Tall Oil Soap Recovery

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Abstract

This article describes what tall oil soap is and how much should be recovered based upon the wood supply, and season of the year. It further describes the benefits of good recovery including improved evaporator and recovery boiler throughput and reduced effluent toxicity. Process variables that affect soap solubility are discussed and related to how pulping process changes affect where soap separates. Soap removal during washing is discussed as well as those variables that most affect soap skimming efficiency. Methods for improving soap skimming efficiency and guidelines for soap handling equipment are also discussed. Factors affecting soap liquor separation during storage and handling prior to acidulation are also discussed. Considerations affecting the recycle of tall oil plant brine are presented.

Introduction

What is Tall Oil Soap?

The alkaline pulping of softwoods in the kraft process converts the resin acids and fatty acid precursors in wood to their sodium salts. Associated with the salts are neutral or unsaponifiable compounds, including phytosterols. The salts and unsaponifiables separate from the spent kraft cooking liquor as "black liquor soap". A good rule of thumb is that it requires about 2 tons of soap to produce 1 ton of crude tall oil.

"Black liquor soap naturally separates from black liquor at various points in the pulping process. The soap separates as a lamellar liquid crystalline phase (36). It is this phase separated material that may be observed floating in pulp washer vats, at the surface of filtrate and weak black liquor tanks, and in large amounts at the foam tower and black liquor soap skimmer. The black liquor soap skimmings are collected from various locations and are pooled together in a central holding tank where the skimmings are held prior to acidulation" (37).

Black liquor soap skimmings (BLSS) consist of a mixture of fatty and rosin acid salts, (i.e., anionic surfactants), fatty and rosin acid esters, and neutral components. Black liquor soap skimmings, being a natural product, contain hundreds of different compounds. The predominance of a given constituent varies with tree species, pulping chemistry and genetic factors. The fatty acids are predominantly oleic and linoleic acids with small quantities of linolenic, stearic and palmitic acid. The rosin acids are monocarboxylic diterpene acids having a general formula $C_{20}H_{30}O_2$. The predominant rosin acids are abietic and de-hydroabietic acids, although numerous distinctive isomers occur. Both abietic and dehydroabietic acids contain three six-membered rings. Dehydroabietic acid contains one aromatic ring, and thus differs from abietic acid, which contains three unsaturated rings. The neutral fraction, often called unsaponifiables, is a mixture of a variety of substances including phytosterols, fatty and wax alcohols, terpenes and hydrocarbons (4).

Table 4.3.1. Composition of crude tall oil

	South-eastern USA	*Northern USA & Canada*	*Scandinavia*
Acid No. (1)	165	135	132
Saponification Number (2)	172	166	142
Resin Acids %	40	30	23
Fatty Acids %	50	55	57
Unsaps %	8	15	20

1. Acid Number - The number of mil-equivalents of potassium hydroxide required to neutralize one gram of tall oil. (1)
2. Saponification Number - The number of mil-equivalents of sulfuric acid required to neutralize one gram of tall oil that has been saponified with potassium hydroxide.

The extractives in black liquor are partially solubilized and, as a result black liquor is a colloidal system. The extractives may be in several different states in black liquor, including true solution, micellar solution, liquid crystalline phases and, eventually, neat soap. Most of these colloidal states occur simultaneously and are in a sort of equilibrium with one another. The aggregative state of the soap depends on the concentration of the dispersed soap as well as on the salt content and solids content of the liquor. Since the weak black liquor is concentrated in evaporators prior to combustion in the recovery furnace, the black liquor colloid is continually undergoing stresses. The stresses result from a continual increase in solids content as the water is evaporated from the black liquor. As the water is removed, the salt content of the liquor increases, causing a natural salting out of any organics present.

The fatty acid and rosin acid salts form micelles that solubilize the neutral fraction of the extractives. Micelle formation, which indicates the onset of phase separation, depends on a number of factors. These include salt content, fatty to rosin acid ratio and temperature. Generally, as the salt content increases, the concentration of soap at which micelles form decreases; i.e., the soap is less soluble. The separation of the soap is dependent on many variables such as wood species, dissolved solids content of the liquor, temperature and residual effective alkalinity. (1, 2, 3)

How Much Tall Oil Soap Is Present and Recoverable?

The quantity of tall oil soap recovered by a given mill varies according to wood species, season of the year, and wood storage practices. The quantity of tall oil available in several southeastern wood species has been determined by solvent extraction (5). This method tends to overstate the true availability but is valid for assessing the different wood species by the same method.

Table 4.3.2. Tall oil availability by species

Pine Species	*Tall Oil kg /1000 kg OD Wood*	*Tall Oil lb./ODT*
Longleaf	43.5	87
Slash	41.5	83
Loblolly	35.5	71
Shortleaf	34.5	69
Spruce	31	62

Tall oil soap recovery is usually somewhat lower than what is available in the wood due to wood storage practices and differences in operating practices. Crude tall oil soap recovery is regularly reported by the Pine Chemicals Association for its member companies. Most members are located in the southeastern U.S. The annual recovery of tall oil soap for the mills from various wood procurement regions is as follows:

Table 4.3.3. Typical tall oil yields

Region	*Tall Oil kg /1000 kg OD Wood*	*Tall Oil lb./ODT Wood*
Piedmont	24	48
Coastal	26	52
Canada	11.5	23
Southwestern	31.5	63
West of Cascades	7.5	15
Finland	19.5	39
Sweden	25	50

Tall oil precursors in the wood vary seasonally. The seasonal variation in tall oil soap recovery is very pronounced in southeastern U.S. mills. This is due to the warmer weather that promotes biological degradation during chip storage. Figure 4.3.1 shows the seasonal variation of tall oil soap availability using data from two southeastern U.S. mills in the coastal plain.

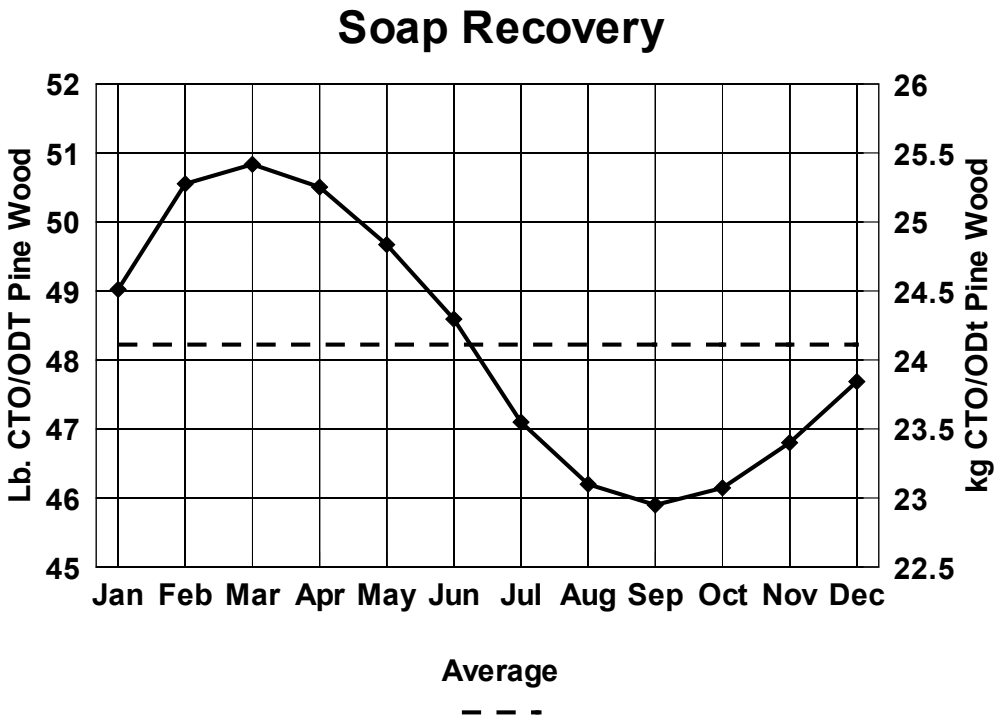


Figure 4.3.1 Soap recovery seasonal variation curve

The type and duration of wood storage also affect tall oil soap recovery. Tall oil soap loss from wood occurs very rapidly during the first two months of storage (6). Figure 4.3.2 shows that tall oil losses can be 50 -65% after two months of storage. This loss is highly dependent upon the manner in which the wood is stored. The tall oil soap loss is lower if the wood is stored as roundwood rather than when stored as chips.

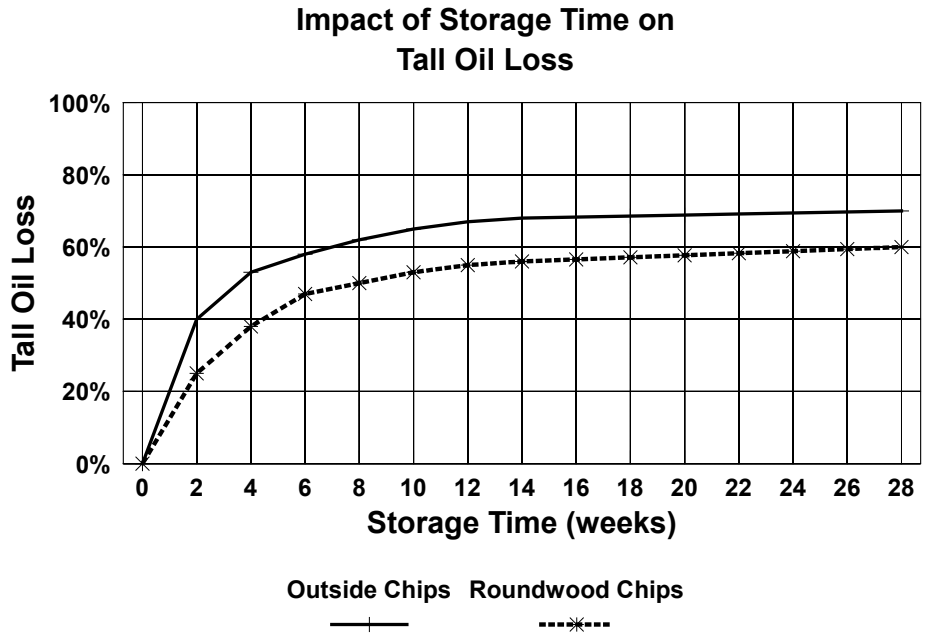


Figure 4.3.2 Impact of storage time on tall oil loss

Why Should the Tall Oil Soap Be Removed?

- Tall oil soap should be recovered to:
- Improve evaporator operation,
- Reduce effluent toxicity,
- Improve recovery boiler operation,
- Reduce caustic room load,
- Reduce accidents due to slips and falls
- It is a valuable byproduct of the alkaline pulping operation.

Improve Evaporator Operation - In 1975, a study (7) was done to define the nature and extent of scaling problems in the alkaline pulping industry. Over 75% of the mills responding reported encountering one or more types of scales. The most commonly encountered scales were calcium scales and soluble Na_2CO_3-Na_2SO_4 scales. Others (8,9) have shown that soap is a significant scale component, particularly in soluble carbonate-sulfate scales in evaporators and concentrators. Mill and pilot plant studies (10) were done to clarify the importance of soap in evaporator scale formation and quantify its effect on scaling rates. The results are represented in Figures 3 and 4. Grace similarly found that tall oil soap addition to black liquor increased calcium scaling by about 30%.

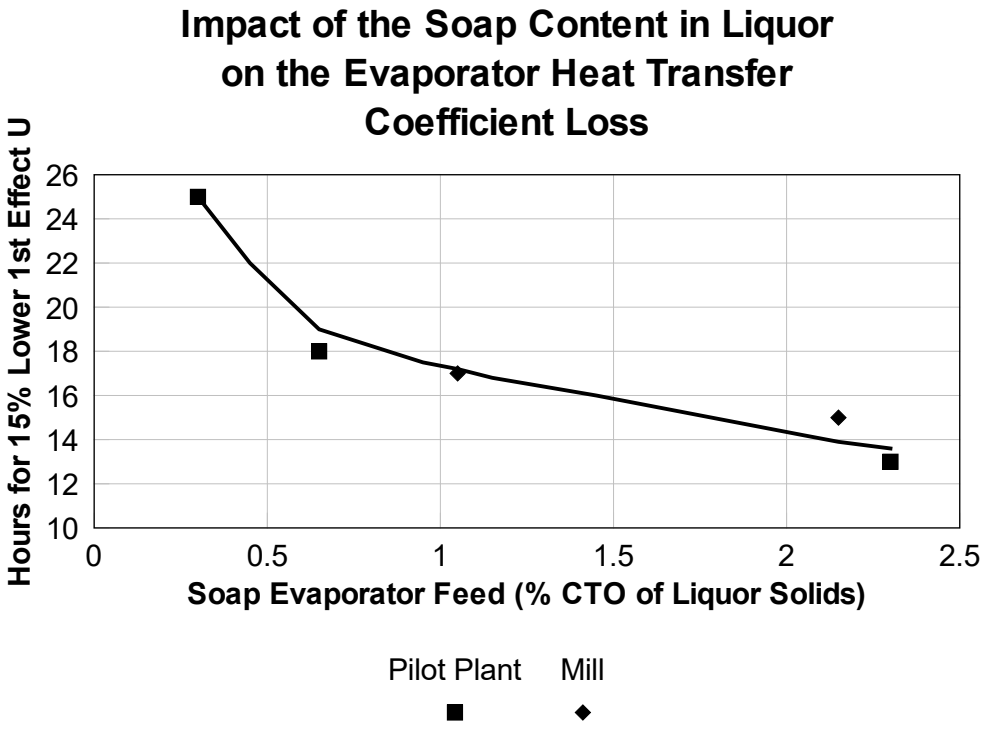


Figure 4.3.3 Impact of soap content in liquor on evaporator heat transfer coefficient loss, time for a 15% reduction in heat transfer coefficient.

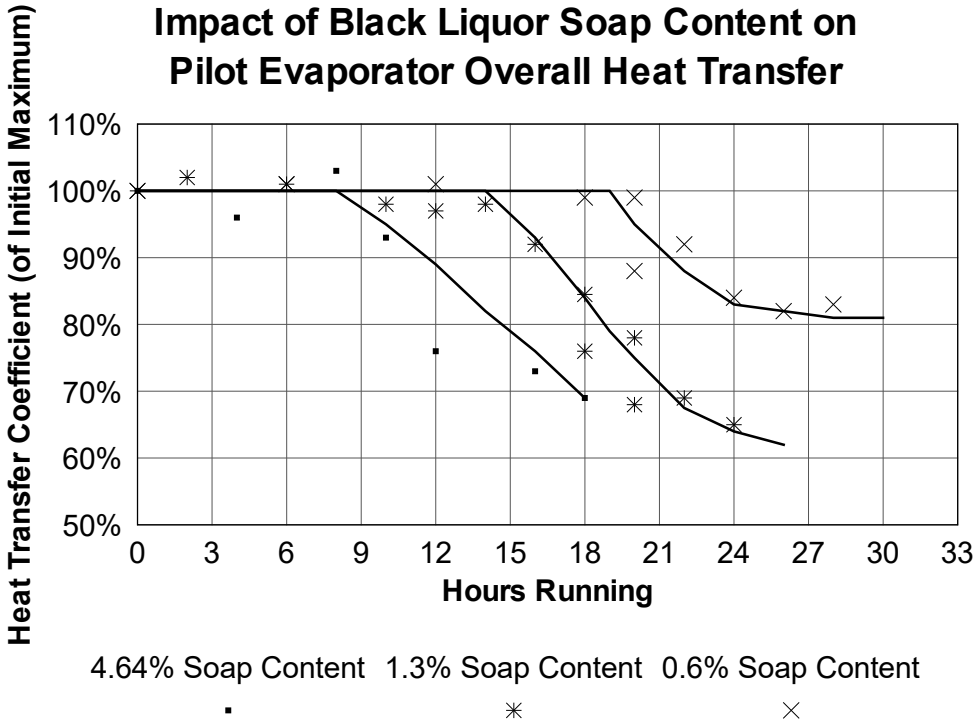


Figure 4.3.4 Impact of soap content in liquor on evaporator heat transfer coefficient loss.

In Figure 4.3.5 and Table 4.3.4 the impact of poor soap recovery on a full scale LTV evaporator is demonstrated. It further validates the pilot studies.

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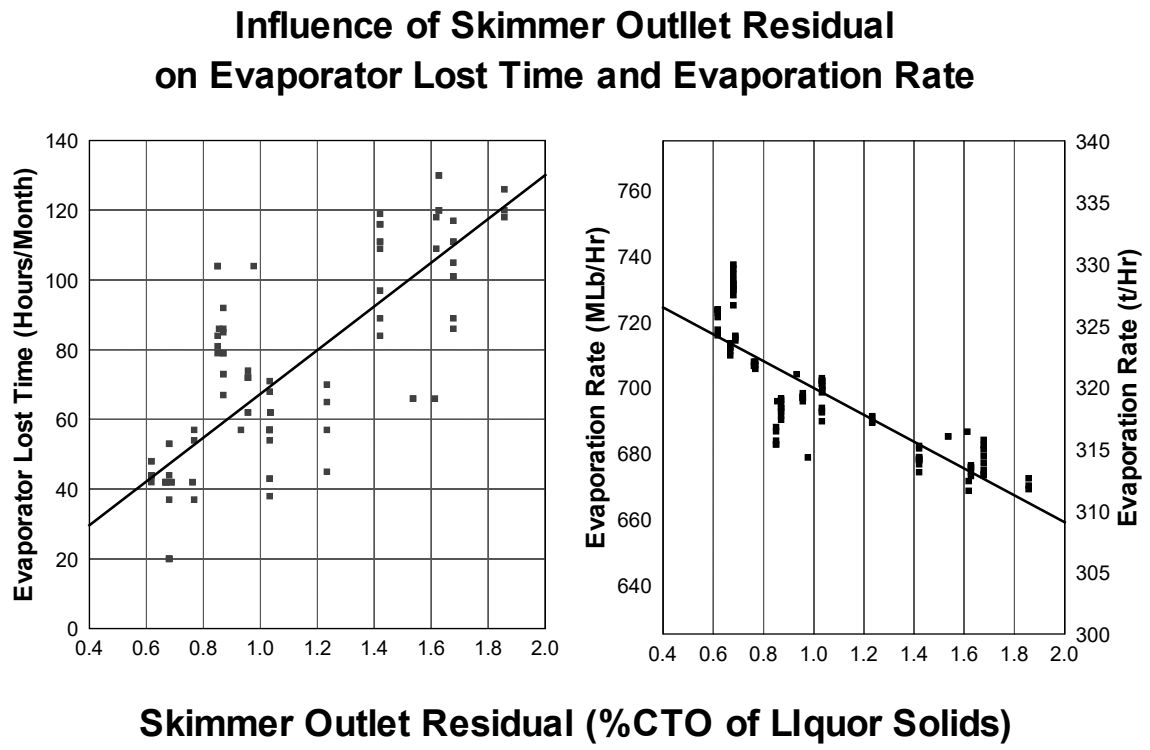


Figure 4.3.5 Influence of skimmer outlet residual on evaporator lost time and evaporation rate

Table 4.3.4. Influence of skimmer outlet residual on evaporator lost time and evaporation rate

	Good Skimming	*Poor Skimming*	*Change*
Skimmer Residual (%)	0.6	1.1	0.5
Downtime (hr./month)	45	75	30
Evaporation Rate (Mkg/hr)	323	315	-8
Production (Tonnes)			
Unbleached	34500	32100	-2400
Bleached	24700	23000	-1700

Soap in the liquor contributes significantly to liquor carryover in the evaporator feed effects. This is particularly true in the weak liquor effects in falling film evaporators. The liquor carryover is essentially that of a foam. Several observations about this foam:

1. The foam is generated shortly after liquor boiling begins to occur.
2. The foam contains water vapor and some TRS.
3. Foam liquor carryover will occur if the height of a column of foam is taller than the height of the vapor space in the evaporator.

Foam Height = Vol. Evap. Rate*Average Bubble Life
Foam Column Area

4. The volumetric evaporation rate increases at the lowest pressure effects.
5. The average bubble life is increased by lower temperatures and increased soap content.
6. The foam column area is fixed by the evaporator dimensions.
7. Removal of the soap prior to evaporation will dramatically reduce the average bubble life and reduce liquor carryover permitting increased evaporator throughput.

Reduce Effluent Toxicity - Drew and Propst (1) summarized the findings of several extensive studies of southern kraft mills, northwestern mills and Canadian mills. "As early as 1931, it was recognized that resins and resin acids present in the waste streams of the kraft mills were the cause of fish kills and resin-like taste to fish. ... Later it was shown that the sodium soaps of the resin acids were the primary cause of the toxicity. The resin acids had little toxicity relative to the soaps of these materials (34). ... At B.C. Research, Vancouver, Canada studies have provided specific toxic materials in effluent from a kraft mill that are acutely toxic to Coho salmon (35). Soaps of resin acids contributed over 80% of the toxicity of the effluent. Sodium salts of the unsaturated fatty acids accounted for the remaining toxicity."

Impact on Recover Boiler Capacity - Besides the evaporator scaling impact, soap reduces the liquor burning capacity of solids limited and steam-side limited recovery boilers (28). In solids limited recovery boilers, a given mass of soap will displace an equivalent mass of black liquor solids. In a steam-side limited boiler, a given mass of soap will displace about twice the equivalent mass of black liquor solids. Pulping capacity will be directly affected.

It has been found (28) that the burning of soap, even at low concentrations, increased total reduced sulfur (TRS) emissions. The boiler fouling rate was also increased at a given liquor firing rate. Kubes (11) has shown that a connection may also exist between liquor soap content and the occurrence of blackouts in kraft recovery boilers.

Furthermore, soap that accumulates in heavy liquor storage tanks generally does not form a well-defined bed. As a result, it tends to be fed to the recovery boiler in "slugs". To prevent black outs, operators are forced to increase the primary air supply. This results in more oxidation of the bed and lower reduction efficiencies. In one mill that improved its soap recovery from 20 lb. to 35 crude tall oil/1000 lb. black liquor solids, reduction efficiencies increased from about 84% to about 92%, in addition to the anticipated 10% improvement in evaporator throughput. They also experienced improved green liquor clarification.

If a mill is caustic room limited, soap represents a larger causticization load / ton of solids fired in the recovery boiler than do black liquor solids. This is because soap burns to sodium carbonate (Na_2CO_3), whereas black liquor solids burn / reduce to a mixture of sodium carbonate and sodium sulfide (Na_2S). The sodium sulfide does not require causticization after dissolution in the green liquor.

Soap Removal Methods

Factors Affecting Soap Removal

Drew and Propst (1) have prepared an excellent summary of the various laboratory and mill studies affecting the recovery of tall oil soap. Most of the studies were conducted on southeastern U.S. mills. A later study (2) on Canadian mills provided some clarification of several controversial effects such as the impact of hardwood liquor.

Liquor Solids and Temperature

Tall oil soap solubility in black liquor is highest in weak black liquor. It reaches a minimum between 20 and 30% black liquor solids. The minimum solubility of the tall oil soap varied somewhat from mill to mill

but was typically 7-15 lb. soap/ton of liquor solids (3 - 8 kg. soap/tonne). The concentration of soap in unskimmed softwood black liquor varies from 70-110 lb. soap/ton of liquor solids (30 - 50 kg./tonne).

Micelle formation is independent of temperature between 20°C and 80°C, but the soap becomes much more soluble at higher temperatures (38). The temperature in the soap skimmer is normally fixed by the operating temperature in the effect that feeds it. However, the advent of new pulping and washing processes has tended to increase the solids content of the liquor before evaporation. This has resulted in a greater tendency of the soap to separate in weak liquor storage tanks. The solubility of tall oil soap as a function of both temperature and solids content is illustrated in Figure 4.3.6.

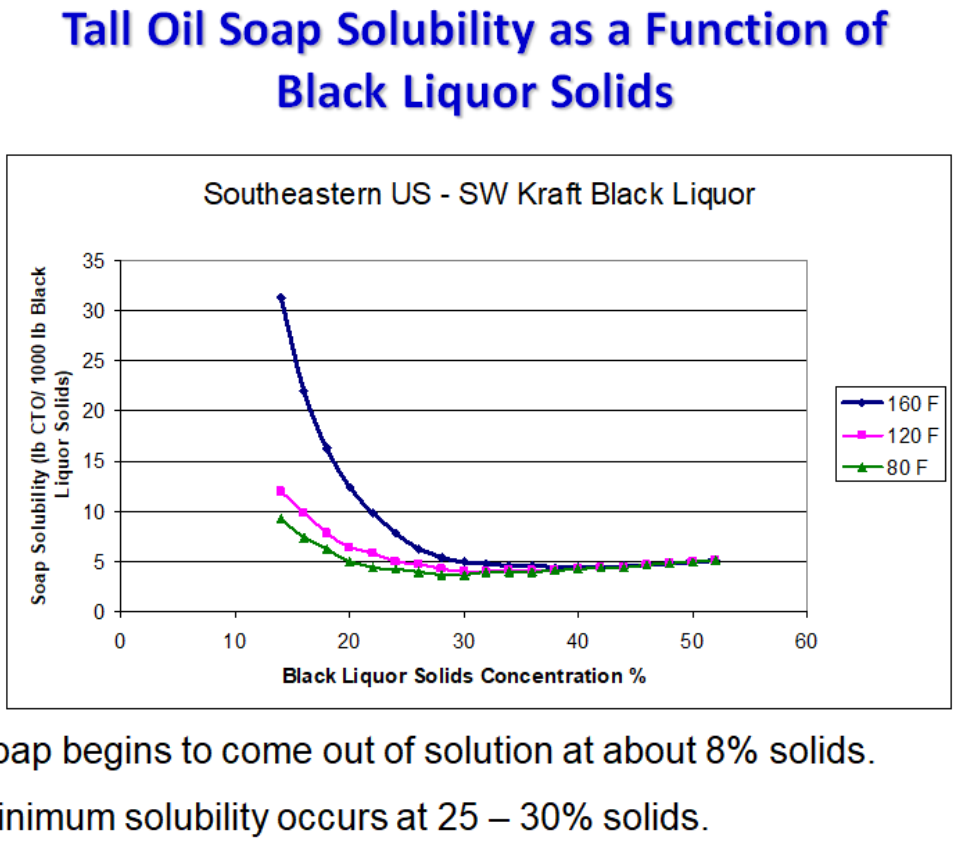


Figure 4.3.6 Tall oil soap solubility as a function of temperature and solids content

The following graph, based on data from Finnish mills, shows how soap solubility is affected by black liquor solids concentration and settling temperature.

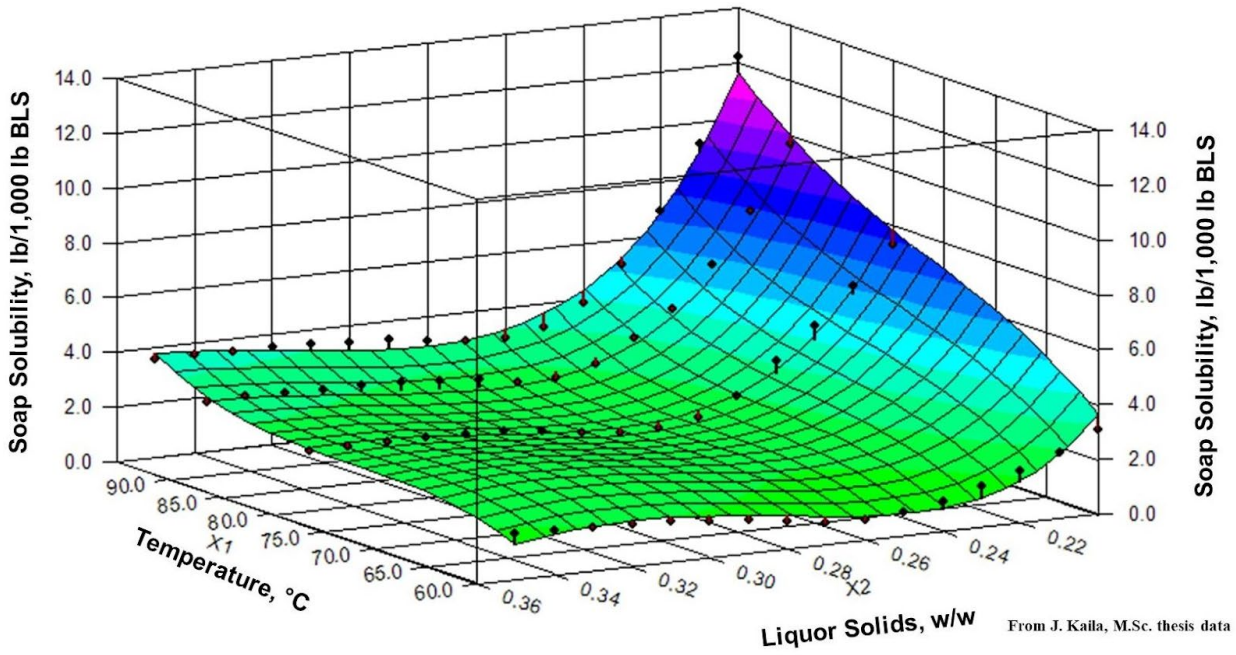


Figure 4.3.6a Tall oil soap solubility as a function of temperature and solids content - Finnish mill black liquor, Courtesy Jarmo Kaila

Since black liquor viscosity increases rapidly as the temperature decreases, it is unlikely that lower evaporator skimmer temperatures would result in increased skimming efficiency (2).

Higher solubility at higher temperatures and lower solids is similar to the southeastern black liquor data in Figure 4.3.6 above but absolute concentrations are different due to the wood species being pulped, and the rosin acid to fatty acid ratio in the soap. (see below).

The implementation of alternative pulping and washing processes has tended to increase the solids content of the liquor before evaporation, resulting in a greater tendency for soap to separate in weak Liquor storage tanks prior to the evaporators.

Although It has also been suggested that cooling the liquor before soap skimming would increase soap skimmer recovery, the increased black liquor viscosity at reduced temperatures reduces soap separation. Therefore, it is unlikely that lower evaporator skimmer temperatures would result in increased skimming efficiency (2).

Composition of Tall Oil Soap

Mixed micelles, where the ratio of fatty to rosin acid soaps is between 1:1 and 2:1, are more stable than micelles of either singular soap. Depending upon the species of the woods being pulped, the ratios of fatty acid to resin acid vary. Soaps containing a higher ratio of fatty acids to resin acids showed lower solubility.

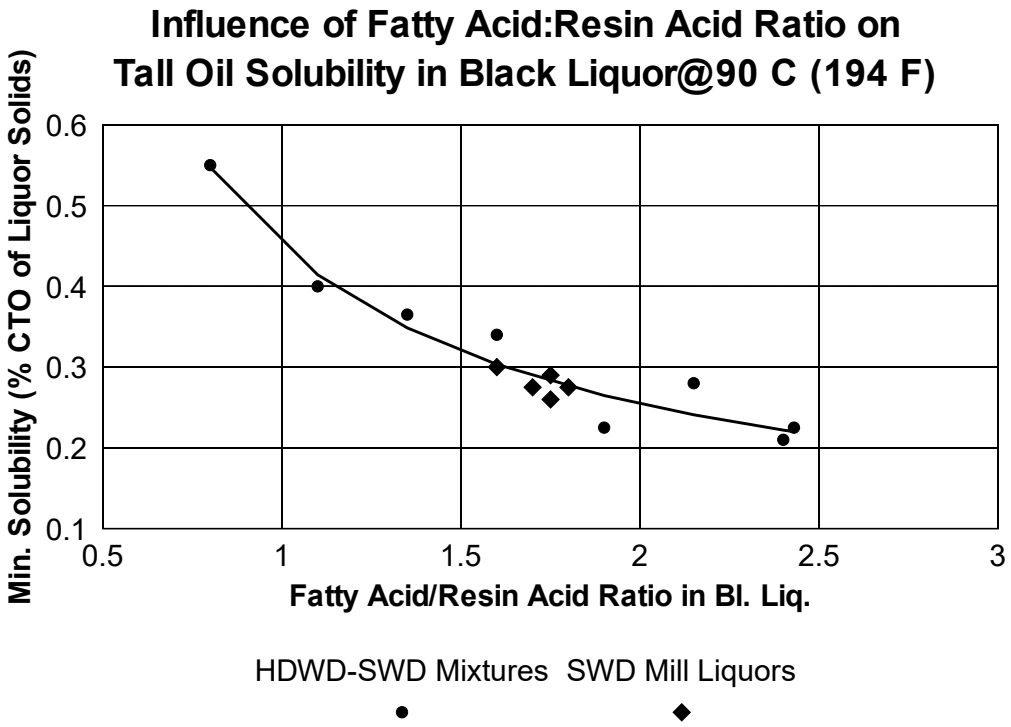


Figure 4.3.7 Relationship of fatty acid : resin acid ratio to minimum soap solubility in black liquor.

A recent study using a newly developed analytical procedure (37), has shown that the bulk of the fatty acid component of the extractives is removed from the black liquor during the recovery process. The rosin acid soaps are more soluble in the black liquor and make up the majority of the soaps that are eventually burned in the recovery furnace. This conclusion leads one to think about which component of the black liquor is really involved in problems such as evaporator scaling, evaporator fouling and recovery furnace blackouts due to incomplete combustion of liquor solids.

Effect of the Residual Effective Alkali Content of the Black Liquor

Residual effective alkali (REA) content of the black liquor has a marked effect on the minimum solubility of soap in black liquor.

For good recovery it should be kept above 6 g/l. The combined effect of lower effective alkali content and fatty acid: resin acid ratio is illustrated in Figure 4.3.8.

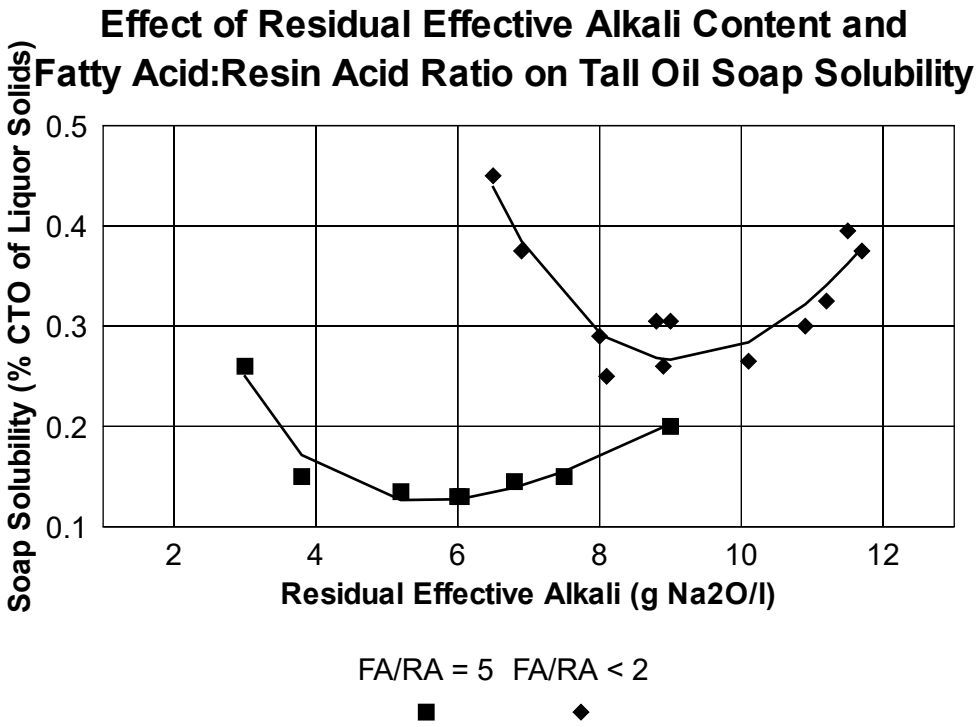


Figure 4.3.8 Effect of fatty acid : resin acid ratio and effective alkali content to minimum soap solubility in black liquor.

Hardwood - Softwood Liquor Blending

Observations of the influence of hardwood liquor blending have often been contradictory. First a distinction should be made between hardwood liquor resulting from the kraft process and that from the NSSC process. Gooding and Wilkinson (12) showed that when hardwood liquor was blended with pine liquor from 0 - 25% on a solids basis, there was a slight decrease in the residual tall oil soap content of the skimmed liquor. After 25% NSSC liquor solids the soap solubility increased sharply. With kraft hardwood liquor, up to about 50%, there was a slight decrease in the residual tall oil soap content of the skimmed liquor (2). Above about 60% kraft hardwood solids content the solubility of the tall oil soap appeared to increase rapidly (Figure 4.3.9).

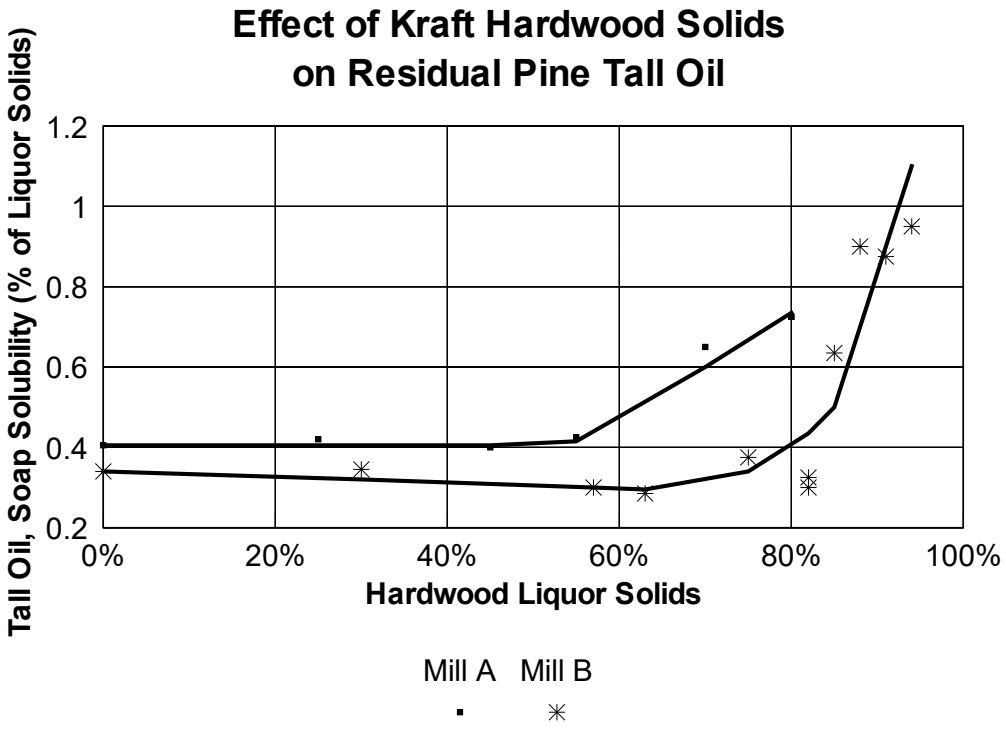


Figure 4.3.9 Effect of hardwood liquor on soap solubility at 194°F (90°C)

At high hardwood concentrations, the residual effective alkali level was reduced enough so that the soap was solubilized. This explanation would also account for much of the increase in solubility of the NSSC-pine kraft liquor mixtures (12).

Overall Tall Oil Balance

The choice of tall oil soap recovery equipment is dependent upon the type of process equipment. The change from conventional batch digesters and vacuum drum washers to cold blow digesters and diffusion, pressure drum or belt washers has dramatically altered where soap separates from the liquor. The increase in black liquor solids levels before evaporation has resulted in greater soap separation in the weak liquor storage system. A comparison of soap balances around a batch atmospheric diffusion washer system appears in Table 4.3.5.

Table 4.3.5. Tall oil material balance

Pulp Type:	*Linerboard*	*Bleach Pulp*	*Linerboard*
Digester:	*Batch*	*Kamyr*	*Kamyr*
Washer:	*Vacuum Drum*	*Diffusion*	*Vacuum Drum*
Year:	*1972*	*1985*	*1987*
	lb./ODT	*lb./ODT*	*lb./ODT*
Tree	112	91	
Chips to Digester	75	74	63
Unwashed Pulp	74	70	57
Filtrate Recirculation		63	46
Washer	12	7	8
Decker	8		
To Weak Liq. Tank	62	67	52
From Weak Liquor Tank	60	21	31
From Evap. Skimmer	12	9	7
To Recovery Boiler	11	9	7
To Effluent Treatment System	4	1	2
Weak Liquor Soap	2	46	21
Evaporator Soap	48	11	24
Heavy Liquor Soap	2	0	0
Total Soap	51	58	45
Recovery Efficiency	68%	78%	71%

The first stage wash liquor in 1972 (13) had a dissolved solids content of about 13 %. The Kamyr liquor in the 1985 study (14) was about 17% dissolved solids. This resulted in a dramatic increase in weak liquor soap separation and recovery.

In some recent batch cold blow systems, the recirculation of soap saturated liquor presented significant operating difficulties. The soap evolved much earlier in the washing process and produced large volumes of foam. Changes in the management of the liquor during heat recovery stages of the process dramatically reduced the soap recirculation. The changes were dictated by soap solubility.

Soap Removal During Washing

Rotary Drum Washing

There is very little data on the removal of soap in the washing process. A study of a three stage vacuum drum washer was done in 1972 (13). It was designed to determine the response relative to shower water flow and temperature. No correlations could be found between tall oil soap recovery and wash water flow rate or wash water temperature (see Figure 4.3. 10).

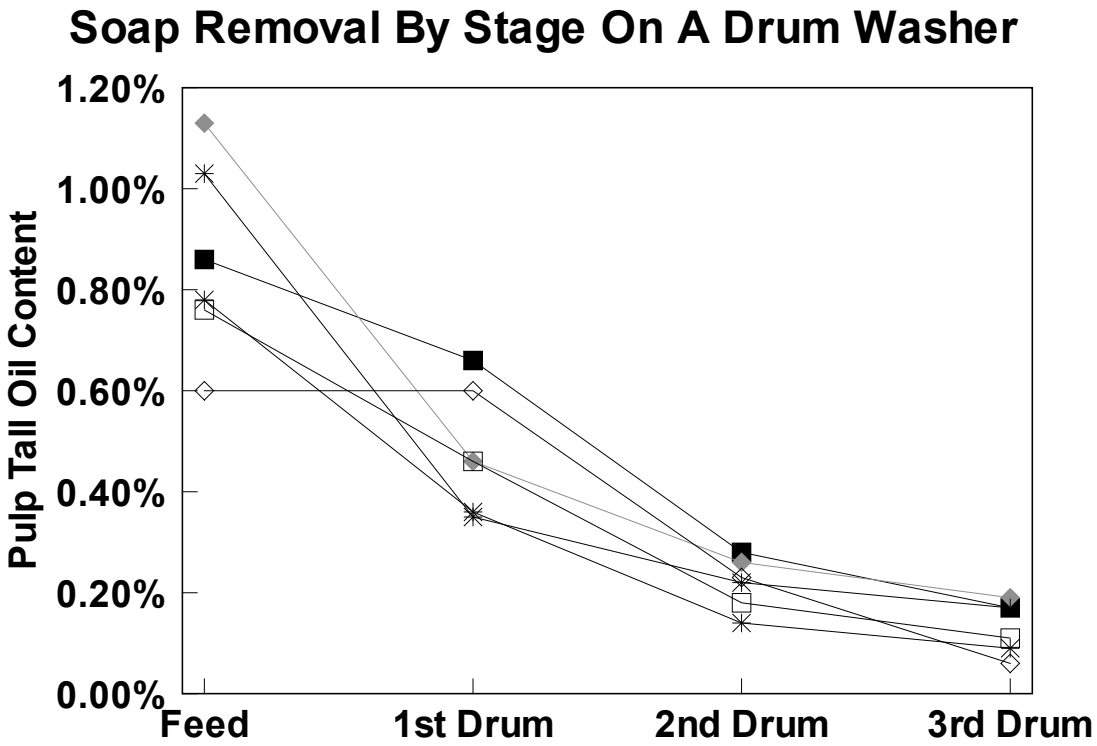


Figure 4.3.10 Soap removal by stage on a drum washer

The tall oil soap in the washed pulp from any stage was directly proportional to the amount present in the feed to that stage. The washer was more efficient at removing dissolved solids than removing tall oil soap. In the later stages of washing, dissolved solids were removed, while the soap was not. The negative displacement ratios indicate that steady state conditions had not been achieved (14). This study highlights the importance of removing the soap foam before it has a chance to contaminate the next washing stage (see Figure 4.3.11)

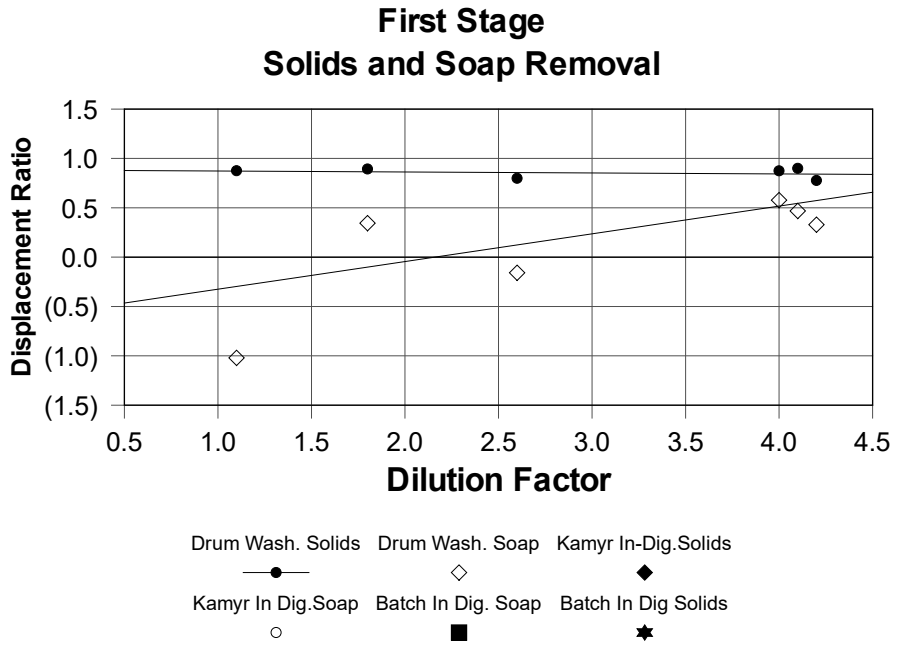


Figure 4.3.11 First stage drum washer solids and soap removal.
Table 4.3.6. Conventional drum washer

Drum	*Dilution Factor*	*Solids D.R.*	*Soap D.R.*
First	1.8	89%	35%
Second	2.3	81%	40%
Third	2.3	71%	-72%

In-Digester Washing

Kamyr™

Probably the most common in-digester washing system is that employed in the high heat washing zone of the Kamyr™ digester. In this system, wash water from earlier stages is introduced at the bottom of the digester and passes upward, counter-current to the pulp flow. The wash liquor is removed at the extraction screens. Contact of the hot cooking liquor with the relatively cool wash water quickly quenches the cooking reaction. Once again there is very little data on soap removal during washing in the system. One unpublished report has studied soap washing at a dilution factor of 1.7. In this study the in-digester washer was effective at removing both dissolved solids and soap.

Table 4.3.7. Kamyr™ in-digester wash

Stage	*Dilution Factor*	*Solids D.R.*	*Soap D.R.*
In-Digester	1.7	97%	71%
First Drum	3	99%	46%
Second Drum	3	64%	-10%

Pilot cooking studies have shown that at the completion of the cook, most of the tall oil soap remains in the cooked chips. About 10% of the soap diffuses out of the chips into the cooking liquor. Therefore the objective of the in-digester wash must be to provide time for the soap to migrate out of the cooked chips. The wash liquor enters at about 190°F (88° C) and 3-5% dissolved solids. At this point essentially all of the soap is in solution. When the liquor is extracted from the digester, it is at 13-15% dissolved solids and 300-320°F (149-160° C). It is probable that the elevated temperatures permit the soap to remain in solution.

Cold Blow Batch

Cold blow batch processes (15, 16) have been introduced to improve the energy efficiency of the batch digestion process. Only unpublished data exist on the soap balance around such systems. This data has shown that in-digester washing of batch pulps is about as effective as in the Kamyr™ digestion process with regard to dissolved solids removal. However, the soap removal is significantly less effective, even at higher dilution factors.(see Table 4.3.8 below)

Table 4.3.8. In-digester wash comparison

	Dilution Factor	*Solids D.R.*	*Soap D.R.*
Kamyr	1.7	97%	71%
Cold Blow Batch	2.7	84%	7%

The cooked chips are not in contact with the washer filtrate for as long a period of time as in the Kamyr™ in-digester wash. The shorter contact time does not allow enough time for the soap to diffuse from inside the cooked chip mass to the liquor outside the chip. Furthermore when the dissolved solids content reaches its peak, the liquor temperature is about 200°F (93°C) as compared with over 300°F (89°C) in a typical Kamyr™ system. Thus much of the soap that might be removed is not in solution.

Soap Removal from Weak Liquor Tanks

Soap removal from weak liquor before evaporation is increasingly important. As Table 4.3.5 above indicates, typically 40% - 80% of the soap recovered, evolves in the weak liquor system.

Washer Filtrate Tanks

Weak liquor soap removal begins in the washer filtrate tanks. E.C. Cobb (17) has detailed the design considerations for vacuum drum washers.:

“As is shown in Figures 12 and 13a, liquor and foam handling from the first stage of any multi-stage washing system is the most important. Later stages cannot offset poor quality washing in the first stage when using normal amounts of wash water.”

“If the air bubbles in the filtrate are not allowed to rise to the surface continuously in each liquor tank, the dissolved solids and soap will be recycled and washer performance will be decreased.

Figure 4.3.13a illustrates the roles of several critical elements of the filtrate tank / foam tower soap system. From the foam tank, the soapy high solids black liquor should be pumped continuously to the weak liquor storage tank, and **should never be recycled into the washing system** ”

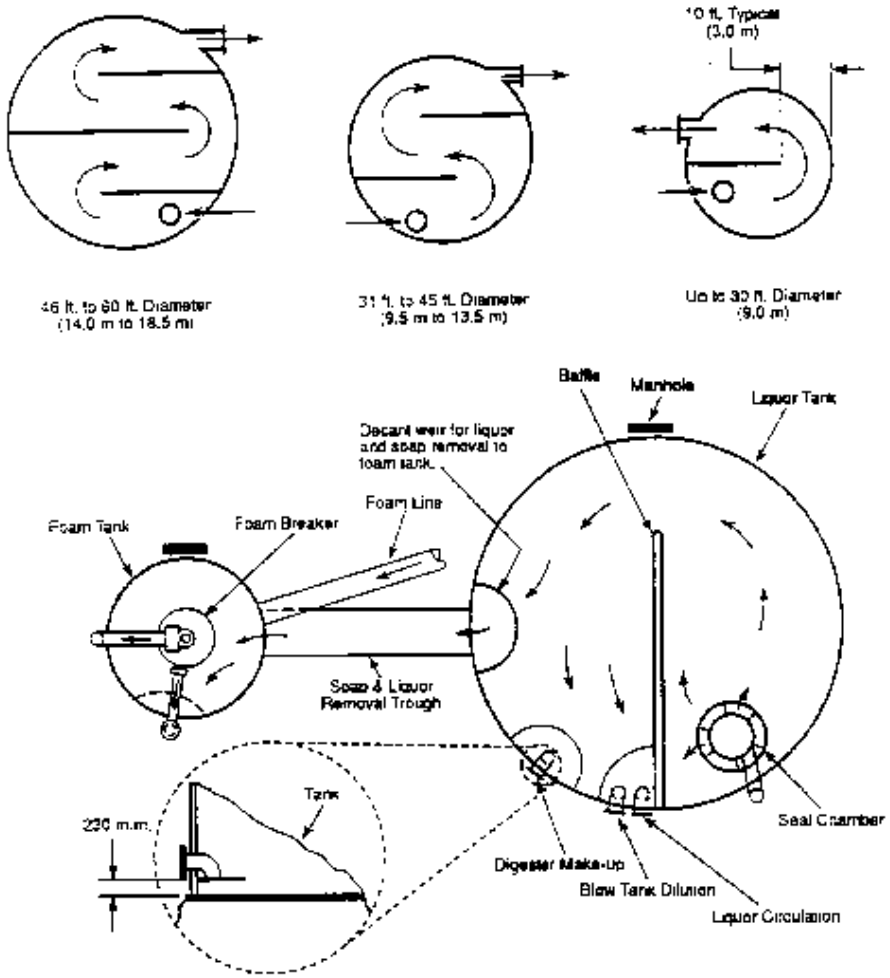


Figure 4.3.12 Liquor tank baffling, first stage tank and foam tank plan view

It should be realized that the entrained air in the liquor is a critical element for floating soap to the surface of washer filtrate tanks. The air bubbles increase the rise rate of the soap. In pressurized rotary drum filters, the filtrate tanks must be sized to allow the soap to rise to the liquor surface without the flotation effect of large volumes of air.

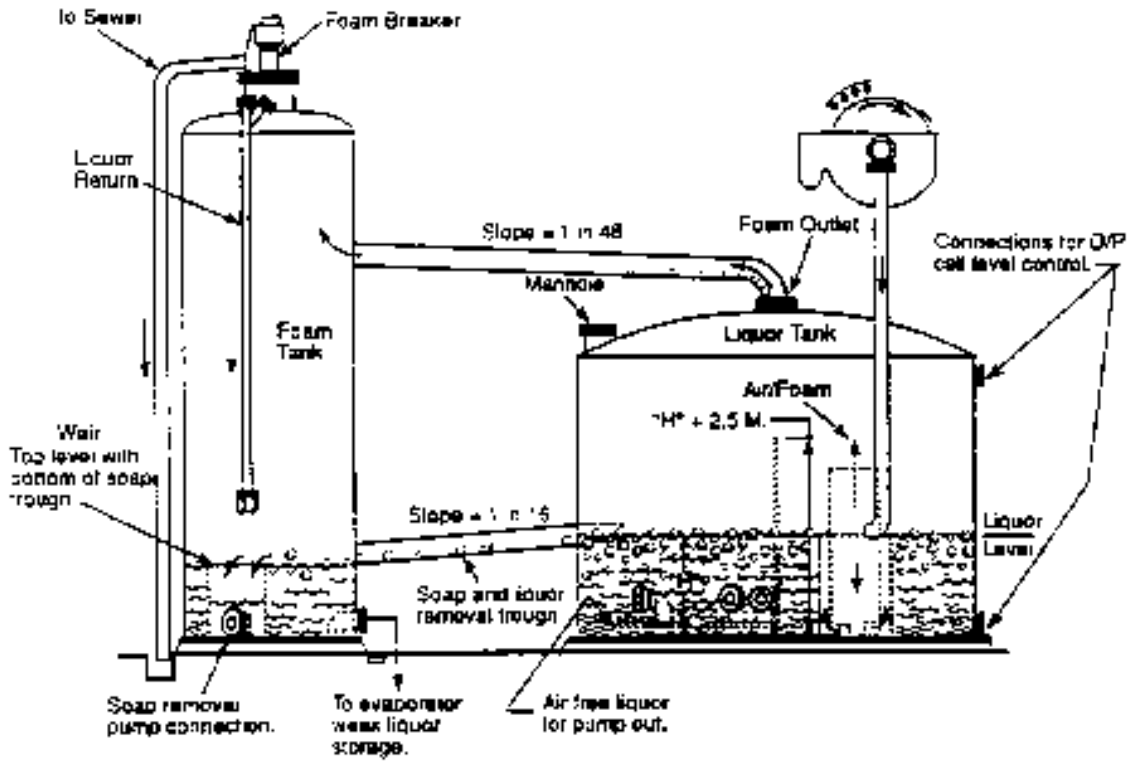


Figure 4.3.13a First stage liquor tank and foam tank arrangement

The air and foam released in the seal chamber and surface of the liquor, fills the upper portion of the filtrate tank. Some foams break down by themselves, back into liquor, soap and air. All rotary drum pulp washers continuously put air into the drop legs. This air must be continuously vented from the foam tank. The foam line slopes upward so the as foam breaks down while moving from through the foam piping, the condensed liquor flows back into its respective liquor tank. The liquor tank system air (hot vapor) leaves the foam tank through mechanical foam breakers located on top."

"Light foam carried with the vapor is readily broken down by mechanical foam breakers. The returned liquor from the foam breaker is brought back into the foam tank, above the liquor level, and discharged out of the system. Foam-free vapor discharges from the foam breaker, through a large vent line. In the event of system overloading, some foam will discharge to the sewer. This could indicate the need for more foam breakers, incorrect foam breaker rotation, or some plugged conditions ... Where odor abatement systems are used, the foam breaker may vent directly to such a system. However, care must be taken not to have auxiliary systems reduce foam breaking action!"

"Total washer system air must be released from each tank via individual foam lines to the foam tank. These lines should enter the foam tank at various elevations. The heaviest foam should be introduced at the lowest elevation to prevent sending strong first stage foam backward to the second or third stage filtrate tanks."

The liquor passing on to the evaporators overflows from the filtrate tank to the foam tower. The overflow channel to the foam tower not only allows liquor to overflow, but also allows the densest foam/soap in the filtrate tank to overflow to the foam tower. It is critical that as the washer capacity is increased, the overflow line size must increase also. This is illustrated in the following diagram from a mill that dramatically increased washer capacity but did not increase the overflow line size. The increased liquor height in the overflow line prevented foam / soap overflow to the foam tower.

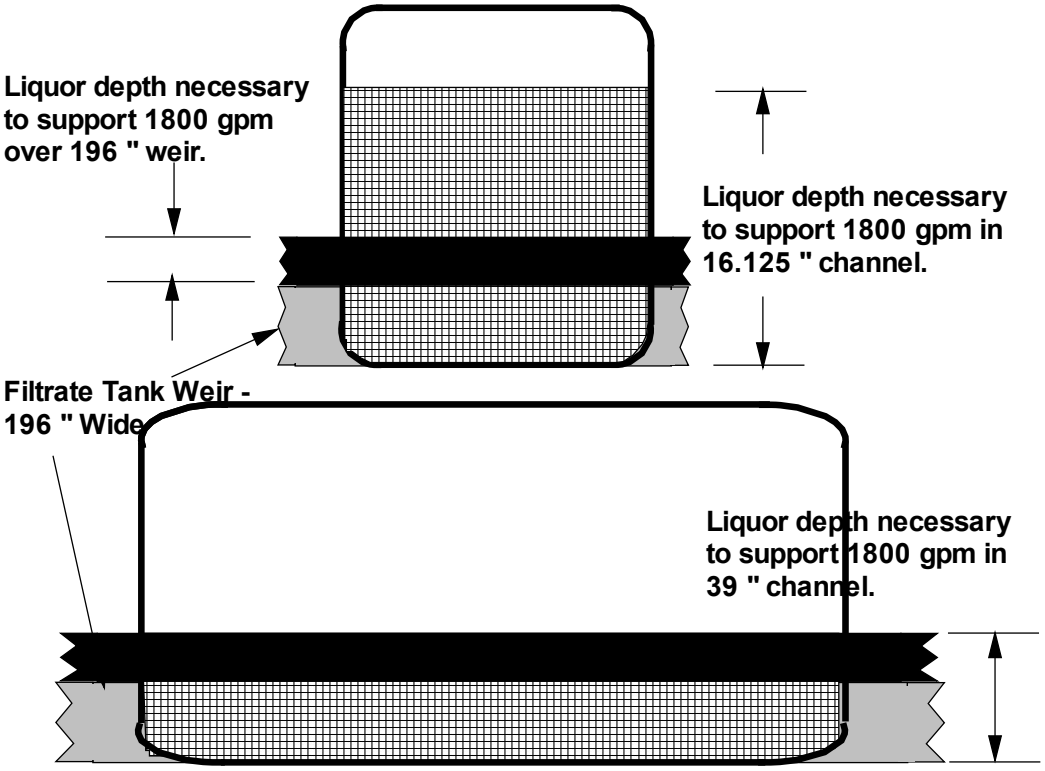
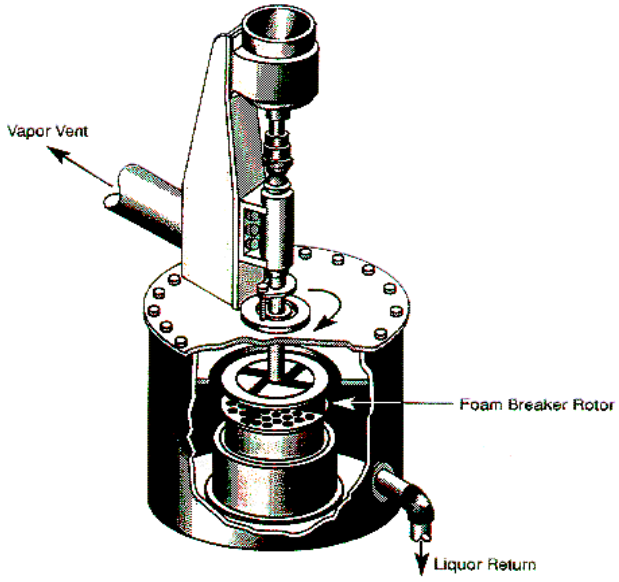
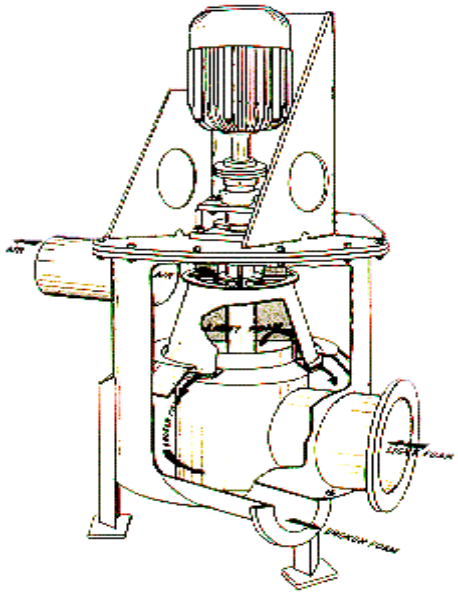


Figure 4.3.13b - How increasing the overflow channel width increases the area for foam / soap removal

Foam Breakers

The initial means of soap removal is by foam breakers. These devices (see Figure 4.3.14) increase soap density from less than 0.5 up to 3 lb./gal. (0.06 up to 0.36 kg/l). It is best to send the broken foam and its associated liquor to a common collection point for further densification. Recombining the broken foam with the main liquor stream leads to soap fouling of operating equipment and re-entrainment in the liquor fed to the evaporators.





Foam Breaker, Courtesy Ingersoll - Rand, IMPCO DIvision

Foam Concentrator, Courtesy A.H. Lundberg Associates, Inc.

Figure 4.3.14 Foam Breaker - Foam Concentrator

Weak Liquor Tank Soap Recovery

Manual Systems

In the weak liquor storage tanks, the soap that separates may be removed by withdrawal ports on the side of the storage tanks (see Figure 4.3.15). These removal ports should be at least 12 in (30 cm) diameter. Determination of the soap/liquor interface is usually done manually. Both thermal conductivity and viscosity sensors have been used to detect the soap /liquor interface successfully (30). Besides the significant amount of operator attention, the main disadvantage of manual collection systems is the risk of carrying over large volumes of liquor to the soap storage tanks.

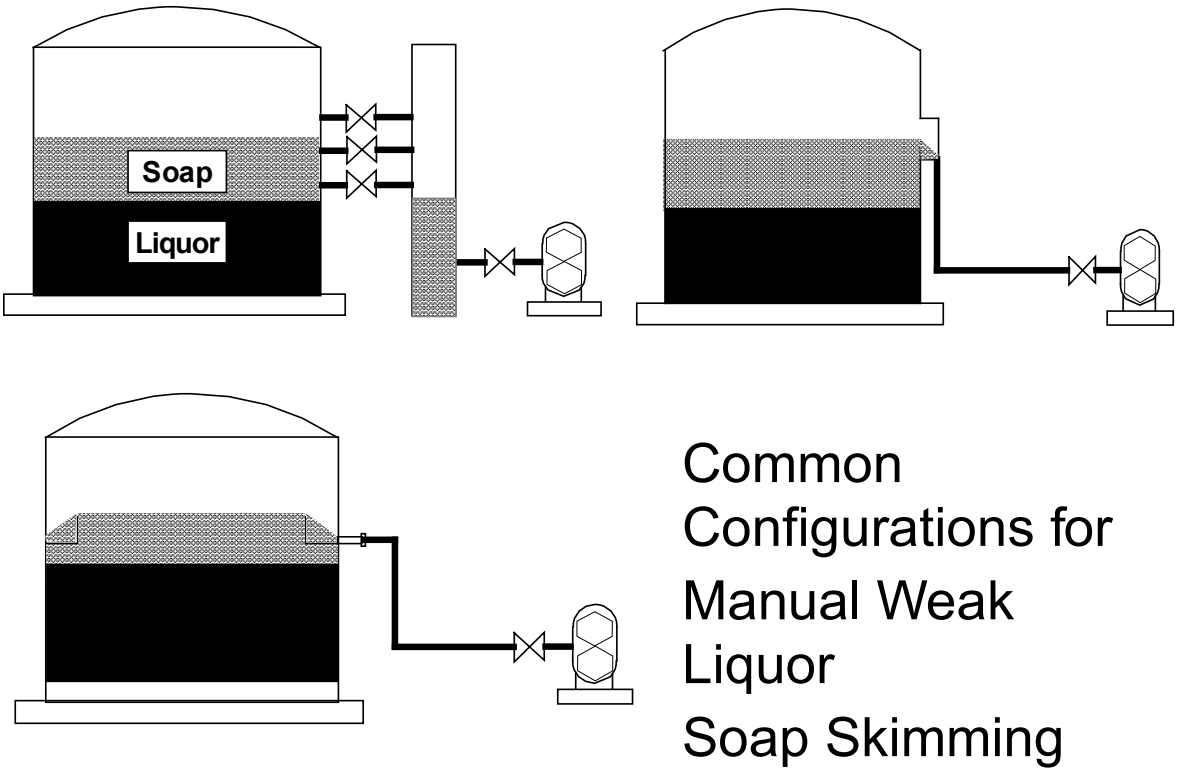


Figure 4.3.15 Common Configurations for Manual Weak Liquor Soap Skimming

Automatic Systems - Floating Soap Skimmers

Since tank levels vary considerably, another device that has been used with success for weak liquor skimming is the floating soap skimmer (34). Floating soap skimmers offer several advantages over manual systems:

- Lower risk of liquor carryover to the soap storage tanks.
- Can be fully automated allowing operators to give more attention to other areas of operation.
- Continuous removal reduces the risk of soap surges to the evaporators.
- Can yield better soap quality overall.

The floating skimmer permits continuous soap recovery over a wide range of operating depths (see Figure 4.3.16). The skimmer is a steel collector placed in a vessel whose buoyancy is adjusted so that it floats at the soap/liquor interface. The collector is connected to ten-inch (25 cm) stainless steel piping by ball joints. Gauge board level indicators mounted on the side of the tank normally measure the skimmer level and the amount of soap. Normal practice has been to maintain a six to ten-foot head of soap/foam above the skimmer to maximize soap density and minimize liquor entrainment. One mill uses pump pressure to detect when the soap / liquor interface has been reached. Due to the high viscosity of soap, the pump discharge pressure decreases sharply when liquor is being pumped. The pressure sensor then automatically shuts off the pump.

SOAP COLLECTION SYSTEMWITH A FLOATING SOAP SKIMMER

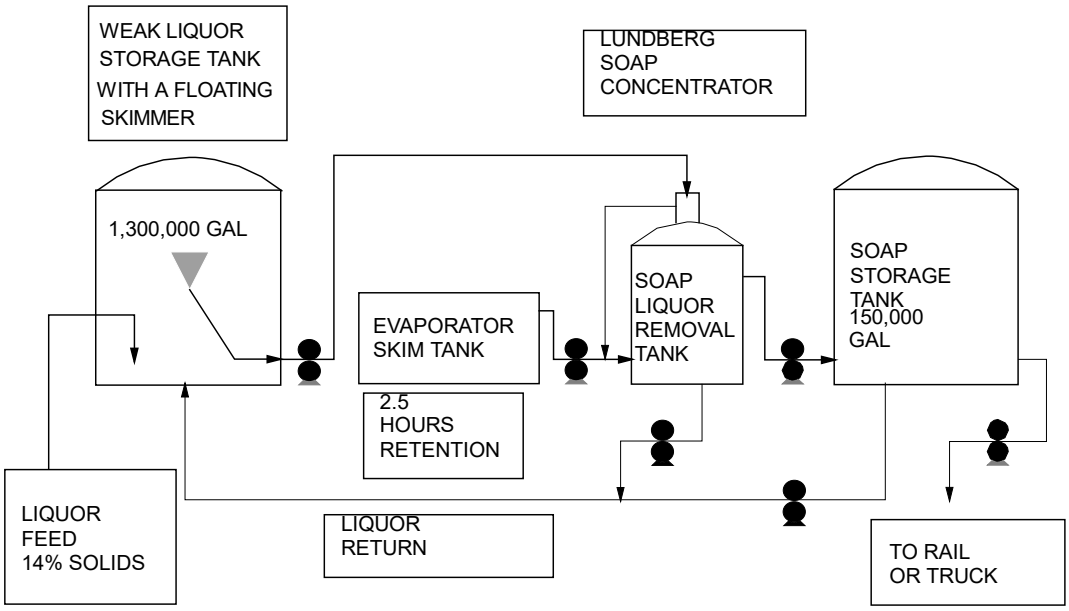


Figure 4.3.16 General equipment configuration for a mill with excellent weak liquor soap skimming

WEAK LIQUOR SKIMMING DETAIL

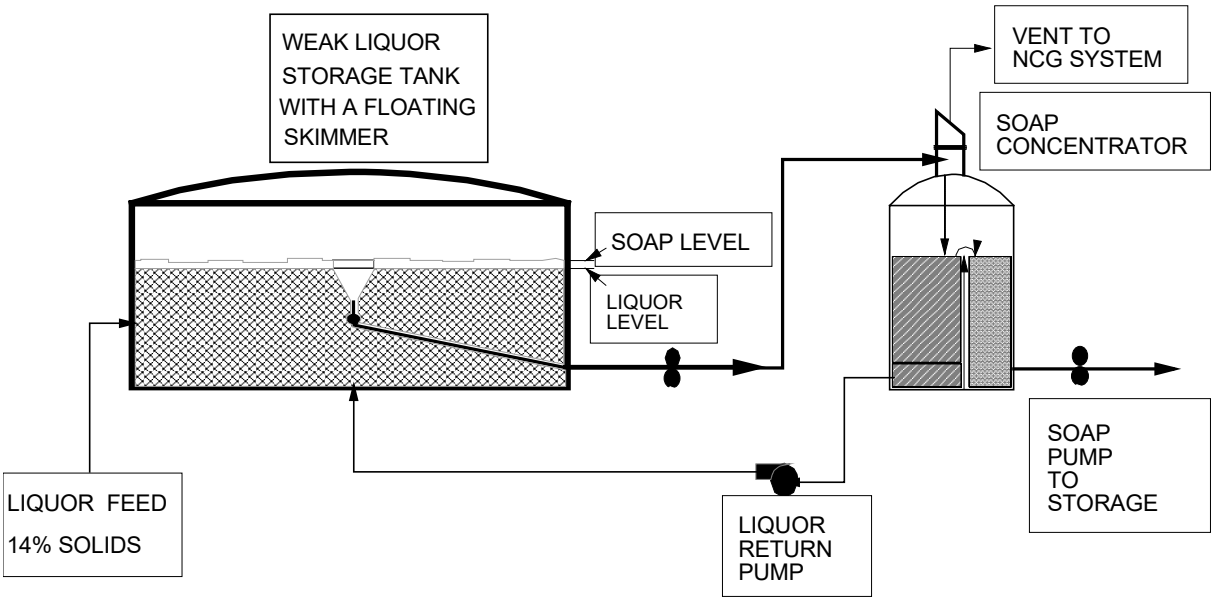


Figure 4.3.17 Weak liquor skimming detail

European Soap Recovery Practice

In Europe there is usually a single intermediate liquor tank (evaporator soap skimmer). The difference compared to soap recovery practice in the USA is that usually at least 80 % of all soap is recovered from weak liquor and feed liquor tanks, that is, before the evaporators. The soap is recovered by overflowing the tanks. (40)

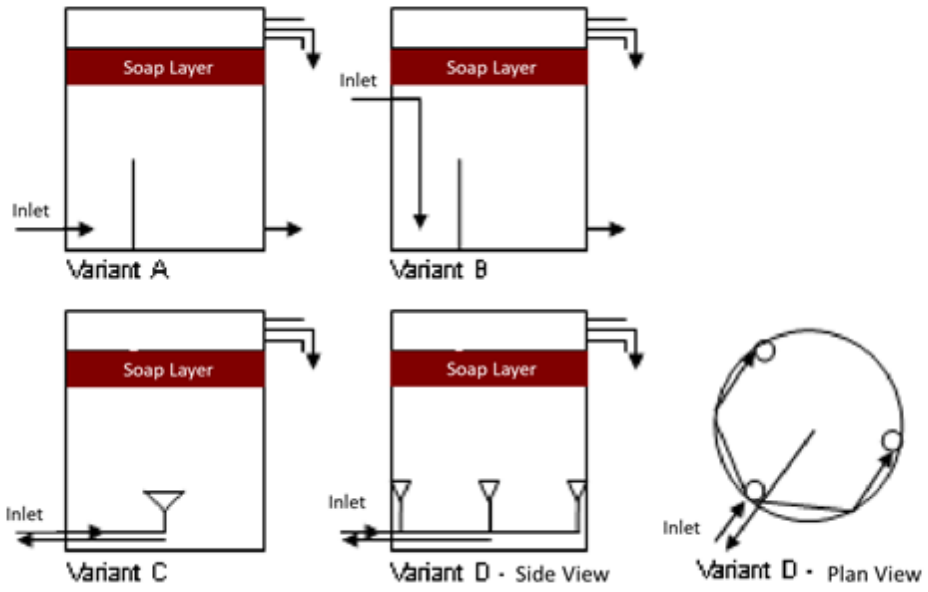
There are usually two feed liquor tanks @ 20 – 22 % solids, operated either parallel or in series. In some cases, they have three feed liquor tanks.

Best practice is that if the feed liquor tanks are in series, the first tank should be operated full all the time, to utilize the maximum retention time. A small volume of soap will overflow continuously from the first tank. The second tank will then act as a buffer for flow changes, and occasionally the level is increased to overflow the accumulated soap layer over from the top.

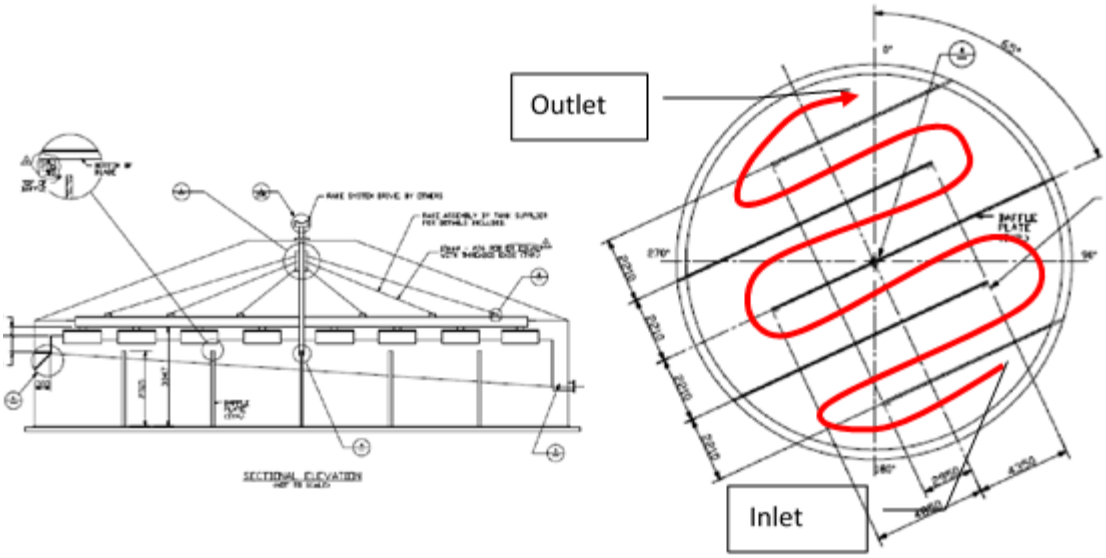
Parallel tanks are usually skimmed in sequences, e.g. once / day. This means the level will be increased to overflow the soap, and the same procedure will follow for the other tank too. This sequence is performed daily.

The intermediate tanks are usually skimmed once or twice per week, some even less often, based upon the experience of operators. One big difference is that there is not continuous soap removal using rotating skimmers (see below), but the soap is recovered by overflowing the tanks instead. Usually the problem is, that there is no visible soap in the intermediate tank, so that it could be skimmed more often.

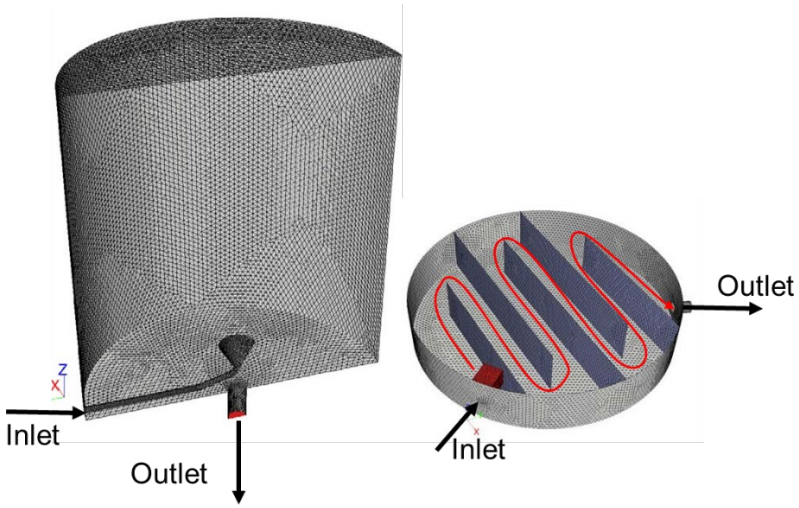
Computational Fluid Dynamics Study of Common Soap Skimmer Designs
An excellent study using computational fluid dynamics (CFD) has been done on several different soap skim tank designs found in a number of Swedish mills (41).



The CFD simulations of three existing liquor tanks showed that the previously used design-rules based on superficial liquor velocities are inadequate as the actual flow velocities within the tanks are two orders of magnitude larger than those previously used as reference (the superficial liquor velocity). The CFD simulations also show that the black liquor flow and the soap separation is very sensitive to density variations of the inlet black liquor due to either temperature or concentration. Temperature variations as small as 1 °C can significantly affect the liquor flow patterns. These skimmers, also referred to as intermediate tanks, are generally 5 to 10 times as large as a typical North American baffled skimmer.



Elevation and top view of the simulated soap tank of the North American model, the red arrow shows the main liquor flow path.



European Soap Skimmer Type C

North American Baffled Soap Skimmer

The relative size of both designs is correctly depicted.

Soap Removal from Evaporator Soap Skimmers

Skimmer Design

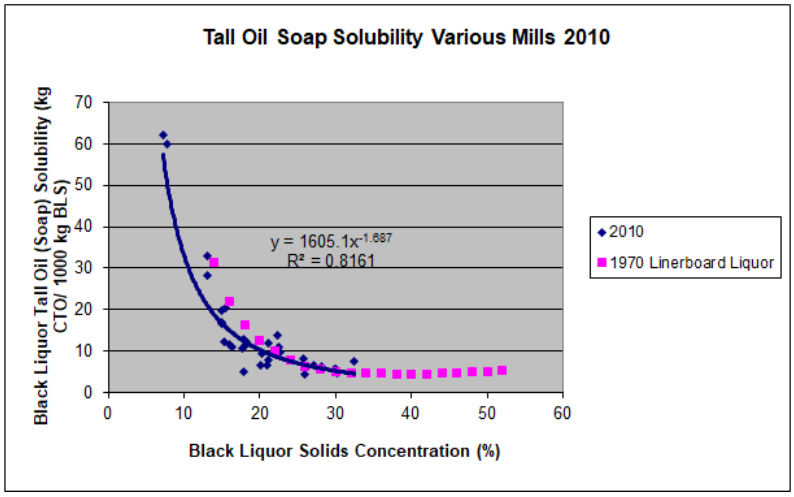
Skimmer Efficiency Determination

The efficient operation of a soap skimmer is best determined by comparing the difference between the feed and discharge tall oil residual (PCA 24) with the difference between the feed and the solubility limit. Placing the skimmer at the location where the dissolved solids content is about 25% is usually optimal. A study (19) was done on a variety of Canadian soap skimmers. The study observed wide variations in soap removal efficiency. It was apparent from this study that simply having a large skimmer residence time was not sufficient to ensure high soap skimming efficiency.

Soap Skimmer Efficiency

$$\frac{(\text{Inlet Soap} - \text{Outlet Soap})}{(\text{Inlet Soap} - \text{Soap Solubility})} = \frac{(3.3\% - 0.7\%)}{(3.3\% - 0.5\%)}$$

$$= 93\%$$



Temperature Effects

Variation on both the incoming temperature of the black liquor and convective cooling along the walls of the skimmer can have large impacts on soap separation. The CFD simulations also show that the black liquor flow, and soap separation, is very sensitive to density variations on the black liquor inlet and temperature variations as small as 1 °C can significantly affect the liquor flow. This is especially true for mills that have larger ambient temperature differences between summer and winter. Black liquor in the soap tanks is hot relative to the ambient air, and the incoming temperature is typically 70°C - 90 °C (158°F - 194°F) or more. The large surface of the tanks in contact with ambient air, about 1000 m^2 (10,800 ft^2) , means that they need to be insulated to reduce heat loss, and typically the tank is insulated with 8-12

inches (2 - 3 dm) of insulation. The insulation reduces the heat losses and the temperature drop in the drain tank.

Soap Particle Rise Rates and Liquor Downdraft

The soap particles that form in the black liquor separate naturally from solution. The yield of soap from the process is directly proportional to velocity at which the soap particles rise from the black liquor. Stokes Law is often applied to estimate the sedimentation rate of particles in a heterogeneous system:

$$V = D_P^2 (\rho_p - \rho_m) g \ / \ 18 \ \mu_m$$

Where:

V = Sedimentation Rate
D_P = Diameter of the particle
ρ_p = Density of the particle
ρ_m = Density of the medium
g = Gravitational constant
μ_m = Viscosity of the medium

The applicability of Stokes law for the case of separation of soap from black liquor was verified and rate constants were determined. The rate of separation of the soap from solution was accelerated by the application of surfactants (39). The size of soap particles varies depending on the presence of organic surfactant, and perhaps on the type of surfactant as well. Other microscopic indicates that a lamellar liquid crystalline phase is present (37).

Soap rises slowly, 3.5-25 ft./hr.(1.2-7.6 m/hr.). (20), soap will not separate if it does not have enough time to reach the liquor surface. Soap particles will not reach the surface if their rise rate is slower than the liquor settling rate or liquor downdraft or superficial velocity. The superficial velocity is defined as the skimmer volumetric feed rate divided by the skimmer surface area.

Feed Rate	1000	gpm	3780	l/m
	8021	ft^3/hr.	227	m^3/hr
Skimmer Diameter	33	Ft.	10	m
Skimmer Area	845	ft^2	79	m^2
Superficial Liquor Velocity	9.5	Ft./hr.	2.9	m/hr.

The removal efficiency plotted against the skimmer superficial velocity is essentially linear. At a superficial velocity of 3.3 ft./hr. (1m/hr.), the recovery efficiency was greater than 90% as expected from earlier studies (20).

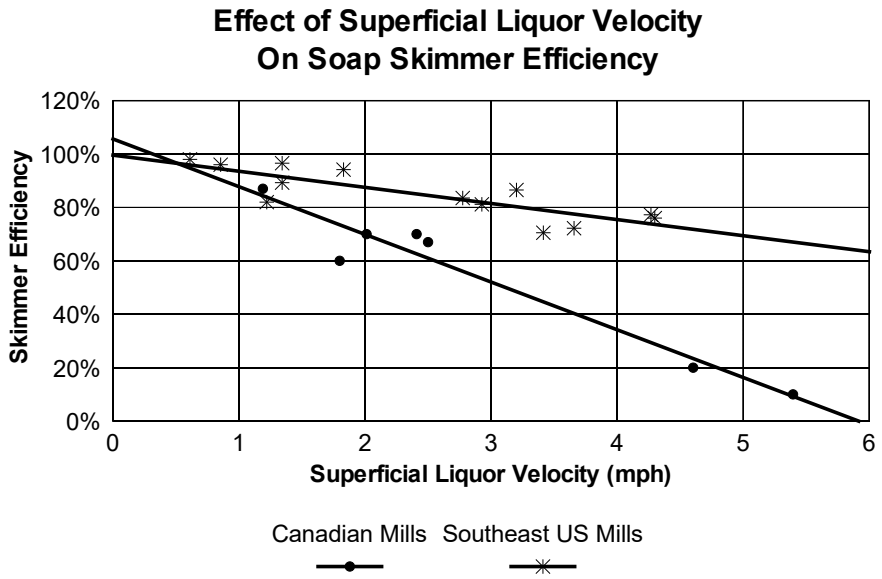


Figure 4.3.18 Effect of superficial liquor velocity on soap skimmer efficiency

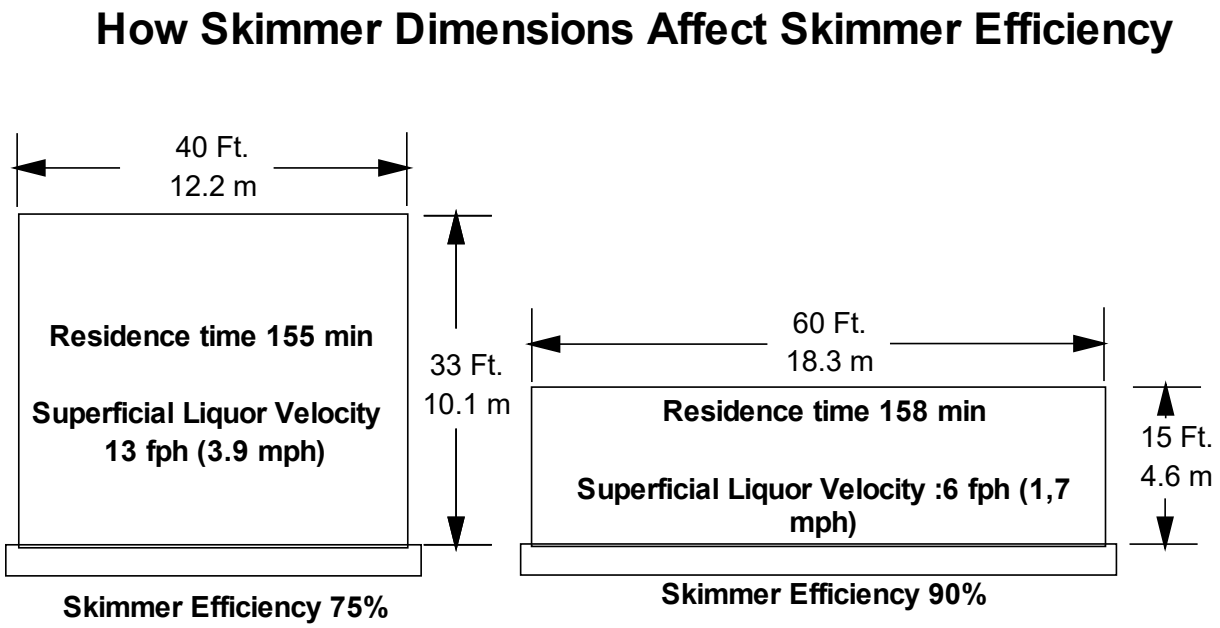


Figure 4.3.19 How skimmer dimensions affect skimmer efficiency

Traditionally residence time was used to specify skimmer performance. However, as Figure 4.3.19 demonstrates, for the same residence time, a taller skimmer will be less efficient because it has a higher superficial liquor velocity than a wide soap skimmer of equal volume.

The CFD study also examined the impact of the height / diameter ratio of a soap tank. Three Type 3 tanks were simulated, and all having the same volume, 3500 m^3, but height / diameter the ratio was varied from 1.6, 1.1 and 0.6. , fewer drops reach the outlet.

Percentage of soap droplets that reach the outlet at two different tank diameters.

	Height to Diameter – 1.1	Height to Diameter 0.6
10 µm	60%	33%
30 µm	58%	32%
100 µm	3%	1%
300 µm	0%	0%

The conclusion of this study is that the height / diameter ratio in the tank should be reduced. If the soap droplets are less than 100 µm, this study indicates that at a fixed volume, the diameter should be increased and the height should be lowered, as this increases the probability that a drop will reach the soap bed and be captured.

Skimmer Baffling

The superficial liquor velocity accounted for 90% of the variability in the data shown in Figure 4.3.18. There are other factors including: liquor short-circuiting, soap/liquor interface location and the relative location of the skimmer feed and outlet. Adjustments to skimmer baffling have resulted in marked skimming efficiency improvement (17). In general, the baffling should be kept simple. The more changes in liquor direction, the more turbulence is generated. Increased turbulence decreases soap removal (see also Figure 4.3.20). There are several recommended baffling alternatives (1).

Rectangular soap skimmers provide high efficiency and circular soap skimmers with the highest efficiency used spiral baffles (22). The liquor linear velocity (feed rate divided by channel area) should be greater than 2.4 ft./hr. (0.73 m/hr.). Lower velocities result in excessive solids settling in the skimmer.

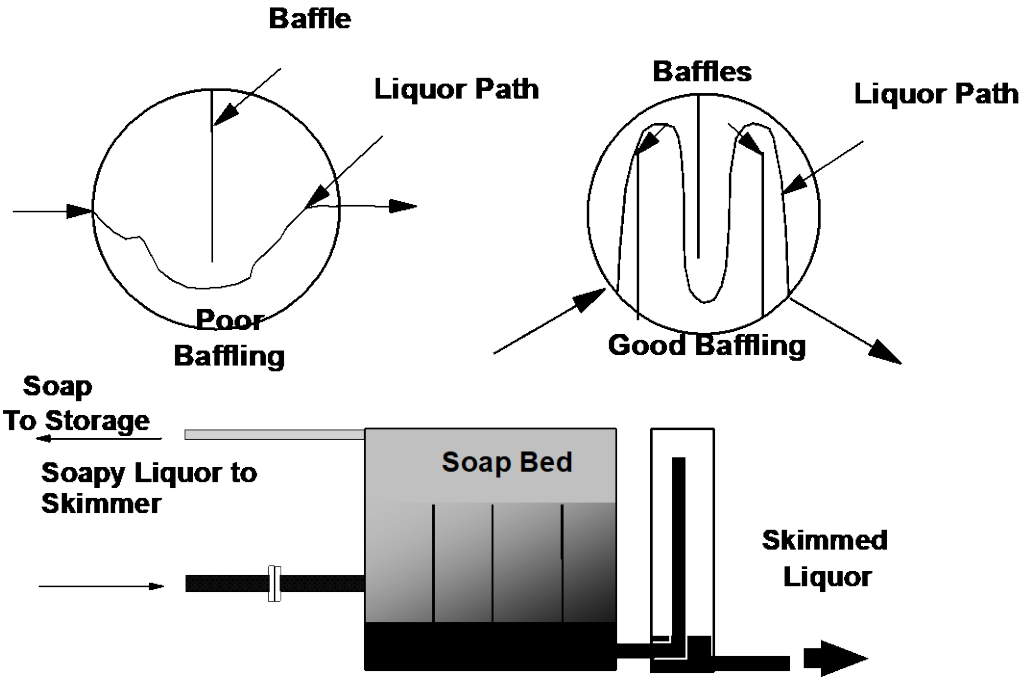


Figure 4.3.20 Skimmer baffling to prevent soap short circuiting

Skimmer Liquor Level Control

Another source of skimmer upset is varying liquor level (22). The most stable control is the overflow standpipe and adjustable weir. This device provides stable level control and a means to control the liquor interface.

Since soap accumulates very slowly, one of the best ways to assess soap production is to install a level transmitter and strip chart recorder for the soap level trough. A strip chart, tracing a steady rise and fall of the soap trough level, (drawing “M’s and W’s” regularly) is a good indication of a correctly adjusted soap skimmer.

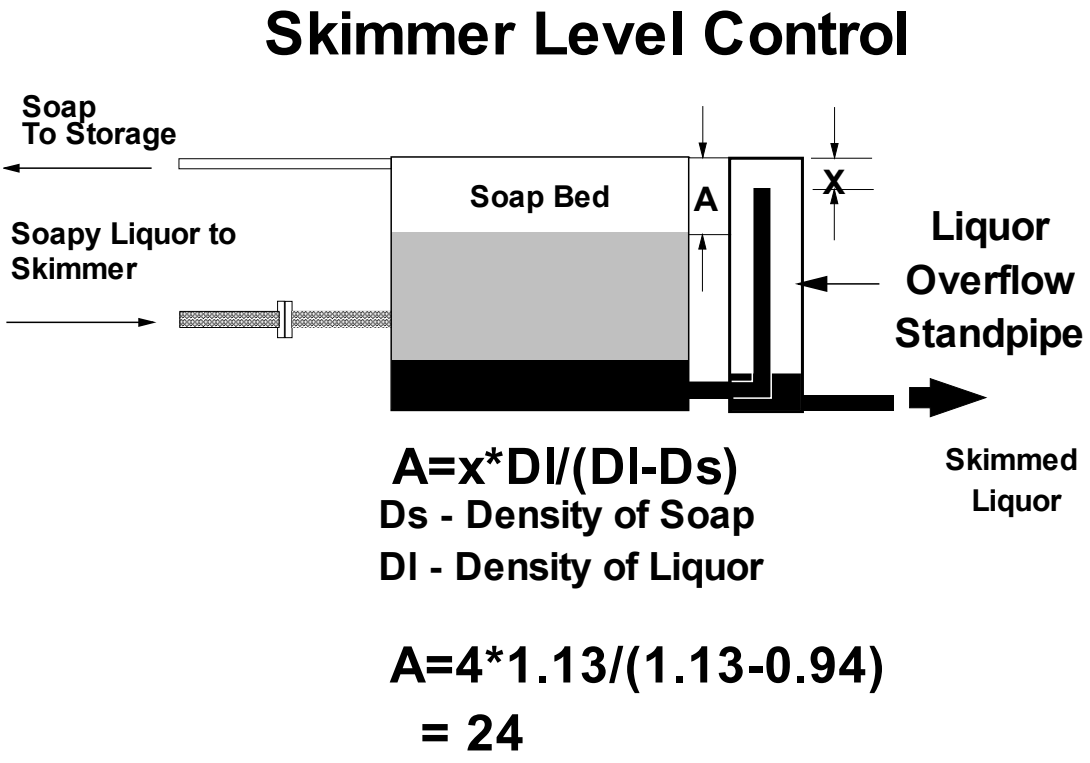


Figure 4.3.21 Skimmer level and soap bed depth control

Soap Bed Depth

The soap bed depth should be minimized directly above the skimmer liquor exit (22,23). Soap beds that are too thick result in re-entrainment of the soap particles in the liquor leaving the skimmer. Soap beds that are too thin result in excessive liquor carryover. Thin soap beds may also contribute to soap re-entrainment due to thermal convection currents and soap scraper convection currents. Soap bed depths should never exceed 2 ft. (0.7 m) immediately before the soap collection trough. One of the best indicators of soap bed depth is temperature. Generally, the soap bed is 20-30°F (10-15°C) cooler than the liquor temperature. Soap taps on the side of an enclosed skimmer can also be used to determine the soap bed depth.

Soap Bed Depth =
(Skimmer Level-Liquor Overflow Level) *(Density Liquor)/ (Density Liquor- Density Soap)

It should be recognized that small adjustments in the skimmer operating level can result in long lasting upsets. As Figure 4.3.21 illustrates, a 1 unit increase in the skimmer depth can result in a 4 unit decrease in the soap bed depth. If the skimmer level is then decreased, the soap bed depth will initially be the same. However, since soap is frequently only about 1% of the total liquor flow, it will take a long time to rebuild to the bed of soap.

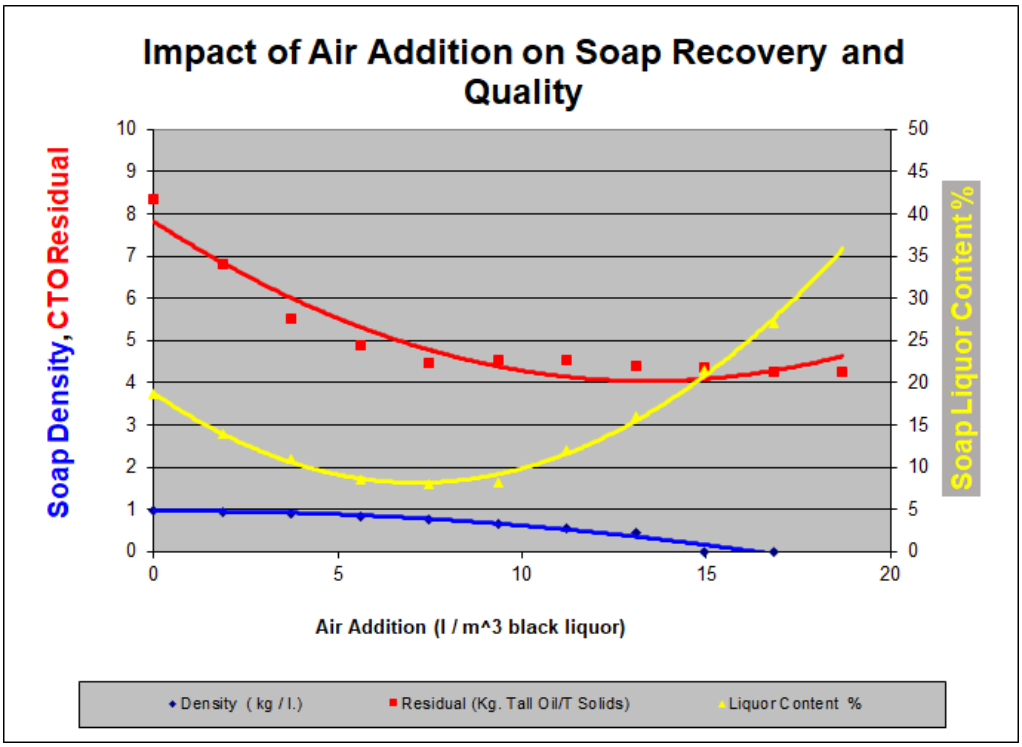
Methods for Increasing Soap Skimmer Efficiency

Basics such as skimmer feed solids, baffling, liquor entry point, level control and bed depth should be optimized first. These basics should achieve outlet residuals below 6 lb. CTO/ 1000 lb. black liquor solids (0.6 kg./100 kg.) on a skimmer with more than three hours retention time.

On smaller skimmers, or skimmers that are very tall or cannot have their baffling altered easily, additional methods should be applied. These are:

Air Injection

The simplest and least expensive method of improving skimmer soap recovery is through air injection. Small quantities of air injected into the skimmer feed improved skimmer efficiency up to 22% (18,19,22). It is critical that the air be finely atomized. Equally important is that although a little bit of air was good, much more air is bad. All three studies indicated that the optimum amount was 1 scfm/1000 gpm (7.5 L/M^3).



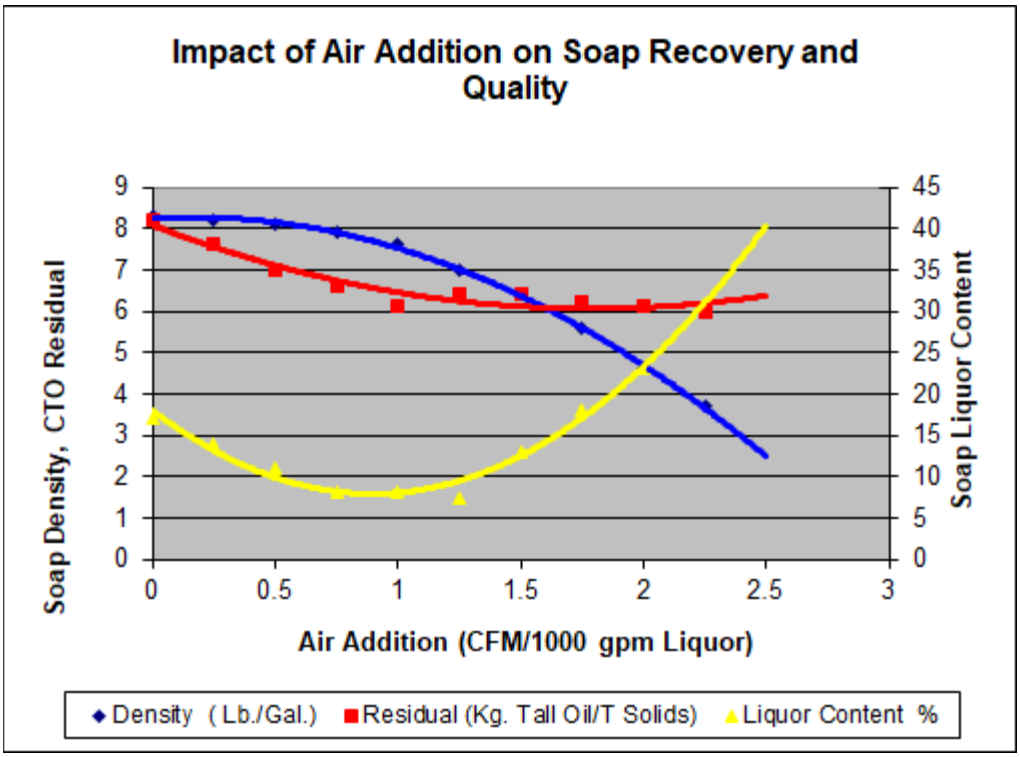


Figure 4.3.22 Effect of air injection on soap skimmer outlet residual, soap density and liquor content

The use of higher air flows reduced skimmed liquor soap residuals slightly. Higher flows also lowered the skimmed soap density and increased the black liquor entrained in the skimmed soap. When correctly adjusted air injection should result in a soap density of about 6.6 lb./gal. (0.75 Kg./L.).

For good atomization most mills inject the air into the suction side of the skimmer feed pump. At air flows of 1 scfm/1000 gpm (7 - 7.5 L/M^3) pump cavitation is not a problem. One mill has used a sintered metal tube to provide finely atomized air on the pressure side of a skimmer feed pump. This would be necessary on most falling film evaporator feed lines to the soap skimmer.

Several mills have applied air injection to large, well designed soap skimmers. They have seen little benefit in skimming efficiency. This is to be expected. However, they have noted that control of the soap bed depth has been more consistent. This should reduce the potential for soap particle re-entrainment.

It should also be noted that since air injection lowers the soap density, it will also affect the soap bed depth. For a given skimmer operating level target, decreasing the soap density will reduce the soap bed depth.

Electroflocculation

The fine particles of tall oil soap that are suspended in black liquor and normally lost in the liquor going to the recovery furnaces can be electrically charged. When charged they agglomerate and form larger particles which separate readily. A corona wind discharge directed against the surface of the black liquor causes the small particles to collect and float to the top of the skim tank. The potential used varies from 10,000 V to 100,000 V. The direct current flow is low, usually fractions of a milliampere (1).

A similar effect can be attained by immersing direct current electrodes into a stream of black liquor. The voltage used is below the decomposition potential of water. A commercial process (24,25) has been reported that by applying an electric field to a liquor stream, they were able to reduce skimmer outlet residuals. The performance of several installations is summarized in Table 4.3.9.

A mechanical air atomizer was used in the feed stream ahead of the electofloccuclator to aid in soap separation. About 10-20% efficiency improvement is due to air flotation.

In one mill that used a digester additive to enhance liquor penetration, the additive increased the soap solubility. This helped soap removal during washing. Unfortunately the soap did not separate effectively in the soap skimmer. It seriously fouled the evaporators. The electroflocculator effectively helped agglomeration of the soap particles and significantly improved recovery.

Table 4.3.9. Electroflocculator results pilot trials in five mills

Mills	*A*	*B*	*C*	*D*	*E*
Tall Oil Leaving Skimmer - No Electroflocculator	12.4	22	10	6.3	13
With Electroflocculator	5.5	15.5	4.3	5.2	5.5
Fatty Acid/Rosin Acid ratio	0.91	0.56	1.43	0.87	0.83
Solubility Limit	5	7	3.5	5	5
Efficiency - No Electroflocculator	80%	56%	67%	87%	63%
With Electroflocculator	99%	75%	96%	98%	98%
Improvement	24%	34%	43%	12%	56%

Chemical Additives

The effectiveness of proprietary additives to help soap recovery has been evaluated. Several commercial additives (19,37,39) were added at the suction of the skimmer feed pump. These surfactants significantly increased soap skimming efficiency in all mills at dosages as low as 0.6 ppm. “Results also show that simple surfactants, their level and point of introduction into the process influence the separation of soaps from black liquor. The additives function by changing the aggregative behavior of the soap micellar solution. The mechanisms by which surfactants influence the separation of soap are not yet fully understood, however, there exists a large amount of knowledge in the colloid chemistry literature that may be applied in solving some of the more practical problems” (37).

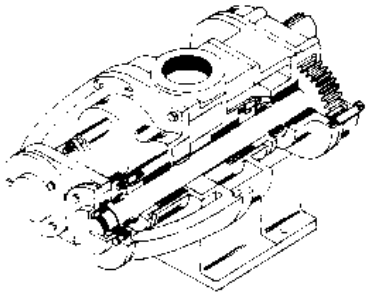
Cationic polyamides, used to flocculate the soap particles have improved skimming efficiency, however their performance has been more inconsistent (19,37).

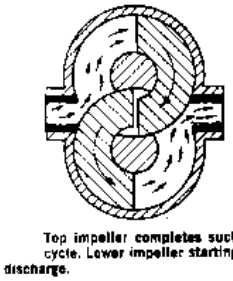
“The mechanism of action of this polymer is not presently understood. It would be expected that the cationic groups would be overwhelmed by the anionic material present in black liquor. Small scale trials in the laboratory with model polymers failed to explain the factors involved in determining the efficacy of the cationic additives. The additive had no effect on soap solubility in the laboratory or full-scale mill studies.” (19)

Soap Handling Equipment

Pumping

Due to its high viscosity, soap is best pumped with a positive displacement pump, typically a gear pump. If the pump contains an internal pressure relief valve, it should be set to about 75% above the system pressure. Failure to set the internal pressure relief high enough will result in frequent soap trough and soap tank overflows. The pumps should be checked regularly for wear. Spare pumps should be valved using positive closure ball valves. When not in service the spare pumps should be completely isolated. Steam clean-out lines should be available and used whenever a soap pump is placed on standby. Check valves should never be used in soap lines since they are readily fouled by the soap.



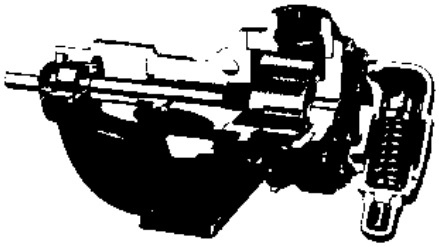


Courtesy Tuthill Corporation, Tuthill Pump Division

Cutaway View - Packed Type Gear Pump



Cutaway View - Mechanical Seal Type Gear Pump



Courtesy Houdaille Industries Inc., Viking Pump Division

Figure 4.3.23 Positive displacement pumps for soap pumping

Soap Densification

The first stage of soap densification occurs in the weak liquor storage area. Traditionally this is done using a foam tower. The foam tower is a tall and narrow tank with a foam breaker at the top. Mechanical soap densification equipment is designed to operate in two ranges. The first range is very low density soap such as washer foam. A foam concentrator is a single stage centrifuge that collapses the foam. The collapsed foam flows along the wall of the centrifuge bowl (see Figure 4.3.24). Air separated from the foam is discharged to the atmosphere. The collapsed foam density is normally 0.5-1 lb./gal. (0.06 to 0.11 kg/L) (27,28). Light soap overflows the weak liquor storage/filtrate tank into the foam tank. The mass of the liquor laden soap partially collapses and densifies the soap. The soap is then transferred to a decanter for liquor removal. The resulting foam is usually less than 2.5 lb./gal. (0.3 kg/L). The liquor content of this dense foam is usually more than 50%. This material is difficult to pump.

The foam tank system is being replaced by the use of a soap collection tank and soap concentrator arrangement (27). Soap recovered from the weak liquor storage is gravity fed into a soap tank. Liquor settles to the bottom and is returned to weak liquor storage. The soap overflows at a point about 1 m

above the liquor return line. The soap then passes through a soap concentrator. The soap concentrator is similar to the foam concentrator, but produces a soap with a density of 5-8 lb./gal. (0.6-0.9 kg/L). and can be readily pumped in conventional soap pumps.

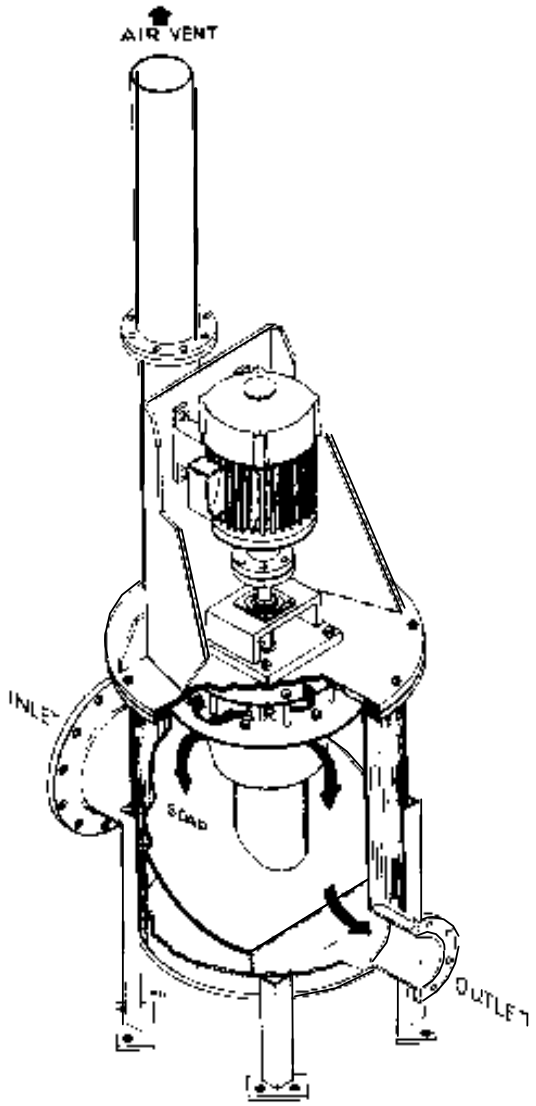


Figure 4.3.24 Soap Concentrator, courtesy A.H. Lundberg Associates.

Soap/Liquor Separation in Storage

Soap storage has been traditionally designed not so much as storage, but as a retention tank. This tank allows time for the liquor to drain from the soap. Soap discharged from the skimmer normally has a liquor content of 10% to 25% by weight. Weak liquor soap can contain as much as 50% black liquor by weight. Black liquor in the soap adds increased costs to the mill for shipping liquor to a tall oil plant. Commonly mills are penalized for excess liquor in the soap. The excess liquor in the soap also increases the cost of acidulation.

To effectively decant the liquor from the soap it is preferable to feed the soap into a tank with a conical bottom. If such a tank is not available, the soap should be cascaded through two soap storage tanks. Liquor that separates from the bottom of the tanks should be returned to weak liquor storage. The distance between the liquor withdrawal port and the soap withdrawal port should be at least 3 ft. (1 m). Soap should only be shipped or pumped for acidulation from the second tank in the cascade (27). A minimum of three days of soap storage should be provided as illustrated in Figure 4.3.25.

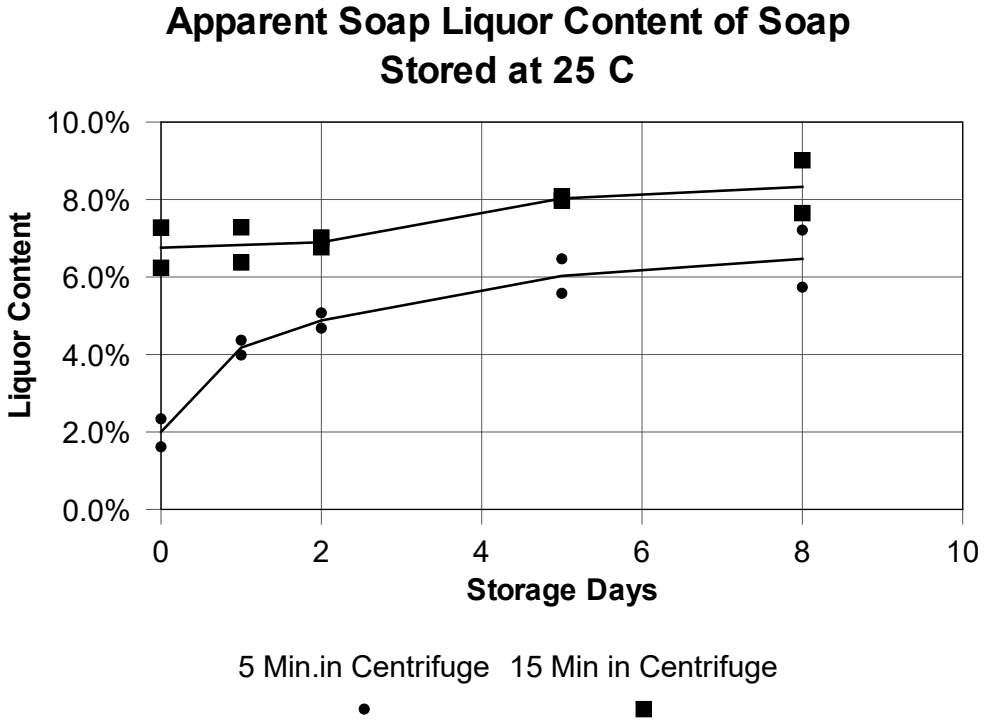


Figure 4.3.25 Effect of storage time on the apparent liquor content of soap

A device for releasing liquor from soap was reviewed (30). It consists of a rotating arm with fingers that gently move through the soap and provide both a collection point and a drainage path for the liquor (see Figure 4.3.26). The rake is installed so that the lower end of the fingers are in the liquor layer at the bottom of the storage tank. The soap rake was able to reduce the liquor content of the incoming soap by 50% or more. The main criteria to ensure good performance is to maintain a uniform feed rate within the design limits and to accurately sense and control the soap /liquor interface. This device should be installed in the last soap storage tank.

Soap/Liquor Interface Detection

The principal problem with interface detection in closed vessels such as soap decanters is soap fouling. Three sensors have been successful. A thermal conductivity probe has been used to control the soap liquor interface (30). This probe uses a three-element head, one of which is a heated probe. This probe melts the soap and avoids fouling. This device only works well in locations where there is not a rapid flow past the probe. The others are a viscosity probe and an ultrasonic probe. Both have been used to start and stop liquor pumps.

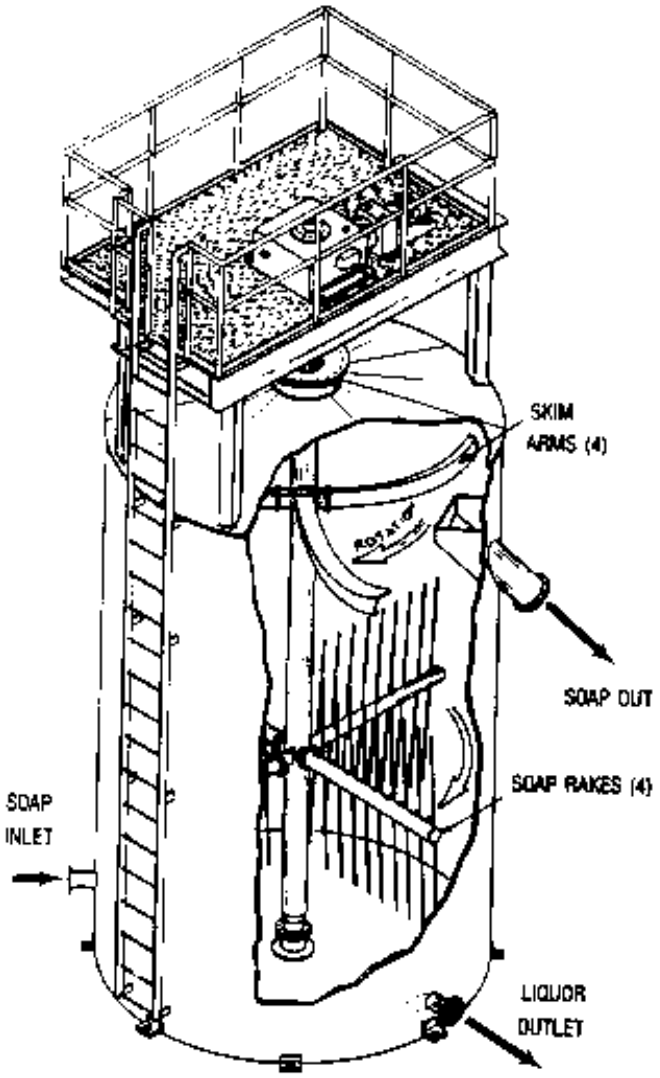


Figure 4.3.26 Soap Rake to enhance liquor removal

Miscellaneous

Fiber Content of Soap

One of the most reliable indicators of liquor fiber content is to measure the fiber content of the soap. Soap acts as a flotation medium for trapping the fiber in much the same way that minerals are recovered from ore. The fiber content of soap is usually 10 - 15 times as high as the fiber content in the liquor. For example, in one mill:

Measured liquor fiber content, 60 - 400 ppm
Skimmer feed liquor 5% soap, average liquor fiber content 200 ppm,
Skimmer product liquor 1.2% soap, average liquor fiber content 192 ppm fiber
Calculated soap fiber concentration, 2105 ppm fiber
Measured soap fiber content, 1800 -2300 ppm

During this period of time the soap fiber content was much more consistent than the liquor fiber content.

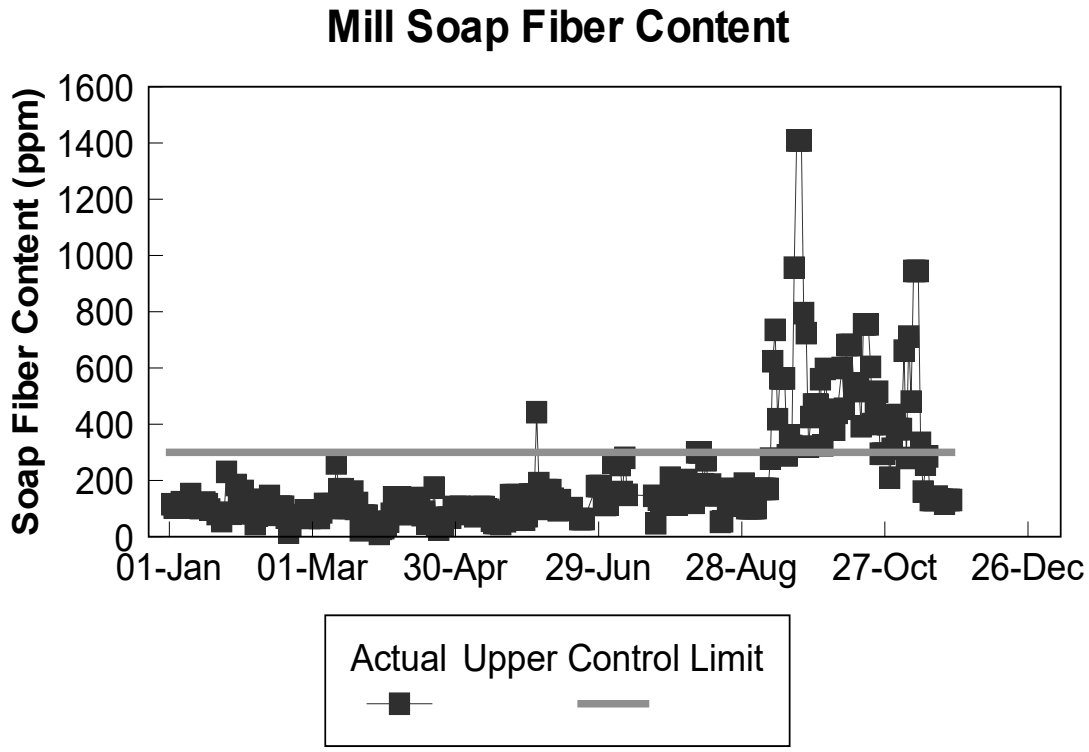


Figure 4.3.27 Mill soap fiber content, normal and upset operation

In Figure 4.3.27 above, weak liquor filter feed sampling failed to identify the source of the fiber contamination. This was because the washer on which the contamination occurred did not run continuously. It was typically in service for 8 - 16 hours at a time. The problem was corrected during an extended outage on the washer.

Useful Analytical Methods

Soap Liquor Content - One of the simplest methods of determining the liquor content (LC) of soap is to centrifuge a 15 ml. sample at 1500 G-force for 15 min. First the sample should be weighed in a tared centrifuge tube. The sample should be kept at 25°C to assist reproducibility. The liquor content can be determined by observing the location of the soap liquor interface.

LC= ml Liquor*1.1/grams of sample

Soap Density

Since most of the processing equipment is sensitive to soap density, this is one of the most useful and simplest measurements. It can readily be determined using a one-liter beaker. The beaker should be filled and leveled using a spatula. The measured density should be adjusted for the liquor content. The adjusted, or liquor free soap density should be used for diagnostic purposes. The measured soap density (MSD) can be adjusted for the liquor content (LC) to calculate the liquor free soap density (LFSD) as follows.

LFSD=MSD*(1-LC)

Black Liquor Tall Oil Residual Content

The residual tall oil (soap) content is probably the single most useful test when determining skimmer performance. The only widely accepted method is the modified Buckeye procedure, PCA 24 (31). A new method has been proposed (37) that appears to have improved accuracy and can distinguish the quantity of rosin acids and fatty acids removed.

The single most important step is sample collection. As was noted above, when liquor cools, at a given solids concentration, soap comes out of solution. Once out of solution, it is very difficult to return the soap into solution. A small portion usually remains on the wall of the sample container. To prevent the soap from coming out of solution during storage before analysis, the liquor should be sampled into water. There should be enough water present to ensure that the diluted solids do not exceed 4% dissolved solids.

Proportions necessary to obtain 4% solids

Bottle Size	*1 Pint*		*1 Quart*	
	473 ml		*946 ml*	
Black Liquor Solids Content	*Liquor* ml	*Water* ml	*Liquor* ml	*Water* ml
55	34	439	69	877
45	42	431	84	862
40	47	426	95	851
35	54	419	108	838
30	63	410	126	820
27.5	69	404	138	808
25	76	397	151	795
20	95	378	189	757
15	126	347	252	694
10	189	284	378	568
7.5	252	221	505	441
5	378	95	757	189

Always dilute the sample directly from the process sample point into water. Never, take an undiluted liquor sample back to the lab and dilute the sample for residual tall oil determination. Soap particles will separate in-transit to the lab and be poured non-uniformly into the dilution bottle. Table 4.3.9 below shows the quantity of water that should be used for collecting 500 ml. and 1 l samples at different feed liquor concentrations.

Calculations:

Let B= ml. black liquor necessary (unknown)
T = Total volume of black Liquor + water desired (ml)
S = Black Liquor solids content (%) 0.04= S*B*0.01/T
Table 4.3.9 Black liquor sampling dilution data

Spent Acid Assimilation

In mills where the black liquor soap is converted to tall oil, an additional complication is how to recycle the Tall Oil Plant spent acid. Although the Tall Oil Plant spent acid is usually called neutralized spent acid, it is neither acidic nor neutral. It should more accurately be called Tall Oil Plant Alkaline Brine. Mills successfully return the TOP brine at three separate locations:

1. To the batch digesters as fillback liquor,
2. In the feed to the black liquor evaporator(s),
3. In the feed to the recovery boiler concentrators.

In all three locations, strict control of the TOP brine pH is recommended. Return of the TOP brine at a pH below 7 will result in the evolution of toxic hydrogen sulfide (H_2S) gas. In most mills the pH is controlled to above pH 10.

At about pH 10 the unrecovered resin acids and fatty acids are fully saponified. Depending upon the point of return, it may need to be controlled to a higher pH. The TOP brine will have some residual salts and contaminants in it, $CaSO_4$ and others. The TOP brine storage tank must be well agitated. A recycle stream off the pump out line is recommended to control pH and to help keep the tank clean.

Batch Digester Fillback

Return of the TOP brine to the batch digesters should be done at a pH above 10. The TOP brine should be returned to fillback liquor holding tank. On low level in the tank, 1st stage washer filtrate should be used for level control. Return to the digesters results in an increased evaporator load. The water is evaporated at about 6 steam economy.

Evaporator Feed

The water in the TOP brine is evaporated at an economy of about 6. Once again, the pH should be controlled above 10. The feed rate should not exceed about 1.5% of the total liquor fed to the evaporator(s). At this rate it will decrease the soluble scale precipitation point 1-2% (33, 10). If the feed rate is likely to exceed 1.5% of the total, the settleable solids fraction in the TOP brine should not be returned. This fraction contains about 80% of the unrecovered soap content of the TOP brine. The soap contained in the TOP brine adds to the load on the soap skimmers. Furthermore, it contains fiber and calcium salts that could accelerate evaporator fouling. By removing the solids, soluble scalants e.g. soap, are also removed.

Studies have shown that the settleable solids in the dilute spent acid (13-17%) are less dense than the black liquor solids at 22-25%. Therefore, this material separates in the skimmers inefficiently. If not removed it represents a voluminous material which can easily plug the evaporator tubes.

Additional NaOH to increase the pH above 12 to fully solubilize the lignin is of marginal value. This would lower the critical solids concentration for Na_2CO_3-Na_2SO_4 saturation. This would likely increase soluble scale formation.

Return to the Heavy Liquor System

If the TOP Brine is returned to the heavy liquor system it must be carefully metered in at a point where it can be well mixed. It will decrease the overall solids level. Evaporation of the water will be at an economy of less than two. If fed to a liquor crystallizer/concentrator its effect on soluble scale formation is minimal since these devices are designed for supersaturated Na2SO4 solutions. It is critical that the brine be treated with 50% NaOH to neutralize any residual acids and to fully re-dissolve the lignin. Typically, about

9 lb. NaOH/Ton (4.5 kg/t) of soap is required. White liquor cannot be used for this purpose, because it can only increase the pH to about 11. This is not high enough to fully re-solubilize the precipitated lignin.

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