

## Tall Oil Soap Recovery

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### Abstract

This chapter 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 soap 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 acids in wood to their sodium salts. Associated with the salts are neutral or unsaponifiable compounds. The salts and unsaponifiables separate from the spent cooking liquor as black liquor soap.

“Black liquor soap naturally separates from black liquor at various points in the pulping process. The soap separates as a lamellar liquid crystalline phase (1). 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”(2).

Black liquor soap skimmings 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 dehydroabietic acids, although numerous distinctive isomers occur. Both abietic and dehydroabietic acids contain three six-membered rings. Dehydroabietic acid contains one unsaturated 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 (3).

Table 4.3.1. Composition of crude tall oil (3).

	<i>South- eastern USA</i>	<i>Northern USA &amp; Canada</i>	<i>Scandinavia</i>
Acid No. (1)	160 - 175	125-135	120-140
Resin Acids %	35 - 45	25 - 35	20 - 30
Fatty Acids %	45 - 55	50 - 60	50 - 60
Unsaps %	7 - 10	12- 18	18 - 24

1. Acid Number - The number of mil-equivalents of potassium hydroxide required to neutralize one gram of tall oil (1)

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 separation 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. (3,4,5)

### 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 (6). 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 (6)

<i>Pine Species</i>	<i>Tall Oil</i> <i>kg /1000 kg OD</i> <i>Wood</i>	<i>Tall Oil</i> <i>lb./ODT</i>
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 process losses and differences in operating practices.

Table 4.3.3. Tall Oil Recovery (7,8,9)

	Bleached Canada	Bleached S.E. US	Linerboard S.E. US
	kg CTO /ADT	kg CTO /ADT	kg CTO /ADT
CTO in Wood	27	61	59
CTO lost on Pulp	4	6	9
CTO lost to Sewers	2	1	2
CTO lost to Recovery Boilers	9	8	5
Recoverable CTO	13	46	43

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 4.3.4. Typical tall oil yields (3)

<i>Region</i>	<i>Tall Oil</i> <i>kg /1000 kg OD</i> <i>Wood</i>	<i>Tall Oil</i> <i>lb./ODT</i> <i>Wood</i>
Piedmont	24	48
Coastal	26	52
Canada	8.5	17
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..

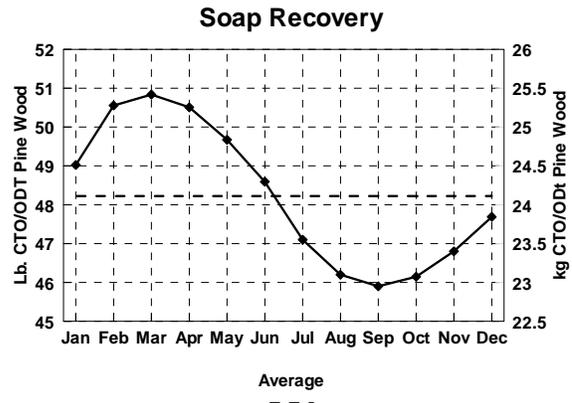


Figure 4.3.1 Soap recovery seasonal variation curve

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 (10). 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.

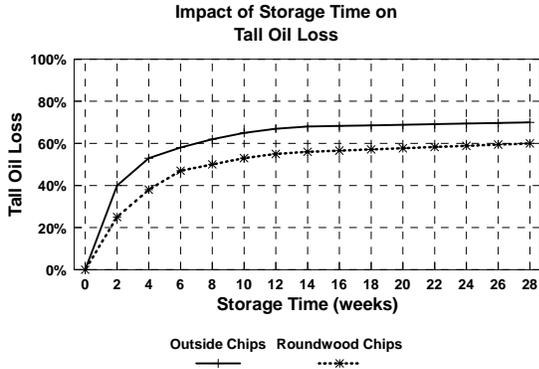


Figure 4.3.2 Impact of storage time on tall oil loss (10)

### 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 loading on the recausticizers,
- Reduce accidents due to slips and falls
- It is a valuable byproduct of the alkaline pulping operation..

**Improve Evaporator Operation** - In 1975, a study (11) 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  $\text{Na}_2\text{CO}_3$ - $\text{Na}_2\text{SO}_4$  scales. Others (12,13) have shown that soap is a significant scale component, particularly in soluble carbonate-sulfate scales in evaporators and concentrators. Mill and pilot plant studies (14) 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% (11).

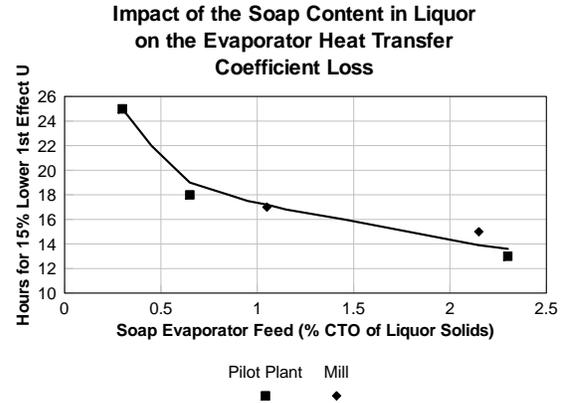


Figure 4.3.3 Impact of soap content in liquor on evaporator heat transfer efficiency expressed as the time for a 15% reduction in the heat transfer coefficient (14).

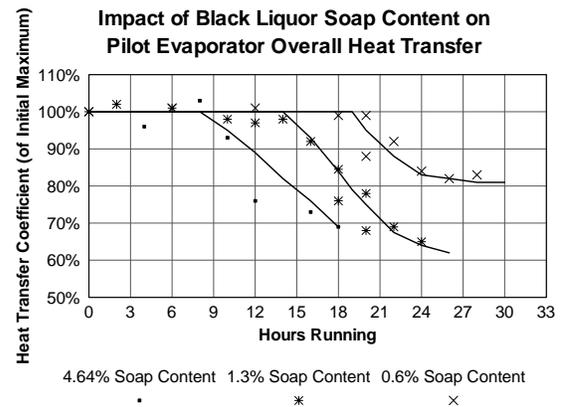


Figure 4.3.4 Impact of soap content in liquor on evaporator heat transfer coefficient loss (14).

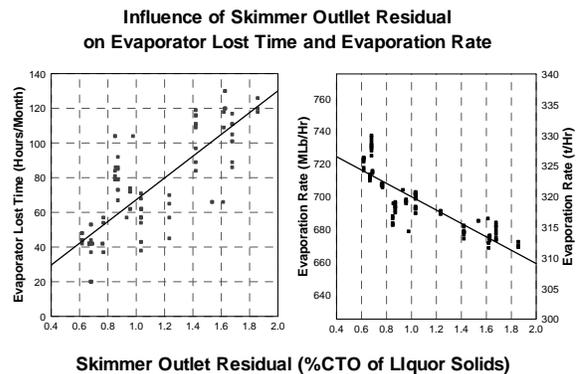


Figure 4.3.5 Influence of skimmer outlet residual on evaporator lost time and evaporation rate

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

Table 4.3.5. Effect of tall oil skimming efficiency on evaporator performance

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

### Evaporator Liquor Carryover

Soap carryover contributes significantly to evaporator liquor carryover and operational problems 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.

$$\text{Foam Height} = \frac{\text{Vol. Evap. Rate} \times \text{Avg. Bubble Life}}{\text{Foam Column Area}}$$

4. The volumetric evaporation rate increases at the lowest pressure effects in the multiple effect evaporator.
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 (3) 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 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 (15).

... 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 (16). 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 (17). 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 (18). Pulping capacity will be directly affected.

It has been found (18,19) 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 (20) 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 to 35 lb. 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.

**Reduced Loading on Reausticizers** - If a mill is reconstituted 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<sub>2</sub>CO<sub>3</sub>), whereas black liquor solids burn / reduce to a mixture of sodium carbonate and sodium sulfide (Na<sub>2</sub>S). The sodium sulfide does not require causticization after dissolution in the green liquor.

## Soap Removal Methods

### Factors Affecting Soap Removal

Drew and Propst (3) 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 (4) 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 (5) but was typically 7-15 lb. soap/ton of dry black liquor solids (3-8 kg. soap/tonne of dry black liquor solids). The concentration of soap in unskimmed softwood black liquor varies from 70-110 lb. soap/ton of liquor solids (35 - 55 kg./tonne).

Micelle formation is independent of temperature between 20°C and 80°C, but the soap becomes much more soluble at higher temperatures (2). The temperature in the soap skimmer is normally fixed by the operating temperature in the evaporator 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.

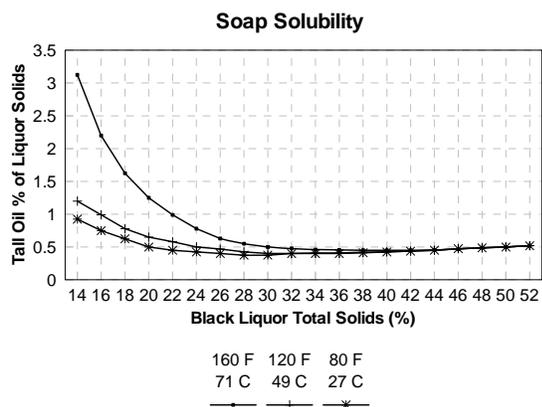


Figure 4.3.6 Tall oil soap solubility as a function of temperature and solids content

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).

### 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 rosin acid vary. Soaps containing a higher ratio of fatty acids to rosin acids showed lower solubility (4).

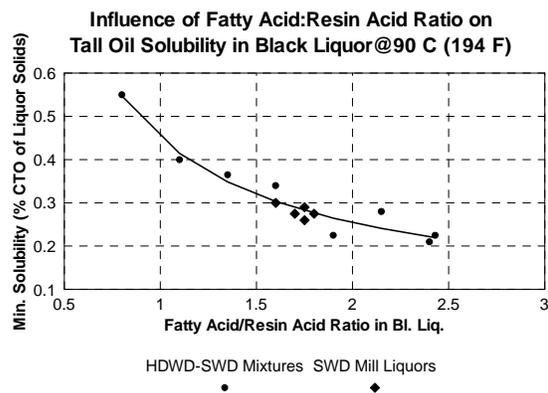


Figure 4.3.7 Relationship of fatty acid : resin acid ratio to minimum soap solubility in black liquor (4).

A recent study using a newly developed analytical procedure (1), 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 (4).

For good recovery it should be kept above 6 g/l in 17 - 20% solids liquor or 2.9% Na<sub>2</sub>O on a dry black liquor solids basis. The combined effect of lower effective alkali content and fatty acid: resin acid ratio is illustrated in Figure 4.3.8.

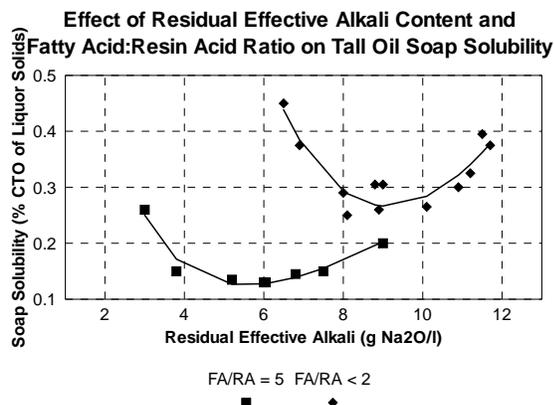


Figure 4.3.8 Effect of fatty acid : resin acid ratio and effective alkali content to minimum soap solubility in black liquor (4).

### Hardwood - Softwood Liquor Blending

Observations on 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 (18) 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 (4). Above about 60% kraft hardwood solids content, the solubility of the tall oil soap appeared to increase rapidly (Figure 4.3.9).

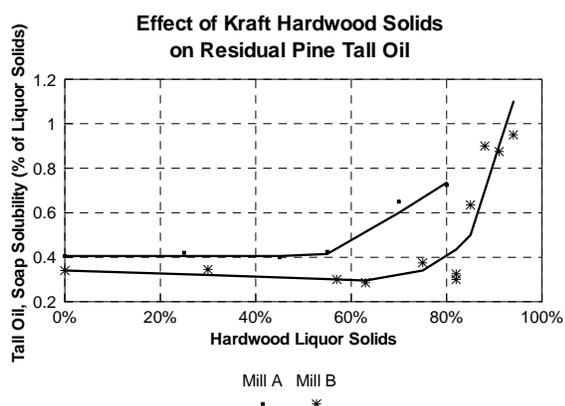


Figure 4.3.9 Effect of hardwood liquor on soap solubility at 194°F ( 90°C) (4)

At high hardwood concentrations, the residual effective alkali level was reduced enough so that the

soap was solubilized (4). This explanation would also account for much of the increase in solubility of the NSSC-pine kraft liquor mixtures (21).

### 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.

Table 4.3.6. Tall oil material balance (8,9)

Pulp Type :	Liner board	Bleach Pulp	Liner board
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		63	46
Recirc. Washer	12	7	8
Decker	8		
To Weak Liq. Tank	62	67	52
Fr. Weak Liq. Tank	60	21	31
Fr. Evap. Skimmer	12	9	7
To Rec. Boil.	11	9	7
Sewer	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%

A comparison of soap balances around a batch digester with 3 stages of vacuum washing, a continuous digester with an atmospheric diffusion

washer and a continuous digester with both in-digester high heat washing and a two stage vacuum drum washer appears in Table 4.3.5 above.

The first stage wash liquor in 1972 (9) had a dissolved solids content of about 13 %. The Kamyr liquor in the 1985 study (8) was about 17% dissolved solids. This resulted in a dramatic increase in weak liquor soap recovery.

In some recent batch cold blow systems, the recirculation of soap saturated liquor presented significant operating difficulties. The soap separated 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 (9). 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).

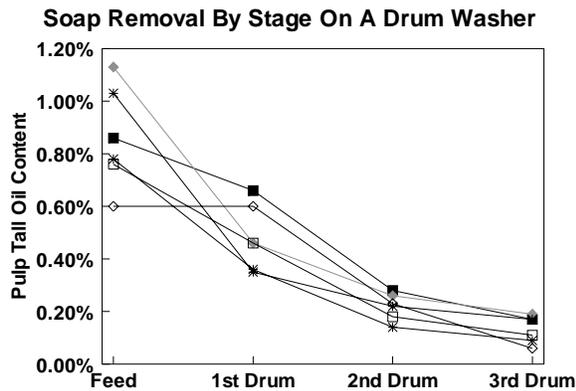


Figure 4.3.10 Soap removal by stage on a drum washer

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 probably indicate that steady state conditions had not been achieved (22). 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).

Table 4.3.7. 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%

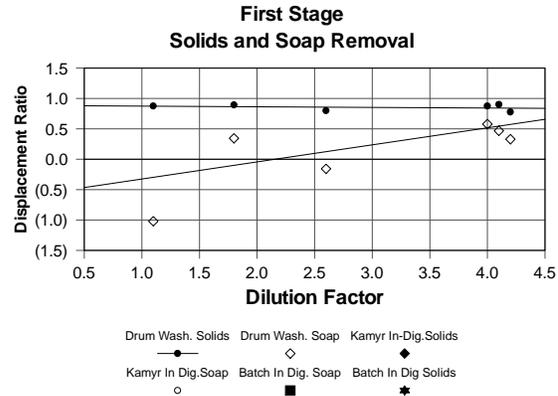


Figure 4.3.11 First stage drum washer solids and soap removal.

### 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 this system.

Table 4.3.8. Kamyr™ in-digester washing efficiencies.

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%

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. (see Table 4.3.8)

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 (23,24) have been introduced to improve the energy efficiency of the batch digestion process. Only unpublished data exists 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 Kamyrtm digestion process with regard to dissolved solids removal. However, soap removal is significantly less effective, even at higher dilution factors.(see Table 4.3.9)

Table 4.3.9. In-digester wash comparison

	<i>Dilution Factor</i>	<i>Solids D.R.</i>	<i>Soap D.R.</i>
Kamyrtm	1.7	97%	71%
Cold Blow Batch	2.7	84%	7%

In the cold blow batch digester system, the cooked chips are not in contact with the washer filtrate for as long a period of time as in the Kamyrtm 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 Kamyrtm 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, can be precipitated and recovered in the weak liquor system.

### Washer Filtrate Tanks

Weak liquor soap removal begins in the washer filtrate tanks. E.C. Cobb (25) has detailed the design considerations for vacuum drum washers.:

“As is shown in Figures 12 and 13, 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.

Liquor Tank Baffle Arrangements for Varying Tank Diameters

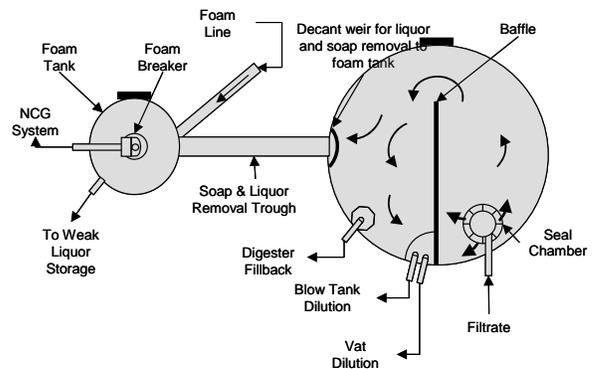
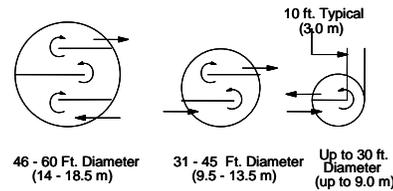


Figure 4.3.12 Liquor tank baffling, first stage tank and foam tank plan view

Figure 4.3.12 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 !**”

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.

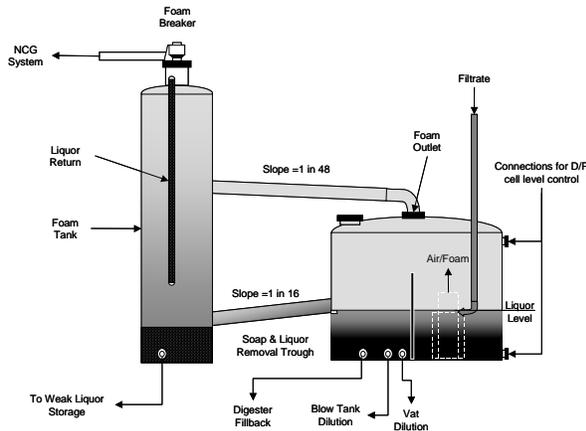


Figure 4.3.13 First stage liquor tank and foam tank arrangement

The air and foam released in the seal chamber and collects on the 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 that as the foam breaks down while moving 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 of each tank.”(25)

“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 foambreaker 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!”(25)

“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.”(25)

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.

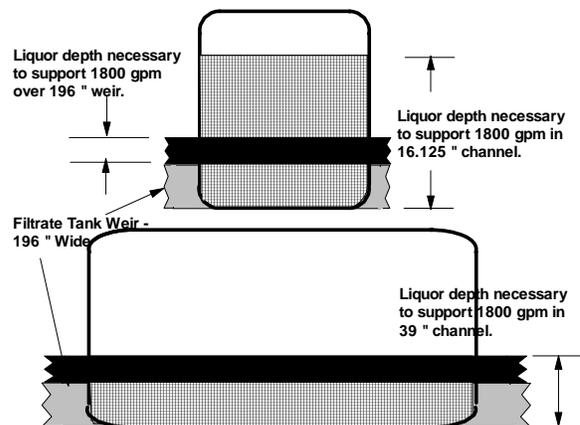
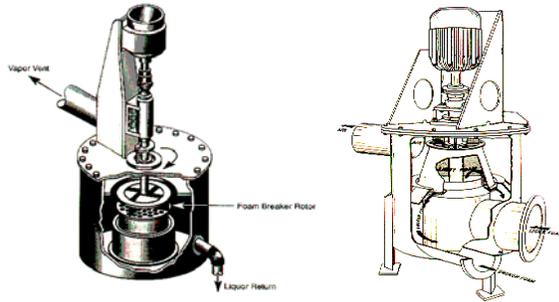


Figure 4.3.14 - How increasing the overflow channel width increases the area for foam / soap removal

Removal of soap accumulation can also occur in diffusion washer filtrate tanks. Such soap/foam accumulations dramatically increase defoamer usage, washed pulp sodium losses and bleaching chemical costs. There have been anecdotal reports of such accumulations in both softwood and hardwood washing systems.

### Foam Breakers

The initial means of soap removal is by foam breakers. These devices (see Figure 4.3.15) 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 4.3.15 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 4.3.16). These removal ports should be at least 12 inches (30 cm) in 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 (26). 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. Tanks larger than about 35 ft (10 m) diameter cannot usually be skimmed effectively from a single outlet location as indicated in the upper two diagrams below. It is generally advantageous to have outlets at multiple elevations within the normal operating range of the liquor storage tank. This is helpful since it is not necessary to raise or lower the tank level to permit soap removal.

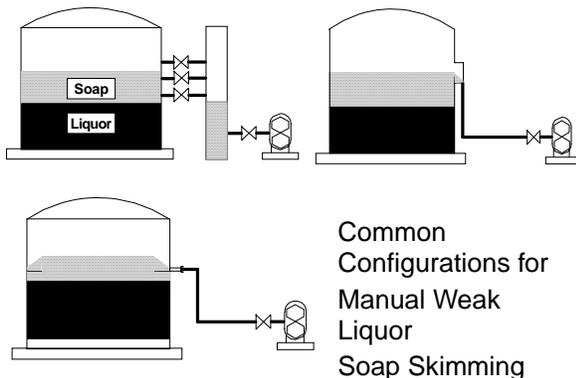


Figure 4.3.16 Common Configurations for Manual Weak Liquor Soap Skimming

### 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 (8). The floating skimmer permits continuous soap recovery over a wide range of operating depths (see Figures 17 and 18). 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 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. Other mills have used a proprietary viscosity sensor. However, on balance, the automatic controls for floating skimmers have required a great deal of attention, and have not fulfilled their promise.

The most successful applications pump soap for brief periods of time, (10 -15 minutes), on a regular timed interval (2 - 4 hours). By keeping the collection funnel and internal pipe full of soap, the skimmer remains submerged in the soap bed. If the pump is allowed to run continuously, the internal pipe empties and the skimmers float on top of the soap bed and try to pump air, requiring operator intervention.

### SOAP COLLECTION SYSTEM WITH A FLOATING SOAP SKIMMER

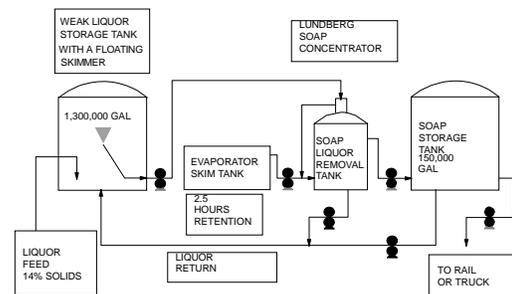


Figure 4.3.17 General equipment configuration for a mill with excellent weak liquor soap skimming

**Weak Liquor Soap Skimming Using a Floating Soap Skimmer**

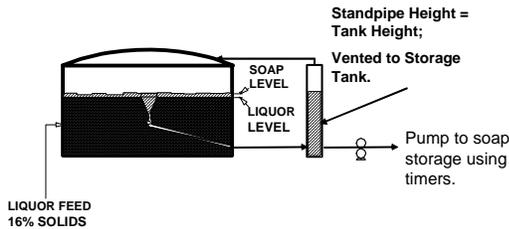


Figure 4.3.18 Weak liquor skimming detail

**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 25 - 30% is optimal. A study (17) 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 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:

$$V = \frac{D_p^2(\rho_p - \rho_m)g}{18 \mu_m}$$

Where :

- V = Sedimentation or Rise Rate
- D<sub>p</sub> = Diameter of the particle
- ρ<sub>p</sub> = Density of the particle
- ρ<sub>m</sub> = Density of the medium
- g = Gravitational constant
- μ<sub>m</sub> = 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 (27). The size of soap particles varies depending on the presence of organic surfactant, and perhaps on the type of surfactant as well. Other microscopic examination indicates that a lamellar liquid crystalline phase is present (28).

Soap rises slowly, 3.5-25 ft./hr.(1.2-7.6 m/hr.). (29), 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, also called liquor downdraft or superficial liquor velocity. The superficial liquor velocity is defined as the skimmer volumetric feed rate divided by the skimmer surface area.

Feed Rate	1000 gpm	3780 lpm
	8021 ft <sup>3</sup> /hr	227 m <sup>3</sup> /hr
Skimmer Diameter	33 ft	10 m
Skimmer Area	845 ft <sup>2</sup>	79 m <sup>2</sup>
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 (17).

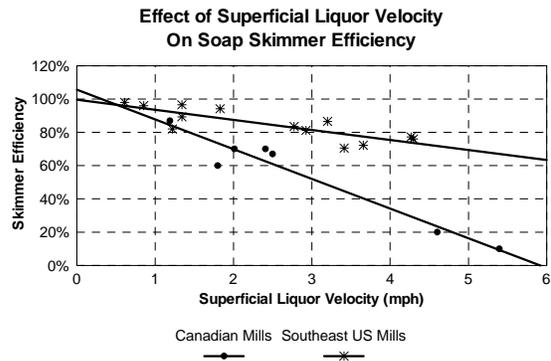


Figure 4.3.19 Effect of superficial liquor velocity on soap skimmer efficiency

### How Skimmer Dimensions Affect Skimmer Efficiency

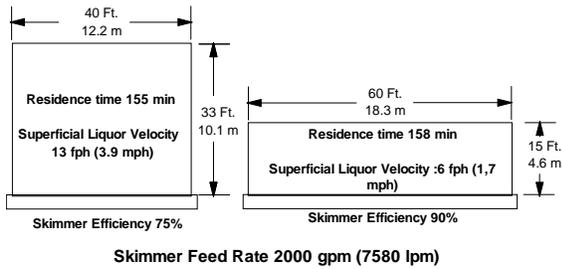


Figure 4.3.20 How skimmer dimensions affect skimmer efficiency

Traditionally residence time was used to specify skimmer performance. However, as Figure 4.3.20 demonstrates, for the same residence time, a taller skimmer will be less efficient because it has a higher superficial liquor velocity than a larger diameter soap skimmer of equal volume.

### Skimmer Layout

Although very few soap skimmers are rectangular in shape, their layout embodies the most important elements of skimmer design.

#### Rectangular Soap Skimmer Layout

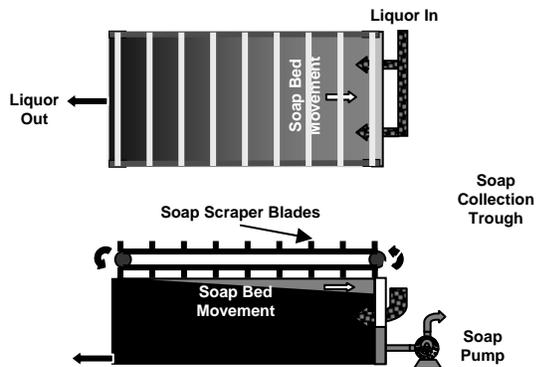


Figure 4.3.21 Rectangular soap skimmer layout

With reference to Figure 4.3.21, In rectangular soap skimmers:

1. The feed liquor enters at one end and the discharge liquor exits at the opposite end, thus maximizing the isolation of the inlet from the outlet;
2. The separated soap is pushed counter-current to the liquor flow;
3. The soap bed depth is thinnest above the liquor discharge;

4. The soap bed is thickest and most deliquored as it overflows into the soap collection trough;
5. The soap collection trough cannot overflow since it is at the same elevation as the rest of the soap skimmer;
6. Soap can easily be pumped away using simple start/stop level control in the soap collection trough;
7. Skimmer liquor level control is easily established either using a standpipe (see below) or level control using a level transmitter connected to an automatic control valve.

The following diagram illustrates how a circular soap skimmer should be arranged and baffled to achieve the same critical features of the rectangular soap skimmer.

#### Circular Soap Skimmer Layout

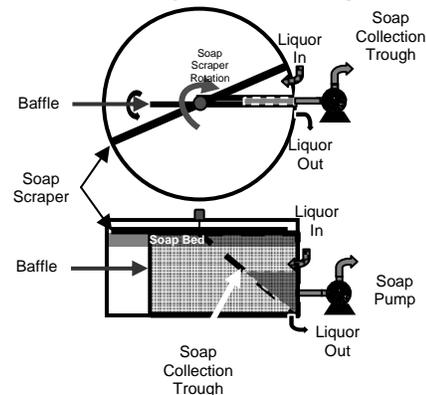


Figure 4.3.22 Circular soap skimmer layout

### Skimmer Baffling

The superficial liquor velocity accounted for 90% of the variability in the data shown in Figure 4.3.19. 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 (30). 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 4.3.23). There are several recommended baffling alternatives (3).

Rectangular soap skimmers provide high efficiency as do circular soap skimmers with baffling that provides a serpentine path. Circular skimmers with spiral baffles (31) have been very effective. However, spiral baffling is not recommended due to

“line-of-sight” considerations with respect to confined space entry when maintenance or cleaning is required. 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.

### Skimmer Baffling to Prevent Soap ShortCircuiting

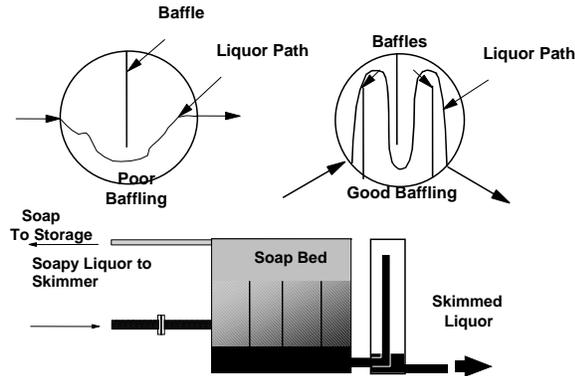


Figure 4.3.23 Skimmer baffling to prevent soap short circuiting

### Skimmer Liquor Level Control

Another source of skimmer upset is varying liquor level (31). If the skimmer diameter is significantly larger than the diameter of the evaporator body, small variations in a level of the soap skimmer result in large level changes in the evaporator body. For example, if the soap skimmer diameter is approximately three times that of the evaporator bodies. This would mean that the soap skimmer has a surface area approximately nine times as large as the evaporator bodies. Therefore, a very small variation in the indicated soap skimmer level, could result in the level of the evaporator body changing by nine times as much. Since the precision of level transmitter is limited to about 1%, the evaporator bodies level could be changing by as much as 9% due to noise from the level transmitter.

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. On most soap skimmers with a diameter greater than about 40 ft., the skimmer level is controlled by the use of a standpipe. Because the standpipe is a much smaller diameter, only real level changes in the soap skimmer result in changes in the standpipe level. Furthermore, changes in the standpipe level do not result in significant changes in the level in the evaporator body. For example, an 8% change in the level of a 5 ft. diameter standpipe would result in less than half percent (0.5%) change

in the level of 20 ft. diameter, evaporator body. For this reason, the most stable skimmer level control is achieved using an overflow standpipe with an adjustable weir. This device provides stable level control and a means to control the liquor interface. However, it is important that the inner standpipe be properly sized. If the inner standpipe is too small, this will result in excessive hydraulic back pressure that will interfere with the ability to build a soap bed.

Skimmer Solids 29%  
 Temperature 90 Deg C  
 Soap Density 1.03 kg / l

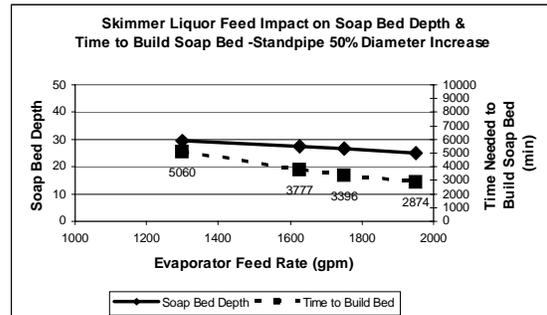
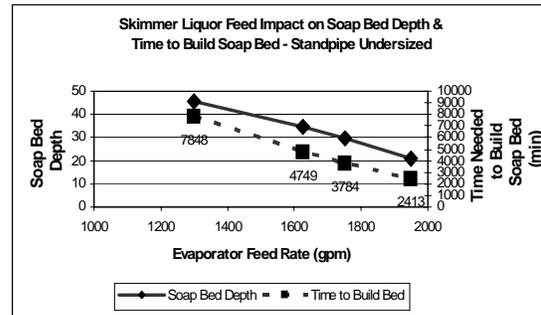


Figure 4.3.24 Influence of Skimmer Feed Rate and Inner Standpipe Diameter on Bed Depth and Time to Build a Soap Bed

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 in the collection 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.

### Soap Bed Depth

The soap bed depth should be minimized directly above the skimmer liquor exit (31,32). 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 and cooling of the liquor being returned to the next evaporator effect. 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.

The hydraulic balance for a soap skimmer is illustrated in Figure 4.3.25. As the figure indicates the impact of the resistance to liquor flow is usually negligible. However, should it not be negligible, increased resistance to flow would tend to reduce the thickness of the soap bed.

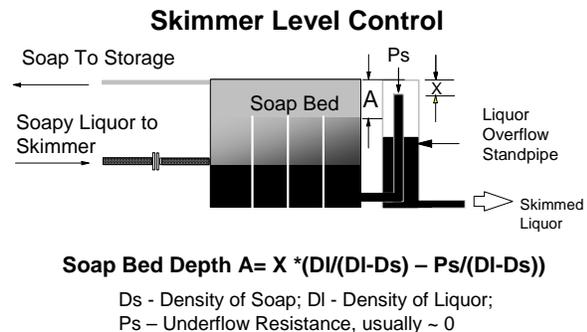


Figure 4.3.25 Skimmer level and soap bed depth control

The equation in the figure can be simplified as follows:

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 4.3.23 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 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% (8,16,31). It is critical that the air be finely atomized. Although a little bit of air was good, much more air is bad (31). All three studies showed that the optimum amount of air was 1 scfm/1000 gpm (7.5 L/M<sup>3</sup>).

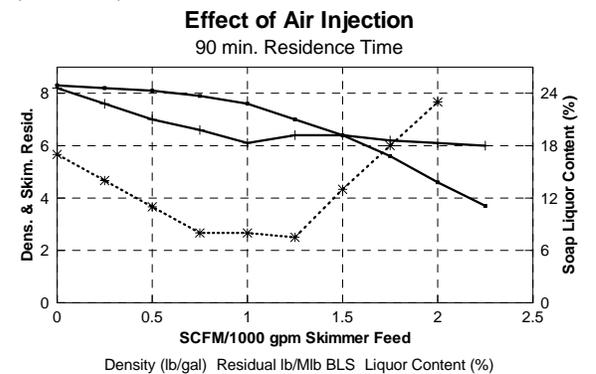


Figure 4.3.26 Effect of air injection on soap skimmer outlet residual, soap density and liquor content of the skimmed soap (31)

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. (0.79 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<sup>3</sup>) pump cavitation is generally not a problem. Several mills have used a sintered metal tube to provide finely atomized air on the pressure side of a skimmer feed pump. This setup 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. Sudden changes in the air addition rate will lower the soap density. If the target skimmer level is not adjusted, the relative depth of the soap bed and the liquor level will change.

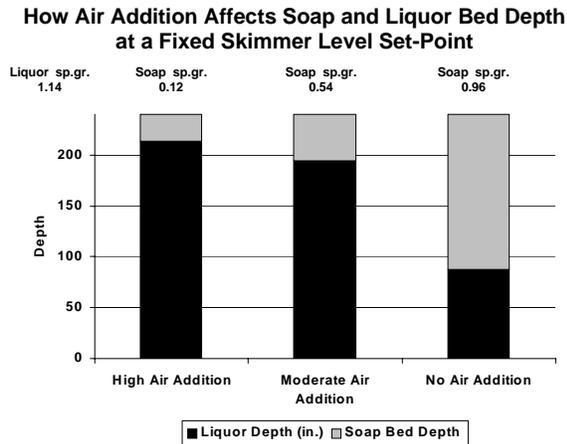


Figure 4.3.27 Effect of air injection on soap and liquor bed depth for a fixed total head setpoint..

Figure 4.3.27 illustrates what would happen if the air addition was suddenly shut off to a tall, narrow soap skimmer that requires high levels of air-addition to effect good soap recovery. To maintain the same total head in the skimmer, the soap density would increase and this would result in an increase in the soap bed depth and a decrease in the skimmer liquor depth. This would also tend to upset the material and heat balance in the evaporator effects after the soap skimmer, by displacing an increased liquor volume to those effects. Similarly, a sudden increase in the air addition rate would displace a large amount of soap and increase the large volume of liquor in the soap skimmer. In-effect, this would temporarily reduce the liquor flow to the evaporator effects after the soap skimmer.

In summary, air-flow adjustments to the soap skimmer should be made very gradually, and should be accompanied by adjustments in the skimmer level set point. Increasing the air flow will require lowering the skimmer level set-point slightly to maintain a relatively constant 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 (3, 33,34). 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 (3).

Mills	A	B	C	D	E
Tall Oil Leaving Skimmer -					
No	12.4	22	10	6.3	13
Electroflocculator With	5.5	15.5	4.3	5.2	5.5
Electroflocculator 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	80%	56%	67%	87%	63%
Electroflocculator With	99%	75%	96%	98%	98%
Electroflocculator Improvement	24%	34%	43%	12%	56%

Table 4.3.10. Electroflocculator results during pilot trials in five mills (33)

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 (33,34) has been reported in which by application of an electric field to a liquor stream, they were able to reduce skimmer outlet residuals. The performance of this device in several installations is summarized in Table 4.3.10. A mechanical air atomizer was used in the feed stream ahead of the electroflocculator 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.

### Chemical Additives

The effectiveness of proprietary additives to help soap recovery has been evaluated. Several commercial additives (2,17,27) 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 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” (2).

Cationic polyamides, used to flocculate the soap particles have also improved skimming efficiency, however their performance has been more inconsistent (2,17) than that of the proprietary additives discussed above.

“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.” (17)

## Soap Handling Equipment

### Pumping

The operating principle of centrifugal pumps and positive displacement pumps are quite different. Centrifugal pumps operate by imparting velocity energy to the fluid, which is converted to pressure energy upon exiting the pump casing. The flow delivered by a centrifugal pump during one revolution of the impeller depends upon the head against which the pump is operating.

A positive displacement pump moves a fixed volume of fluid within the pump casing by applying a force to moveable boundaries containing the fluid volume. The positive displacement pump delivers a definite volume of fluid for each cycle of pump operation regardless of the head against which the pump is operating.

### Positive Displacement Pumps Produce Essentially Constant Flow That Is Almost Independent Of Pressure

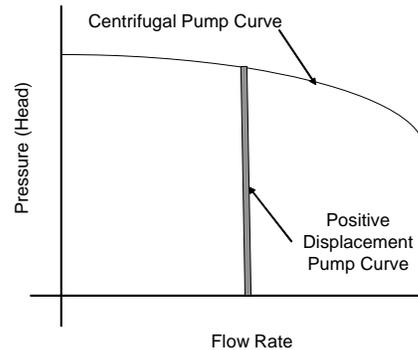
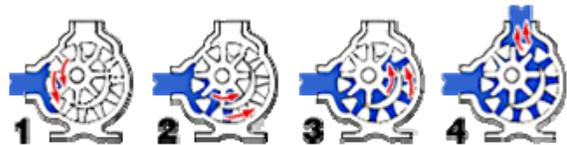


Figure 4.3.28a – Positive displacement pumps deliver a constant flow independent of the discharge pressure.

Unlike the centrifugal pump that decreases flow as the discharge pressure increases, positive displacement pumps maintain an essentially constant flow regardless of the discharge pressure due to tight tolerances and minimal liquid leaks from the discharge of the pump back to the pump suction at increased viscosities. Due to its normally high viscosity, soap is best pumped with a positive displacement pump, typically an internal gear pump or a circumferential piston pump.

Internal Gear Pump – Operating Principle  
Courtesy Viking Pump, Inc.



Circumferential Piston – Operating Principle  
Courtesy Tuthill Corporation, Tuthill Pump Division

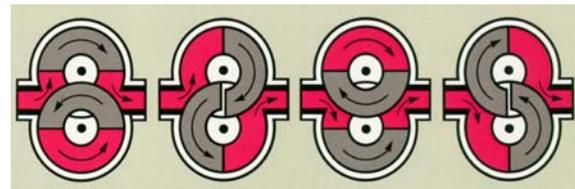


Figure 4.3.28b Positive displacement pumps for soap pumping

**Pressure Relief Valves** - A positive displacement pump operating against a closed discharge valve, will continue to produce flow until the pressure in the discharge line is increased until the line bursts or the pump is severely damaged - or both. **A relief or safety valve on the discharge side of the positive displacement pump is therefore absolutely necessary.**

The relief valve can be internal or external. Normally the pump manufacturer has the option to supply internal relief or safety valves. The internal valve should in general only be used as a safety precaution, an external relief valve installed in the discharge line with a return line back to the suction line or supply tank is recommended.

If the pump contains an internal pressure relief valve, it should be set 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.

**Effects of Viscosity on Positive Displacement Pumps** - Unlike centrifugal pumps, positive displacement pumps maintain, or increase their flow rates at increased viscosity. As the viscosity of a liquid increases, the maximum speed at which a positive displacement pump can properly operate decreases.

Since tolerances play a critical role in the pump's operation, worn rotors will greatly reduce pump efficiency. Positive displacement pumps can only handle a limited capacity range and become significantly inefficient when pumping low viscosity fluids such as black liquor at less than 30% dissolved solids content. This due to slippage, the rate at which liquid leaks from the discharge of the pump back to the pump suction.

**Soap Viscosity Characteristics** - The rheological nature of the soap, is that of a pseudo-plastic, or shear-thinning fluid. It has a lower apparent viscosity at higher shear rates. Such fluids are usually solutions of large, polymeric molecules in a solvent with smaller molecules. It is generally supposed that the large molecular chains tumble at random and affect large volumes of fluid under low shear, but that they gradually align themselves in the direction of increasing shear and produce less resistance. This is a good description of soap micelles in a liquor matrix.

For most soap pumping applications, the viscosity will be in the range from 500 to 3,000 cp at 25°C (77°F). However, very well de-liquored soap that has been in storage for some time can have a viscosity of over 25,000 cp. **Therefore the soap pump must be sized so that it can pump liquor at about 10 cp or soap as high as 25,000 cp.** In general choose larger size pumps that are designed to operate at low rpm, generally less than 200 rpm.

Occasionally, operators inject water in the soap pump suction to assist pumping. This dramatically lowers the viscosity of the mixture and makes it almost

Newtonian. Although this lowers the viscosity, it increases the volume to be pumped and significantly reduces the pump efficiency due to increased slippage, frequently making a bad situation worse. Water addition should be limited to about 2 % of the rated pump flow.

Furthermore water dissolves a portion of the soap. This dilute soap mixture ultimately drains from the soap and is recycled to the black liquor system. Since it tends to be pumped off intermittently and contains high concentrations of soap, it can cause significant and unexpected operating upsets, particularly in the feed effects of an evaporator. It is important that soap pumps be repaired as quickly as possible to avoid such problems.

**Pump Inspections** - As stated above, tolerances play a critical role in the pump's operation, worn rotors will greatly reduce pump efficiency. Soap pumps should be checked regularly for wear.

**Piping Considerations** - Spare pumps should be valved using positive closure ball valves. When not in service the spare pumps should be completely isolated. Steam heated water 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. Never heat trace soap lines as this will tend to dry out the soap and plug the lines.

Avoid piping restrictions in the pump suction. The viscosity of soap varies widely dependent upon the temperature composition and especially upon the liquor content (3).

Repeated frequent repairs are frequently a sign of restrictions in the pump suction piping.

### **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) (32,35). 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.

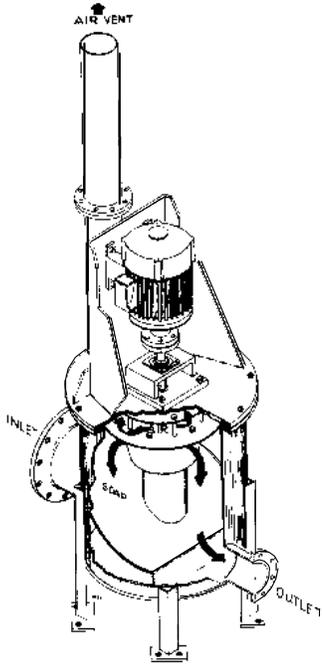


Figure 4.3.29 Soap Concentrator, courtesy A.H.Lundberg Associates (36)

The foam tank system is being replaced by the use of a soap collection tank and soap concentrator arrangement (8,36) in some mills (see Figures 17,18). 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.

The low-density soap results from entrained air. Historically, installation of a soap concentrator has been recommended for increasing soap density. Because of the separation tank associated with the concentrator, these devices require an installation footprint of about 10 m<sup>2</sup> (~100 ft<sup>2</sup>) and tend to have frequent overflows.

An innovative solution recently employed at one mill, applies a medium consistency pump connected to a vacuum pump to pump the soap to a soap collection tank. The device is capable of pumping

liquids containing up to 70% air. This combination of pumps were installed to replace a conventional positive displacement pump that leaked excessively when pumping weak liquor soap. The evacuated medium consistency pumping system was leak-free. The deaerated soap / liquor mixture density was increased from about 0.35 kg/l to about 1 kg/l. The installation footprint for this system was about 1.5 m<sup>2</sup> (15 ft<sup>2</sup>).

### 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 entrained 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 and the potential for high total reduced sulfur (TRS) gas emissions.

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 (37). A minimum of three days of soap storage should be provided as illustrated in Figure 4.3.30.

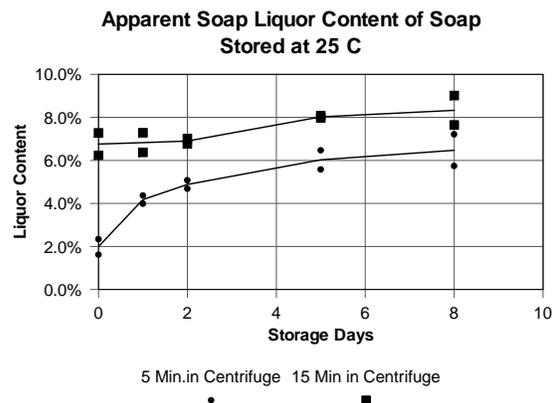


Figure 4.3.30 Effect of storage time on the apparent liquor content of soap. Longer storage times allow more liquor to drain from the soap than in standard centrifuge tests.

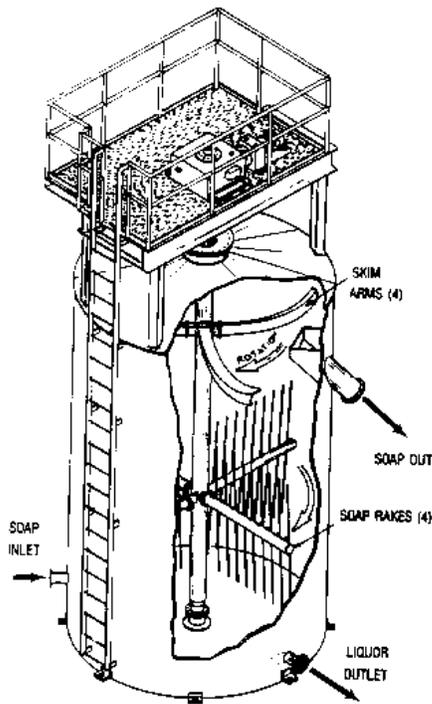


Figure 4.3.31 Soap Rake to enhance liquor removal

A device for releasing liquor from soap was reviewed (26). 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 4.3.31). The rake is installed so that the lower end of the fingers are in the liquor layer at the bottom of the storage tank (38). 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. Four sensors have been successful. A thermal conductivity probe has been used to control the soap liquor interface (26). 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 that have been used to start and stop liquor pumps.

In recent years a new sensor system has been introduced (41) and is gaining acceptance. The sensor system consists of three principal components, an external float, a sensor hose and a microwave radar transmitter. The interface level transmitter senses the position of an external float located at the interface by measuring the changing resistor attenuation signal inside of the sensor hose, which passes through the float assembly. The float assembly is designed to float only at the liquor/soap interface. The microwave radar transmitter measures the distance between the top of the liquor storage tank and the top of the soap layer.

## 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

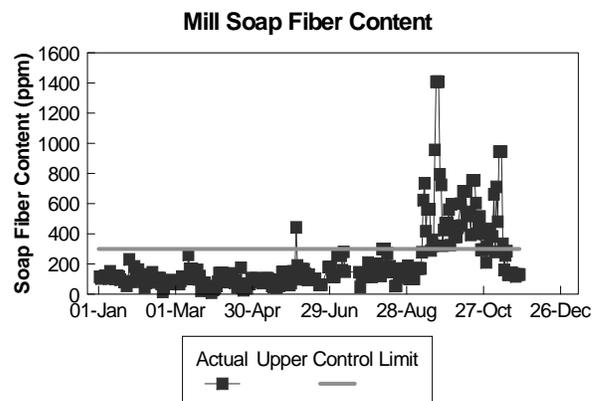


Figure 4.3.32 Mill soap fiber content during normal and upset operation

In Figure 4.3.32 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. During this period of time the soap fiber content was much more consistent than the liquor fiber content.

**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. The sample should first 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.

$LC = \text{ml Liquor} * 1.1 / \text{grams of sample}$

**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

Table 4.3.11 Black liquor sampling dilution data

**Proportions necessary to obtain 4% solids**

Bottle Size	1 Pint		1 Quart	
	Liquor	Water	Liquor	Water
Black Liquor Solids Content	ml	ml	ml	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

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 (38). A new method has been proposed (2) that appears to have improved accuracy and can distinguish the quantity of rosin acids and fatty acids removed on each unit operation.

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.

*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 4.3.11 above 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 (%)

$0.04 = S * B * 0.01 / T$

**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.

**Acidulation Process Description** - Spent acid is a byproduct of the black liquor soap acidulation process. Kraft black liquor soap is converted to crude tall oil in a variety of ways. The most common method is by reaction with sulfuric acid in batch, semi-continuous and continuous processes (3,39, 40).

For each tonne of well de-liquored tall oil soap, approximately 100 kg (220 lb.) of concentrated sulfuric acid is added along with about 0.6 tonne of water and steam to increase the reaction mixture to 95 - 100°C (200 - 212°F). Upon completion of the reaction, the reaction mixture, at pH 2 - 3, separates into several phases, that usually include: precipitated calcium sulfate, a sodium sulfate brine solution at 15 - 20% dissolved solids, a precipitated lignin-tall oil layer and a crude tall oil layer.

Historically it has been most common to separate these layers by gravity separation. In recent years, the tall oil layer is more frequently being isolated by centrifugation at about 4000 g-force.

Independent of the separation process, the combined sodium sulfate and lignin layers, commonly called Tall Oil Plant spent acid are usually treated with caustic soda for return to the kraft process.

**Brine Assimilation in the Kraft Process** - 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<sub>2</sub>S) gas. In most mills the pH of the tall oil plant brine is controlled above pH 10.

At 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 dirt in it. CaSO<sub>4</sub> 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 the fillback liquor holding tank. On low level in the tank, 1<sup>st</sup> stage washer filtrate should be used for level control. Return to the digesters results in an increased evaporator load. The water is evaporated at 4-5 steam economy in most mills.

#### **Evaporator Feed**

The water in the TOP brine is evaporated at an economy of about 4-5 in most mills. 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% (12,27). 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 in 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.

The settleable solids material in the dilute spent acid (13-17%) is 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 caustic soda (NaOH) used to increase the pH above 12 to solubilize the lignin is of marginal value. This would lower the critical solids concentration for Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> 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 one. If fed to a liquor crystalliser/concentrator, its effect on soluble scale formation is minimal since these devices are designed for supersaturated Na<sub>2</sub>SO<sub>4</sub> 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 re-solubilize the precipitated lignin.

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