts to calculate the rise rate have been reported in the literature, but the results vary widely depending on the input values. The difference of density between soap and liquor is small, and minute changes of the input values produce quite different rise rates.

Kahila (1) studied factors influencing soap separation in 1967, and measured among other factors the yield as a function of time. A graph redrawn from Kahilas results is shown in fig. 1.



Fig. 1. Soap yield as a function of time in laboratory conditions.

The results indicate that part of the soap rapidly moves to the surface, but the remaining part, however, rises very slowly. The yield was surprisingly low. The soap that remains in the liquor consists of dissolved soap and particles that are so small that they do not rise to the surface in a reasonable time.

The literature on soap separation has been comprehensively reviewed by Niemelä (2) in another report of this project.

4 METHODS

A mill study was performed comprising six mills. The rising of the soap in black liquor was studied by examining particles in a microscope. Photographs were taken of liquors from the tanks, and occasionally from other locations along the evaporator train. The examination was performed at the mill immediately after sampling, in order avoid changes with time. The images were afterwards scrutinized for features describing separation mechanisms.

A method for determining the particle size distribution was developed, based on the images. Rise rates were determined on the basis of the changes of particle size distribution with time. Simulations were performed in order to reproduce the observed changes in particle size distribution, and thus to model the event.

Samples were taken of liquor from the cooking department entering the feed liquor tank, feed liquor leaving the tank, liquor entering the intermediate liquor tank and leaving the tank. Occasionally samples were also taken from evaporator effects. The preparation technique was as follows: A ring of silicon grease was applicated on a microscope glass. A drop of the liquor was taken with a pipette, and transferred to the glass inside the silicon ring. The grease prevented the liquor from escaping the area, and served as an aid in controlling the thickness of the preparate, when another glass was pressed on top. The preparate was then transferred to the microscope, and images were taken with a digital camera. The magnification in the microscope was normally 100 x but occasionally others, although zooming in the camera and subsequent treatment in the computer rendered the final magnification undefined. Therefore a microscopic scale was always photographed at the same occasion, and when the images of the scale and the particles were processed the same way, the size of the particles could be established.

5 OBSERVATIONS ON MECHANISMS

In the series of images presented below, the development of the soap appearance is shown along the evaporator train in the six mills.

5.1 Images from the mills

Mill A

Mill A cooked birch, pine and spruce in continuous cooking and SuperBatch cooking.

Images taken of wash liquor are shown in fig 2 a - b. In this mill the soap occurred as free spheres or to a limited extent bound to each others to agglomerates.

The liquor leaving the feed liquor tank is shown in fig 3. In the feed liquor unexpectedly large particles were still present. Large particles have a high rise rate (this is also evident from the results later in this report), and may not be expected to be present in the liquor leaving the tank. Possible explanations are that there is a short circuiting, i.e. the liquor travels directly from the inlet to the exit, without experiencing the desired retention time in the tank. Another explanation is that particles continuously merge in the tank, and larger particles are produced all the time. Later in this report this is shown to be true.



Fig 2 a - b. Mill A, weak liquor entering the feed liquor tank.



Fig 3. Mill A, liquor leaving the feed liquor tank.

Fig. 4 a and b show the liquor that enters the intermediate liquor tank. The soap material is the same that has leaved the feed liquor tank, but the appearance is quite different. The individual soap particles are smaller, and they are lumped together, or agglomerated. This is a result of the influence of the evaporator effects. The liquor repeatedly passes through pumps and runs along heat surfaces. This shatters the particles into numerous smaller particles. However, the mixing also brings particles together, and they stick together. The agglomeration obviously increases their buoyancy, and enhances their rise rate.

Two different factors can be distinguished from the graphs: Reduction of the particle size induced by pumping, which reduces the rise rate, and agglomeration, which enhances the rise rate.

The liquor leaving the intermediate tank is shown in fig. 5. In this liquor there is as well extensive agglomeration, but also free individual particles. However, the size of the individual particles is considerably smaller than in the incoming liquor.



Fig 4 a -b. Mill A, liquor entering the intermediate liquor tank.



Fig. 5. Mill A, liquor leaving the intermediate liquor tank.

Mill B

Mill B was a softwood cooking mill with continuous cooking. It had air injection for improvement of soap separation in the feed liquor tank. The injection was placed before the fiber sieve, so the wash liquor was already influenced by it.

The wash liquor is shown in fig. 6. The appearance of the soap is quite different from in mill A. The degree of agglomeration is extensive, and only small particles occur as free spheres.

In the feed liquor (fig 7) large particles are absent.

The images of the intermediate liquor were not satisfactory and are not presented.



Fig. 6. Mill B, wash liquor.



Fig. 7. Mill B, feed liquor. The image was exceptionally taken in 400 x.

Mill C

Mills C cooked birch, spruce and pine in continuous cooking. The mill had two feed liquor tanks in parallel, but the liquor was exchanged between them, so that both tanks contained both hardwood and softwood liquors. In this mill wash liquor is pumped several kilometers from another mill along a pipeline. In fig. 8 is shown the wash liquor from the main mill, and in fig. 9 is the wash liquor from the adjacent smaller mill.

There is a considerable difference in the appearance of the liquors. After being pumped through the pipeline, the soap from the smaller mill is completely shattered into an immense number of small particles. By polarized light it could be verified that the particles actually are soap (fig. 10). This gives further evidence of the influence of pumping.



Fig. 8. Mill C, wash liquor.



Fig. 9. External wash liquor coming in to mill C after pumping through a pipeline.



Fig. 10. The same liquor in polarized light. Soap particles appear lighter.



Fig. 11. Mill C, feed liquor.

The feed liquor is shown in fig. 11. The fine particles in the external mill liquor have disappeared. The liquor in this mill has a strong tendency of agglomeration. Most of the soap occurs in large agglomerates, and the space between them only contains minor amounts of small free particles. Comparing the images of the wash liquors and the feed liquor, it is evident that extensive merging of small particles has taken place in the feed liquor tank.

In the liquor entering the intermediate liquor tank (fig. 12), the extent of agglomeration is very large. Like in mill A, it is obvious that the soap has been shattered in the evaporator effects.

In mill C, some lumps of soap seem to escape the intermediate liquor tank (fig. 13).

The striking feature in mill C is the tendency of agglomeration that prevails all the way along the evaporation line. There also seems to be a strong tendency of merging, which appears also in the intermediate liquor tank. The individual particles in the agglomerate are larger than in the liquor entering the tank.



Fig 12. Mill C, Liquor entering the intermediate liquor tank.



Fig. 13. Liquor leaving the intermediate liquor tank.

Mill D cooked softwood by SuperBatch.

Images of the liquors are shown in figs. 14 - 17. The remarkable feature in mill D is the absence of agglomeration, in contrast to mill C. This feature prevails all the way to after the intermediate liquor tank. The particles appear small compared to the other mills. Problems with soap separation were not reported.

Comparing figs. 15 and 16, the shattering in the evaporator effects is visible.



Fig 14. Mill D, wash liquor. Slight polarization was applied in order to enhance the particles.



Fig. 15. Mill D, liquor leaving the feed liquor tank.



Fig. 16. Mill D, liquor entering the intermediate liquor tank.



Fig 17. Mill D, liquor leaving the intermediate liquor tank.

Mill E

Mill E was a softwood cooking mill with continuous cooking. It had air injection in the feed liquor tank. The air injection was temporarily shut off and on during the microscope study, in order to study its effect.

The wash liquor with the air injection on is shown in fig. 18 a - b. The images can be compared with fig. 19, where the air injection was shut off during the study. The size distribution and the degree of agglomeration are clearly different. Air injection scavenges the liquor from particles, and causes an increase in agglomeration. It appears that the injection has the intended effect. When the injection is on, only small particles remain free in the liquor.

The feed liquor leaving the tank is shown in fig. 20. It is fairly free from large particles.

The liquor entering the intermediate liquor is shown in fig. 21. Having passed through the rear end of the evaporator train, the particles have largely agglomerated. Few particles are completely free.

The liquor that leaves the intermediate liquor tank is shown in fig. 22. It has a remarkably low content of soap. They yield appears to be very high in this mill.



Fig. 18 a - b. Mill E, wash liquor, air injection on.



Fig. 19. Mill E, wash liquor, air injection off.



Fig. 20. Mill E, feed liquor leaving the tank.



Fig 21. Mill E. Liquor entering the intermediate liquor tank.



Fig. 22. Mill E, liquor leaving the intermediate liquor tank.

Mill F

Mill F was a continuously cooking mill, cooking both softwood and hardwood with SuperBatch.

Mill F was exceptional in that the wash liquor contained soap at one point of time, but at another point of time hardly any soap could be detected. This is shown in figs. 23 and 24. The feed liquor was also very poor in soap (fig. 25). This was thought to be a feature of SuperBatch cooking, where the liquor that enters the evaporator may vary with time. Another reason to the situation probably was that the study was made right before midsummer, and the soap content of the wood had probably already diminished. Mill F was less informative for the study than the other mills.

The feed and intermediate liquors contained a grainy material that could not with certainty be identified as soap. This is shown in figs. 26 - 30.



Fig. 23 Mill F. Wash liquor.

Fig. 24. Mill F, wash liquor at a later point of time.



Fig 25. Mill F, feed liquor.



Fig. 26. Mill F, the same liquor taken in 400 X magnification.



Fig. 27. Mill F, liquor entering the intermediate liquor tank.



Fig. 28. Mill F, the same liquor, 400 X.



Fig. 29. Mill F, liquor leaving the intermediate liquor tank.



Fig. 30. Mill F, same liquor, taken in magnification 400 x.

5.2 Various observations

5.2.1 Merging

The images of the mill study provided material for some other observations. One such observation is the process of fusion or merging of particles into each other. Fig 31 shows such a fusion in proceeding.



Fig. 31 Mill F. Wash liquor, after 3 h. Big particle has collected smaller ones.

It is clearly visible how the bigger particle has collected smaller ones, and they have begun to merge. The process is, however, slow. It was followed a number of times during the microscope study, where a single group of particles could be held at the focus for some time. The process requires hours, but in particular in the feed liquor tank the retention time is sufficient to effect rather substantial merging. When such merging occurs, it obviously increases the rise rate.

In the liquor leaving the feed liquor tank unexpectedly large particles were occasionally found, even larger than in the incoming wash liquor, as is seen for example in the images 2 and 3 from mill A. This is obviously due to that the wash liquor just has passed a pump, and the soap has been shattered to some extent. The liquor leaving the tank has been in silent conditions for many hours, with subsequent fusion or merging of particles and thus growth.

5.2.2 Different phases

Soap is often considered as one material. However, two immiscible phases are clearly distinguishable. One is more fluid than the other, with a tendency to spread along the surface of the microscope glass. This phase does not polarize light, while the stiffer phase polarizes. This is visible in the images 32 a and b from mill A. The latter image is taken in half polarization, revealing how the stiffer phase polarizes.



Fig 32 a and b. The same material photographed with and without polarization.

How this is related to composition was not attempted to clarify in this study. It is possible that one phase is rich in resin acids, while the other one is rich in fatty acids. The images did not reveal any clear difference between softwood cooking and hardwood cooking mills.

5.2.3 Interaction with fibers

There may be confusion regarding the attraction of soap and fiber to each other. This issue is given clarification in the image series below. Wash liquor from mill E was left to stand on a water bath for 90 min. Liquor was pipetted out from the extreme bottom of the vessel, where some fiber material had settled. Images were taken at different focusing depths of the preparate. The graphs are shown in figs. 33 a - d.







Fig. 33 a - d. Fibers and soap in different focusing depths.

The series of images show that the fibers, when focusing to the bottom of the preparate where they had sunk, did not contain any remarkable amounts of soap (a), at least in the form of particles. When lifting the focusing upwards, to the upper surface of the preparate, the soap particles appeared (b,c,d). In the upper part of the preparate the soap particles are free and not entangled in fibers (d). Thus, the fibers sank to the bottom and the soap floated to the surface. Soap and fibers did not have any remarkable affinity for each other, but were completely free from one another.

5.3 Summary of observations

The present study showed that the commonly adopted model of soap rising in the form of free spheres is oversimplified. The process is much more complicated, involving several different mechanisms. The images allow several conclusions to be made.

The images of samples along the evaporator line in mills A - E clearly show that an essential factor that influences the particle size is the pumping of the liquor, and possibly also the flow along the heat surfaces in the evaporator effects. The soap is shattered into smaller particles. This view of the mechanism is strongly supported by the mill case C (fig. 9), where the long transfer pipeline enhances this process. However, the small particles also seem to agglomerate as a consequence of the agitation. They are more easily brought to contact with each other. Agglomeration obviously must increase the

buoyancy, and enhance the separation. Attempts to model the separation process obviously have to take these factors into consideration in order to be successful.

There are considerable differences in the degree of agglomeration between mills. Particularly striking is the difference between mills C and D, when examining for example the feed liquor. In mill C there are very few free particles, while in mill D almost all particles are unagglomerated. Both cases are softwood liquor. Mill C uses, however, continuous cooking, while mill D has SuperBatch cooking.

6 PARTICLE SIZE DISTRIBUTION

Particle size distributions are of interest in the first place because they can provide basic data for calculation or estimation of the rise rate. A future aim is to be able to model the whole process of soap separation. Such a model could be used for optimizing the process and for trouble shooting. This requires full understanding of not only the rise rate, but also of all other mechanisms that are involved. Issues that may be addressed are for example how does the shattering caused by pumping influence the rising, what are the reasons to agglomeration or not agglomeration, and how does agglomeration influence the rise rate? The yield of soap is influenced by the number or fraction of small particles, because they rise too slowly to reach the surface in the available time, and will therefore remain in the liquor and go to the recovery boiler.

Particles within agglomerates can also be measured, to the extent they have maintained a measurable shape. The information that they provide are in this case somewhat different from that of the free particles. It is more difficult to estimate the rise rate for an agglomerate than for a free particle, because it is more difficult to determine its volume, and because the resistance to movement in the medium is different from that of a spherical particle.

The degree of agglomeration can be roughly estimated by counting the number of particles visible in an agglomerate, seen in the two-dimensional plane, and assuming that the lump has approximately the same shape in the depth or third dimension. This is, however, a cumbersome operation.

6.1 Microscopy and image treatment

The optimal magnification for taking images for particle size measurements was found to be 100 X. In larger magnifications all particles could not be photographed at the same focusing depth. Mostly the images were taken in black and white. This allows faster processing in the computer.

At the beginning of each photographing series, an image of a microscopy scale was taken. The division of the scale was 0,01 mm, i.e. 10 μ m. The image of the scale was processed the same way as the other images. In the subsequent desktop study of the images, a paper printout was taken, including the scale image. A transparent scale stick

was prepared by copying a millimeter scale to such a size that one unit corresponded to 2 μ m on the image. This way the size of the particles could be measured under a magnifying glass in steps of 2 μ m from the paper printout. A number of particles were measured, using 2 - 30 images, until a number of satisfactory statistical representativity was obtained. The sizes were transferred to an Excel table. The particle size distribution was plotted. One size class comprised 2 μ m.

Particles below 5 μ m were not used, because it could not readily be verified that they actually were soap particles, and not some other material. Larger particles could be identified as soap by means of polarized light. Particles below 5 μ m were occasionally abundant, influencing the number distribution too strongly, covering the more interesting larger sizes.

6.2 Number and volume distributions

The basic way of presenting particle size distributions is to plot the number of particles or its fraction as percent versus the particle size. In this type of plot, the smallest particles get a dominating role, since they are usually most abundant. Most of the soap material is, however, located in the large particles. The large particles are therefore of particular technical interest. Studying the plots, it is necessary to pay attention to the large size end. Here frequently occurs only one particle in a size class, but nevertheless it contributes significantly to the quantity of the soap that the plot covers.

A way to get a better conception of how the soap is distributed among the particles, is to use a volume plot may be used. A prerequisite is that there are free spheres of soap whose size can be measured, or at least estimated if they are in an agglomerate. Large agglomerates are complicated to estimate. If there are measurable spheres, not extensively covered by agglomerates, they can easily be recalculated to volume. If desired, the volume distribution plot can be converted into a mass plot by using the density.

6.3 Particle size distributions

Below are shown some selected particle size distributions. The aim is in the first place to present the technique as a tool, and not to make conclusions about process performance in different mills. At the present stage, it is still to a large extent open how the distribution curves can best be utilized in order to optimize the process or to trouble-shoot it. The results presented here are only the first steps in a new direction of research, and the possibilities it may open are only taking shape.

In figs. 34 - 37 the distribution curves for liquors along the evaporation line are shown for mill A.

The typical shape for wash and feed liquors is that small particles are abundant and the number in each class decreases towards larger particles. The distributions greatly remind

those of crystallization. However, there is a long tail towards bigger particles. Here there are usually only one or two particles in each class.

In the feed liquor (fig. 35), somewhat surprisingly, the tail is even longer than in wash liquor (fig. 34), i.e. bigger particles occur. This is in spite of that the bigger particles rise quicker to the surface during the time in the tank. This is explained by that there is a continuous fusion of particles with each other during the tranquil conditions in the tank, in contrast to the wash liquor, where the soap just has been shattered by a pump.

The situation by the intermediate liquor tank is shown in figs. 36 and 37. It is to be noted that in the intermediate liquor the majority of the particles are in agglomerates, and not as free individual particles. Free particles were counted separately, and are included in the graphs.

The liquor entering the intermediate liquor tank (fig. 36) is compositionally the same as the one that left the feed liquor tank. However, the large particles have disappeared. The change is thus the effect of the pumping and movement in the rear end of the evaporator train. Note that here the y-axis is drawn not as percent but as number.

In the liquor leaving the intermediate liquor tank, the largest particles have disappeared, and the remaining soap material is very fine-grained. This material represents the yield loss, together with the soap that is actually dissolved to a true solution. The particles can be regarded as an unnecessary yield loss, because in principle they should be possible to separate mechanically, contrary to the truly dissolved soap.



Fig 34. Size distribution in liquor entering the feed liquor tank. Note long tail of large particles.



Fig. 35. Size distribution in liquor leaving the feed liquor tank. Note biggest particles.



Fig. 36. Liquor entering the intermediate liquor tank. Free particles are presented separately.



Fig. 37. Liquor leaving the intermediate liquor tank.

In Fig. 38 and Fig. 39 are shown distributions from wash liquors of two other mills, E and F. These examples show that considerable differences occur between mills. In mill F the medium size range is coarser, but the biggest tail seen in mills A and E is missing.



Fig. 38. Size distribution in wash liquor of mill E.



Fig. 39. Size distribution of wash liquor in mill F.

6.4 Volume distributions

The distributions for wash liquors were recalculated to volume, and are shown in figures 40 - 42.



Fig. 40. Particle size distribution by volume, mill A.



Fig. 41. Particle size distribution by volume, mill E.



Fig 42. Particle size distribution by volume, mill F.

The measurements of volume distributions illustrate the importance of the large particles relative to the small ones. Although they appear as very few in the number distribution, like for example in fig. 38 Mill E, they contain a very large fraction of the soap. For example in fig. 41 the two biggest particles contain about 40 % of the total soap content in the studied group of particles.

6.5 Largest particles

It is of interest to get a view of how large particles actually have been present in the liquors, especially in the feed and thin liquors. The volume that is taken to a microscopy preparate is rather small, and the bigger the particles, the less abundant they are. The chances that a particle happens to be in the preparate volume is smaller the bigger the particle. However, by examining the material that has floated to the surface or its vicinity, it is often possible to get a view on this issue. Merging of the material is slow,



Fig 43. The largest found particles in mill A, feed liquor, and the scale.

and shapes are usually distinguishable for a considerable time. Fig 43 shows a collection of big particles from mill A. In all other mills the biggest particles were smaller than in this mill. The scale that was photographed at the same occasion is also shown. The largest particles that occurred were slightly below 0,2 mm or 200 μ m.

7 RISE RATE

The rise rate of soap has been subject of considerable interest through the years, and a number of studies have been reported. Mostly the studies have been theoretical, and the results vary considerably depending on the starting assumptions. A model of spherical particles has usually been applied. It is fairly easy to measure experimentally how quickly soap gathers on the surface of the liquor, as was done for instance by Kahila (1). These methods, however, measure a sum of factors, and they tell very little about the underlying mechanisms or the influence of particle size. On the other hand, they allow easier and more accurate determination of the total gathering of soap than will probably ever be possible by modeling or calculating. Therefore the different methods should be seen as techniques that support and complement each other, and not compete with each other.

As is evident from the results presented in the earlier sections, the model of spherical particles rising through the liquor is too simplified to describe the separation process. It does not take into account agglomeration with formation of non-spherical clusters, collection of smaller particles onto bigger ones as these migrate upwards, simple fusion of particles on quiet standing, or interaction between particles that disturb their free movement upwards. Even if accurate figures on the rise rate of a spherical particle can be obtained, it appears too optimistic to calculate the rate of separation solely on this basis. Nevertheless, the rise rate of a spherical particle is of fundamental importance. It can be considered as a reference point, to which other mechanisms can be added.

Particle size distributions, and the changes in them with time, provide a new basis for experimental determinations of the rise rate. The method described in the previous chapter was employed for this measurement. The size distribution was determined after various time periods at different depths, i.e. liquor column heights. Rise rates were then calculated on the basis of the changes in the size distribution.

It is well known that the size of the soap particle influences the rate of movement. When we consider a narrow depth zone in a column of liquor standing still, we may assume that particles of different size migrate into the zone from below and out from the zone upwards. If the height of the column is such that new particles are supplied all the time from the liquor below, we expect no change in particle size distribution. If, however, the studied zone is so close to the bottom that new particles no longer are supplied, we get a depletion of such particles. The large particles will disappear first, and with time smaller and smaller particles will disappear from the distribution curve. Thus, this depletion zone is the one that provides information of the rise rate. If the rise rate of a particle is such that the particle at a given time period moves a distance greater than the distance from the bottom to the height of sampling, then it cannot exist in the sampling zone. Particles are randomly distributed in the liquor, and those that happen to be located higher up migrate out of the zone sooner. Those that are at the bottom of the sample, however, provide the desired information. When the drop is taken out, the biggest particles have already passed, but those that have exactly such a rate that makes them migrate the distance from the bottom to the sampling zone, will be the biggest particles found in the drop. Thus, when the particle size is measured, the edge of the size distribution represents the particles that have a migration rate corresponding to the time and distance.

In principle the method can be employed for non-spherical soap particles as well as for spherical ones. However, determination of the size of a non-spherical particle, i.e. an agglomerate of particles, is considerably much more difficult than in the case of a neat sphere. The two-dimensional image only permits rough estimates of the volume of the irregular agglomerate. For this reason in this study rise rates were investigated only for spherical particles.

7.1 Size distribution changes with time

Immediately after the sampling from the tank the liquor was transferred to a water bath, and was kept there at controlled temperature for a certain time period. The temperature of the bath was adjusted to that of the feed liquor and intermediate liquor tank respectively. At certain points of time after sampling a small amount of the liquor was pipetted from different depths in the liquor. The used column heights were 1 cm and 12 cm. The time span ranged from 0 min to several hours. Mill A was chosen as the primary case, because of a limited degree of agglomeration. Rise rates were investigated in wash liquor and feed liquor.

In figs. 44 a - d the change in particle size distribution is demonstrated. The y-axis is expanded so that the bigger particles are better visible. In a, the wash liquor was directly transferred to the microscope. The biggest particle found was 76 μ m. After 25 min the big particles were thinned out, and the biggest found particle at 12 cm column height was 56 μ m. An image of this liquor is shown in fig. 45. At a column height of 1 cm, the biggest particles were after 45 min 34 μ m. Fig. 46 shows an image of this situation. At 65 min the biggest particles were 22 μ m at the same depth. An image is shown in fig. 47. After 1h 45 min, no bigger particles than 18 μ m were found at 12 cm.

The series of graphs and images demonstrate how big particles disappear from the sample drop as a function of time and sampling height. The same procedure was applied for feed liquor.



Fig. 44 a. Wash liquor, 0 min.



Fig. 44 b. After 25 min, column height 12 cm.



Fig. 44 c. After 45 min, column height 1 cm.



Fig. 44 d. After 65 min, column height 1 cm.



Fig 44 e After 100 min, column height 12 cm.



Fig. 45. After 25 min at 12 cm height.



Fig. 46. After 45 min at 1 cm height.



Fig. 47. After 65 min at 1 cm height.



Fig. 48. After 100 min at height 12 cm.

7.2 Calculation of rise rate

As described above, the largest particle present should represent the size where the rise rate corresponds to the height and time of the sampling point. However, some practical factors cause inaccuracy. The bigger the particles, the less abundant they are. The microscope image covers only a small volume, and it is therefore to some extent a matter of chance if the biggest particle is found. For that reason, many images need to be taken, to cover as large surface as possible. In order to obtain a more precise estimate of the size of the biggest particle "edge", the following procedure was employed: The number of particles in each size class was converted to its natural logarithm. The logarithm was then plotted against the particle size. This causes the distribution to fall on an approximately straight line, at least over a section. A line was then fitted, and its intersection with the x-axis was determined. Based on a larger portion of the distribution curve, a more precise edge point could be pinpointed than if the largest particle was read directly. This approach improved the repeatability and accuracy of the procedure. The process is illustrated in fig. 49.





When the largest particle edge could be determined with satisfactory accuracy, the rise rate could be calculated. The primary subject of the study was mill A, in which the soap particles were rather well shaped as spheres, with a minimal degree of agglomeration. The study was confined to wash liquor and feed liquor, because in the intermediate liquor the agglomeration was too extensive.

In fig. 50 and Fig. 51 the rise rate is shown as a function of particle size.



Fig. 50. Rise rate as a function of particle size, mill A.



Fig. 51. Rise rate as a function of particle size, mill A, the axes expanded in order to show the small particle end clearer.

The results show that the rise rate varies over a very large range depending on the particle size. Particles below roughly 30 μ m have an extremely small rise rate. The rate in this range is in the order of 1 mm/min or less, which means that they will migrate only about 6 cm per hour, and occasionally even less. Such particles have very small chances to reach the surface in a feed liquor tank during a normal retention time of 6 - 10 h. This also becomes evident in scrutinizing the graphs in fig. 44 . For example in 44 d there are still particles of sizes above 30 μ m after 45 min at a height of 1 cm from the bottom of the vessel.

At large sizes, above roughly 100 μ m, the rise rate increases rapidly. The largest particles could start at the bottom of the tank, and reach the top in one hour.

The technical implications of the results may be discussed. The bulk of the soap is contained in the large particles, as can be concluded for instance from the figure fig 41. Here two particles in the measured distribution contain around 40 % of the soap volume, although greatly outnumbered by the smaller ones. Thus, the scarce looking big particles in the distribution curve are far more important with respect to soap separation than the small ones. However, the small ones that never reach the surface by direct migration will influence the residual soap that is not separated, i.e. the yield. The results indicate that the only way the small particle soap can reach the surface is by some other mechanism than direct rising. Such mechanisms may be collection on bigger particles as these rise, merging to bigger particles, or agglomeration to flocks with higher buoyancy than separate particles. Technically, if the objective is to improve the yield, a possible measure would be to employ air injection in the intermediate liquor tank as well as in the feed liquor tank.

The results show that the variation of the rise rate with particle size is much larger than earlier studies have indicated.

Using this method, some caution is necessary. If the largest particles in the initial studied liquor are smaller than the edge size at a studied time and height, the biggest particle will be wrongly estimated, i.e. an even bigger particle would remain if it had only been present in the liquor. Therefore samples should be taken at several points of time, until it is ascertained that the critical edge has moved over the sampling height.

7.3 Comparison with simulations

In order to test our understanding of the rising process, it is expedient to simulate it, and compare the results with the experimental ones. Any deviation indicates the presence of factors that are not included in the simulation model. A simulation system was built in Excel according to the basic simple model described below.

The distance s that a particle migrates in a given time period is:

$$s = v . t$$
 (2)

where v is the velocity or rise rate and t is the time.

If a particle at the starting time is located at the height h_o in the liquor column, then the new position h of the particle after time t is:

$$h = h_0 + v . t$$
 (3)

Thus the model takes into account only rising upwards at constant rate.

A large number of particles, with a size distribution corresponding to a liquor at time zero, are scattered over the depth of an imaginary liquor column, by means of the random number generator in Excel. This is shown in fig. 52. Each particle is then given an initial rise rate. After a period of time, the new position of each particle is calculated according to equation (2). A plot is shown in fig. 53. A depletion zone is formed in which no particles of a certain size are present. As described earlier, the depletion zone is formed at the bottom of the vessel, as a result of that no new particles of the size are provided from below. The size distribution of particles within a narrow depth zone is plotted. The used width of the "height window" or "depth window" was here 2 mm. This was considered to be rather close to the depth range that is suck by the pipette in the practical experiment. Since only a small number of particles will fall inside the height window in the simulation, the generation of random particles was repeated a large number of times, up to thousands of times, by means of a macro. This way a fairly good distribution curve could be obtained. The obtained distributions could then be compared to experimentally determined distributions.



Fig. 52. Particles randomly distributed over a column height.



Fig. 53. Development of a depletion zone and a size edge.

If in the studied zone a size class somewhere to the left of the size edge is examined, the expected development is that the number of particles is not changed with time, because new particles migrate in from below while at the same time others migrate out from the

top. Only when the size edge is exceeded, the feed of particles from below will stop, and the number of particles in the zone will suddenly drop to zero. Thus, looking at different time periods, the number of particles smaller than the size edge should remain approximately unchanged, while the size edge should move from the coarse end towards smaller sizes with time. This is in good agreement with the measured size distributions from the mills.

Below is shown a comparison between measured and simulated results for mill A, feed liquor (fig. 54 - 57). In the figures is shown both the whole fit and a fit with the y-axis expanded, so that the bigger particles become better visible.

The main difference between simulated and measured results is at 1 min. The examined point was close to the surface, only 1 cm below it, and it is possible that large particles crowded in this area, disturbing the free rise of each other. At longer periods of time the agreement is good.

It is very evident from the graphs how the size edge moves to the left as time increases or the column height is reduced. Note that when the y-axis is presented as percent, the value changes because the total number of particles changes as the large ones disappear, and therefore the classes will not remain quite constant.





Fig 54. Simulated and measured distribution at 1 min and 12 cm column height. a) the whole distribution b) expanded y-axis to make the big particles better visible.







Fig. 55 a - b. Simulated and measured distribution at 5 min and 12 cm column height.





Fig. 56 a - b. Simulated and measured distribution at 60 min and 12 cm column height.

61





Fig. 57 a - b Simulated and measured distribution at 60 min and 1 cm column height.

Simulated rise rates as a function of particle size are shown in fig. 58.



Fig. 58. Rise rate according to simulations.

The simulation results shows that the basic model (equation 3) describes the rising behavior of spherical particles in the test conditions quite well. It must be emphasized that the conditions in the experiment were different from those in the mill liquor tanks. The column was low, which means that particles were not fed from below in the same way as in the liquor tanks, where big particles may rise from several meters below. The time period was not long enough to produce extensive merging. Therefore other mechanisms that operate in the mill liquor tanks could be stripped off, and the rise rate alone could be studied.

8 CONCLUSIONS

The mechanisms of the soap separation process were investigated in mill conditions. Plain microscopy was shown to be a useful tool in clarifying separation mechanisms and measuring rise rates. From simple microscope images several conclusions can be made regarding the phenomena that are involved when soap rises to the surface of the liquor tank.

Soap is frequently thought of as spherical particles that migrate upwards in the liquor. It is assumed that the rate at which the soap is accumulated on the surface of the liquor can be calculated if only the rise rate of individual particles is known. Attempts have been made to calculate the rise rate according to Stokes' law, which describes sedimentation, or rising, of spherical particles, as a function of difference of density and viscosity of the medium. From the results of this study it is, however, evident that this model is grossly oversimplified. The microscope images show that there are considerable differences in the appearance or morphology between mills and between different locations in each mill. The most distinct variation is seen in the degree of agglomeration. In the wash liquor and feed liquor, i.e. liquors entering and leaving the feed liquor tank, only in mill D soap occurred almost entirely as free spheres, with a minimal degree of agglomeration. In mill A the degree of agglomeration was so small that the model of free spheres had satisfactory justification. In mills E and F there was more agglomeration, but in mill C only small particles occurred as free, the bulk of the material being completely agglomerated. In the last case there is obviously no possibility to calculate the rise rate by means of the model of free spherical particles. No correlation with wood species could be identified.

In all mills there was a considerable difference between feed liquor tanks and intermediate liquor tanks. In the intermediate liquor tanks the soap mostly occurred as agglomerates of small particles. The only mill with only limited agglomeration was mill D. It is obvious that the soap has been shattered into small particles during its way through the rear end of the evaporator train. For intermediate liquor tanks it is obvious that the model of free spheres is not applicable. The model has some justification only in feed liquor tanks, and there only in part of the cases.

Pumping and flow along the heat surfaces in the evaporator effects obviously are the most important factors that influence the size of individual particles. In mill C wash liquor was pumped a long distance through a pipeline before it entered the feed liquor tank. Fig. 9 shows how this causes the soap to be shattered into numerous minute particles. This observation strongly supports that pumping breaks down the particles. However, the circulation in evaporator effects also produces an opposite factor, i.e. that particles are brought together, and agglomerate. Agglomeration causes formation of larger particles that possess a greater buoyancy, and thus obviously increases the rise rate. Due to the irregular shape, rise rate of agglomerates is difficult to estimate.

Standing still in the liquor tanks on the other hand has the reverse effect than pumping, causing particles to merge. This was observed in many cases during the study. Fig. 31 shows an example of this process. The process is slow, being an issue of hours. However, the retention times in the feed and intermediate liquor tanks are sufficient to bring about changes. This mechanism thus improves soap separation.

The rise rate of small particles was shown to be so slow that they have practically no possibilities to rise to the surface during normal liquor retention times in the tanks. Large particles and agglomerates rise rapidly, while small particles virtually stand still. From this follows that the large particles must collide with the small ones on their way up, thus collecting them. This mechanism is visible in fig. 31. Also this mechanism improves soap separation. Considering that the distance a large particle may migrate through the liquor may be up to the order of 10 m, the probability of collisions is very high. Thus, the possibilities for small particles to rise to the surface are dependent on several mechanisms, agglomeration, merging and collection by bigger ones. Yet another mechanism may influence, i.e. air or gas bubbles. Such bubbles occur also in mills that do not employ air injection.

A method was developed for measurement of soap particle size and particle size distribution, based on microscopy. A problem in the measurement is that soap consists of at least two separate phases, one being more fluid than the other. The latter tends to float out along the surface of the microscope glass, thus making it difficult to judge its original shape when it moved freely in the liquor. The former phase causes polarization in the microscope, the latter one does not. The fluid phase occurred also in plain softwood cooking mills, and is therefore not associated with birch. Measurements of the volume of agglomerates were not attempted. In this case a possible approach appears to be the use of a shape factor.

Measurement of particle size distribution also opens opportunities to measure the rise rate, although restricted to spherical particles, unless proper estimates for the size of agglomerates can be made.

The rise rate of spherical particles could be estimated. As is evident from the results presented above, the model of rising spheres is oversimplified. Even if the rise rate of spheres is available, it appears unlikely that it would be possible to calculate the quantity of soap that can be skimmed from the surface as a function of time. In particular in the intermediate liquor tank, the most common form of occurrence is agglomerate. Agglomerates undoubtedly have different resistance to movement in the liquor than spherical particles.

In spite of that the microscopy method may not be the optimal method for predicting soap collection rate, it is an expedient tool for studying fundamental mechanisms. Insight in the fundamental mechanisms is necessary in solving problem situations in soap separation, as well as in optimizing and modeling the process.

REFERENCES

1. Kahila, S. Suovan eroaminen mustalipeästä, KCL, unpublished results (1967).

2. *Niemelä, K.* Sulfate soap separation and acidulation , Part 2. Composition of the soaps, KCL Reports 2874, 2007, 70 p.

SUOMEN SOODAKATTILAYHDISTYS RY RAPORTTISARJA

- 1/2006 Suomen Soodakattilayhdistys ry Konemestaripäivä 26.1.2006, esitelmät Sokos Hotelli Seurahuone/Laminating Papers Oy, Kotka (16A0913-E0072) 18.1.2006
- 2/2006 Suomen Soodakattilayhdistys ry Soodakattila-alan yhteistoiminta Vuosikertomus 2005 (16A0913-E0073) 30.3.2006
- 3/2006 Suomen Soodakattilayhdistys ry Vuosikokous 30.3.2006, If Vahinkovakuutusyhtiö Oy, Helsinki Pöytäkirja (16A0913-E0074)
- 4/2006 Suomen Soodakattilayhdistys ry Soodakattilapäivä 1.-3.11.2006 Viking Line (16A0913-E0075)
- 5/2006 Suomen Soodakattilayhdistys ry Soodakattilan vastaanottokokeet Materiaali- ja energiatase Esa Vakkilainen, Pöyry Forest Industry Oy (16A0913-E0078) 4.12.2006

SUOMEN SOODAKATTILAYHDISTYS RY RAPORTTISARJA

- 1/2007 Suomen Soodakattilayhdistys ry Konemestaripäivä 25.1.2007, esitelmät Kulttuurikeskus, Kemi / Oy Metsä-Botnia Ab, Kemin tehdas / Hotelli Cumulus Kemi (16A0913-E0079) 12.1.2007
- 2/2007 Suomen Soodakattilayhdistys ry Mustalipeän sisältämien rikkiyhdisteiden haihtuvuudet eri tehtailla Paterson McKeough ja Eero Leppämäki, VTT (tutkimusraportti VTT-R-00513-07) (16A0913-E0080) 22.1.2007
- 3/2007 Suomen Soodakattilayhdistys ry Sähkösuodintuhkan puhdistus ja käsittely Osa III, Kuljetusmuoto ja radioaktiivisuus Kurt Sirén, 12.12.2006 (KCL työ 0522546) (16A0913-E0081) 26.2.2007
- 4/2007 Suomen Soodakattilayhdistys ry Soodakattila-alan yhteistoiminta Vuosikertomus 2006 (16A0913-E0082) 29.3.2007
- 5/2007 Suomen Soodakattilayhdistys ry Ohje soodakattilan päästöjen laskentaan (16A0913-E0084) 19.4.2007
- 6/2007 Suomen Soodakattilayhdistys ry Vuosikokous 29.3.2007, Alstom Finland Oy, Vantaa Pöytäkirja (16A0913-E0085)
- 7/2007 Suomen Soodakattilayhdistys ry Soodakattilan päästömittausten menetelmät Pekka Jussila, Pöyry Forest Industry Oy (16A0913-E0086), 14.6.2007
- 8A/2007 Suomen Soodakattilayhdistys ry Kartläggning av tungmetallsfördelning i och omkring sex sodapannor Freya Emilia Böök, diplomarbete, Åbo Akademi, 11.5.2007 (16A0913-E0087), 25.6.2007
- 8B/2007 Suomen Soodakattilayhdistys ry Soodakattiloiden raskasmetallitaseet Loppuraportti perustuen diplomityöhön, Freya Böök, Jukka Konttinen, Mikko Hupa, Åbo Akademi, 5.12.2006 (16A0913-E0088), 25.6.2007
- 9/2007 Suomen Soodakattilayhdistys ry Soodakattilapäivä 18.10.2007 Sokos Hotel Vantaa (16A0913-E0090)
- 10/2007 Suomen Soodakattilayhdistys ry
 Sulpafate soap separation and acidulation, Part 2. Composition of the soaps.
 Klaus Niemelä, KCL Reports 2874, 30 July 2007 (16A0913-E0091) 30.10.2007
- 11/2007 Suomen Soodakattilayhdistys ry Mechanisms and rate of soap separation Kurt Sirén, KCL Reports 2875, 8 August 2007 (16A0913-E0092) 30.10.2007