Evaluation of soap recovery efficiency from black liquor — analytical tools

JOSEPH E. BOHANNON

ABSTRACT: Soap skimmings ("soap") are typically recovered from black liquor in kraft mills that process a high percentage of softwood. In many mills, the recovery of soap is inefficient, negatively impacting performance of evaporators and recovery boilers and resulting in loss of potential revenue. A thorough evaluation of soap recovery performance in a kraft mill requires measurement of soap content in black liquor at various sampling locations, especially around the soap skimmer.

The standard laboratory method for evaluating soap content in black liquor is a complex, multi-step process that relies on solvent extraction and titration; most mills send these samples to an outside laboratory for this analysis. In this study, 100 black liquor samples, with a wide range of soap concentrations, were tested by the standard solvent extraction method. After additional dilution, each sample was also tested for surface tension with a bubble pressure tensiometer. The results were found to correlate very closely with the solvent extraction tests results. This alternate method, using surface tension measurements of diluted black liquor samples, produces rapid results and can be easily implemented in most kraft mills, which would facilitate much more frequent in-house evaluations of soap recovery performance.

Application: Evaluating soap recovery performance in kraft mills requires measurement of soap content in black liquor at key locations in the mill. This paper presents an alternate, simplified method using surface tension measurements, allowing rapid evaluation of soap content at low cost, as compared to the traditional solvent extraction method.

Black liquor soap skimmings (BLSS, or "soap") are a valuable byproduct of the kraft pulping process. Optimizing the recovery of soap from black liquor requires some regular attention, including the collection and analysis of black liquor samples to evaluate equipment performance. The standard test method, in use for over 60 years, directly measures soap content of black liquor with a multi-step solvent extraction technique, providing very useful data for assessing soap recovery. However, the method is complex and costly, usually requiring outside laboratories to complete the work, which in turn delays results. An alternate method is presented here that uses surface tension as a surrogate parameter, which correlates strongly with soap content in black liquor.

BACKGROUND

Source of soap in kraft mills

In the kraft process, the black liquor produced in the digestion and brownstock washing processes consists of an alkali solution of dissolved lignin, hemicellulose sugars, extractive components, and inorganic components originating from the wood chips and the white liquor introduced to the digesters. Some of the extractive components (predominantly fatty acids and resin acids) are present in the black liquor as soluble sodium salts (soap).

In the highly efficient kraft process, all the components of the black liquor are either used as fuel in the recovery boiler or recovered as smelt (mostly sodium carbonate and sodium sulfide) or as soap skimmings, as shown in **Fig. 1**.

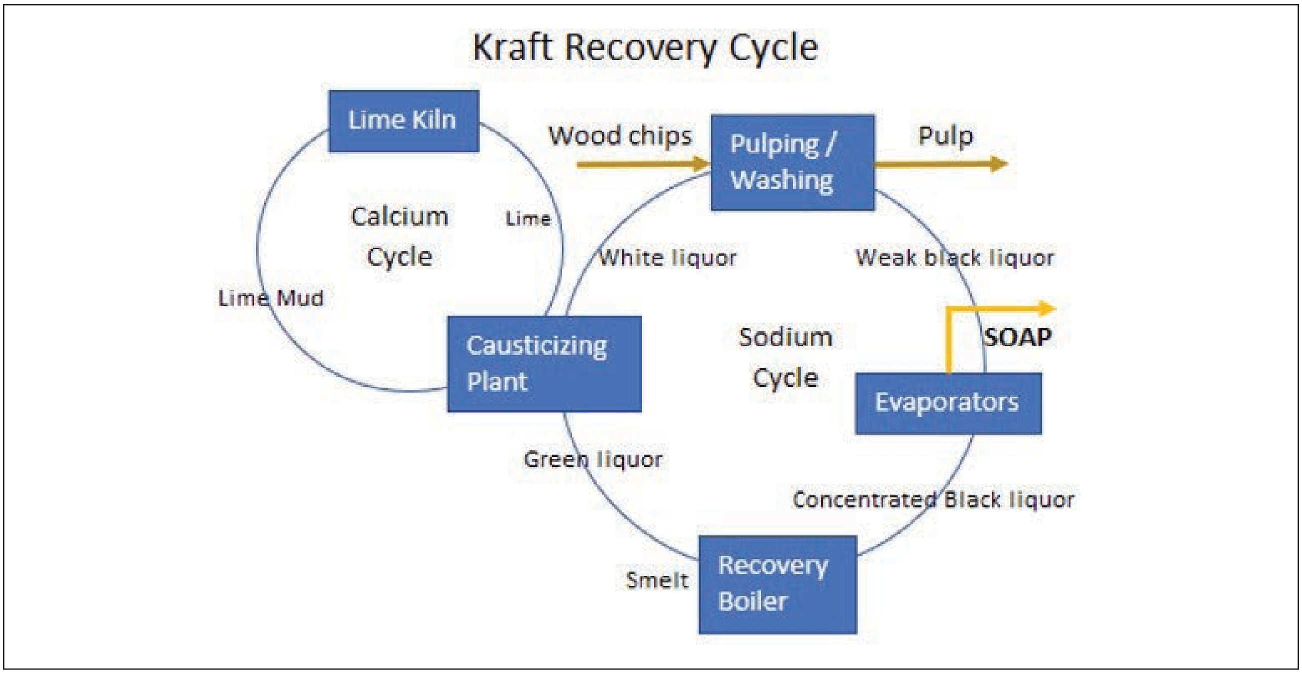
The soap components in black liquor are soluble at low solids concentration, but as the black liquor is evaporated, soap solubility decreases, resulting in the formation of soap micelles, which also "solubilize the neutral fraction of the extractive components" [3]. As the solids concentration of the black liquor increases after the washers (at 12%–14% solids, typically) and through the evaporators (40%–50% solids at the discharge), soap solubility further decreases until a minimum solubility is reached, usually around 25%–30% solids, as shown in **Fig. 2**.

Throughout this concentration process, as more soap micelles form, they begin to agglomerate and form into a distinct layer of "soap skimmings" that can be removed at various points in the process.

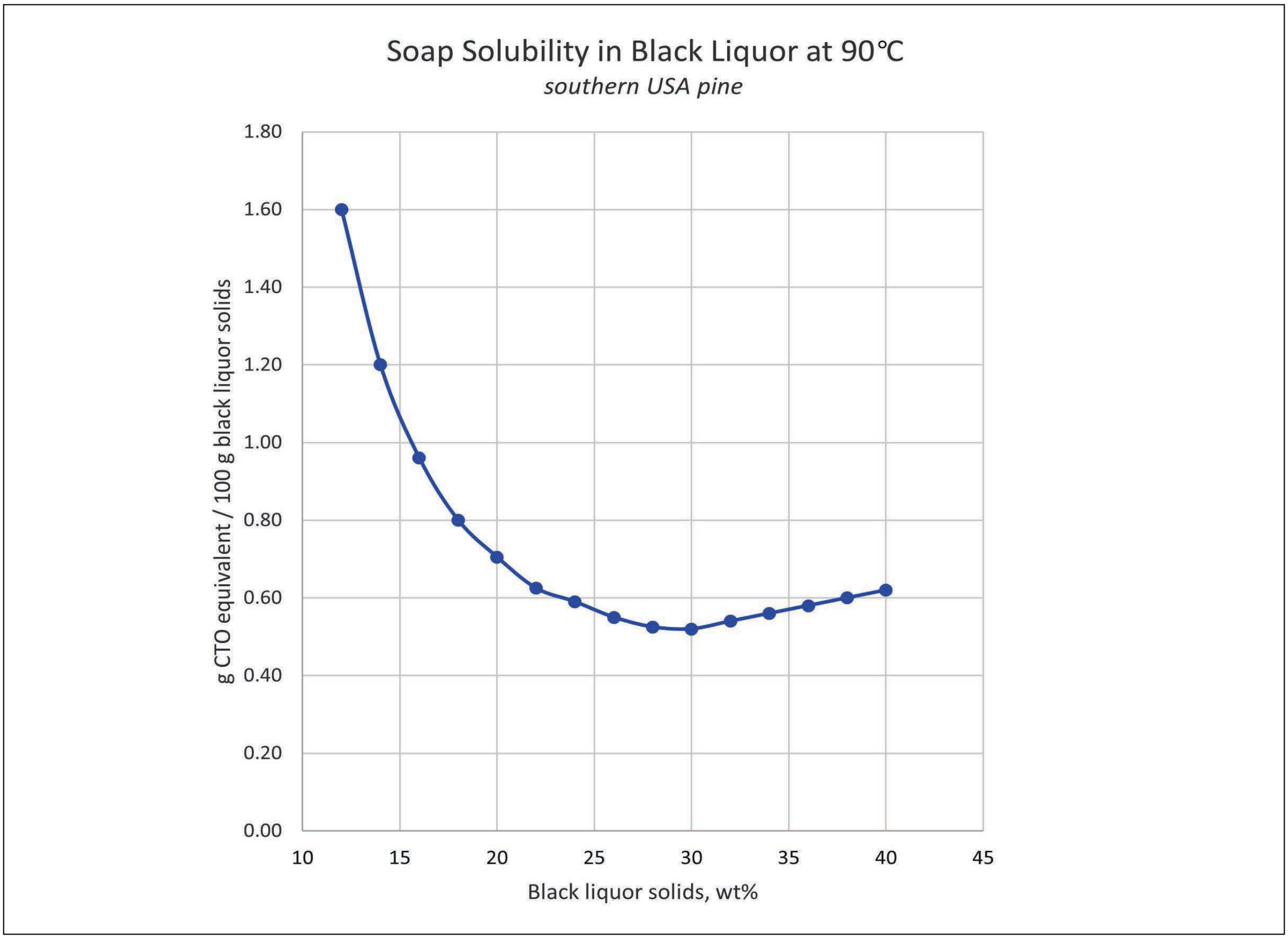
Options for handling soap

Mills have various options for handling soap, including removal in various locations and with different types of equipment involved.

1. No soap recovery.
   a. In this case, the mill allows the soap to pass through the evaporators, and further concentration processes it along with the black liquor so that the soap is eventually consumed as fuel and the sodium content is recovered as smelt in the recovery boiler.



1. Major features of the kraft liquor cycle, consisting of sequential black liquor, green liquor, and white liquor production generated through interlocking sodium-based and calcium-based cycles [1,2].



2. Soap solubility in black liquor at 90°C (CTO = crude tall oil). Data from Uloth et al. [4].

b. In mills processing a high percentage of softwood (especially pine), some soap will naturally accumulate in certain tanks, requiring it to be removed periodically.

2. Soap removal from weak liquor tanks.

a. When black liquor solids increase to over 14%–15% concentration, which is typical in weak liquor tanks between washers and the evaporators, some soap will begin to separate.

b. It is ideal to equip these tanks with: (1) nozzles and valves with chain wheels (or remotely actuated valves) at fixed elevations that can be opened when needed to allow the accumulated soap layer to flow out of the tank to an external storage tank; or (2) a floating skimmer that rides on the surface of the black liquor and is available to receive soap whenever it has accumulated.

c. The soap recovered from weak liquor tanks is usually somewhat lower quality, i.e., often foamy (low density) and may carry over a significant percentage of black liquor with the weak liquor soap.

3. Soap removal midway through the evaporator set with a soap separator (skimmer).

a. This is the optimum location for soap removal from most mills, as the skimmer is typically fed from the effect where the concentration has reached 25%–30% solids, where soap solubility is at the minimum.

b. Soap skimmers are ideally designed with a wide base and minimum height so that soap micelles are not required to rise a great distance before the soap is removed by skimming to a launder. For example, a width-to-height ratio (W:H) of 2:1 would be much preferred to W:H of 1:2 or even 1:1. However, many mills have limited space in the vicinity of the evaporators, which requires use of less-than-optimum soap separation equipment.

c. In most mills, the soap skimmer at a midpoint of the evaporator train produces the most soap of the highest quality.

4. Soap removal at intermediate liquor tank (> 40% solids).

a. Presence of significant quantities of soap in the liquor downstream of the soap skimmer indicates inefficient operation of the soap skimmer, which can occur for many reasons.

b. Some soap may accumulate in intermediate liquor tanks. However, at 40+ % solids, the viscosity of the liquor is higher, and there may not be sufficient residence time for the residual soap to accumulate.

c. When a soap phase accumulates in an intermediate liquor tank, it is usually removed only infrequently (often associated with a mill outage and sometimes only on the frequency when tank cleaning and inspection is needed).

d. With the high solids concentration of the black liquor entrained in this soap, it is often very viscous and difficult to process.

Soap quality

After soap has separated from black liquor and has been removed from weak liquor tanks, soap skimmers, or intermediate liquor tanks, it can be handled in multiple ways. The determination depends on the quality of the soap (which affects its market value for direct sale or for additional processing) and on logistics considerations (availability of rail or truck transport from the mill). **Table I**

	Lower Quality Soap	Higher Quality Soap
Tallates* content	<40%	>50%
Density, lb/gal	< 6.0	>8.0
Fiber, ppm	>1000	<300
Water content	>45%	<40%
Energy value, Btu/lb	<7000	>8000
Viscosity, cP at 100°F	>10,000	<10,000
Wood source	Birch, spruce, aspen, maple, balsam, fir	Pine (loblolly, slash, radiata, et al.)

*"Tallates" as used here designate the sodium salts of fatty acids and resin acids, along with typical neutral components that compose tall oil. In this usage, the term is meant to define the content of the soap that could ultimately be converted to crude tall oil (CTO) after a well-run acidulation process.

- Sodium tallate (CAS Registry Number 061790-45-2) [5] has the synonym "tall oil fatty acids, sodium soap," which is close to the usage here, with the addition of resin acids.
- In the cosmetics industry, sodium tallate has a description similar to the usage here: "Tall Oil Acid is a mixture of fatty acids and rosin acids that is obtained from tall oil, a byproduct from the pulping of pine trees...Sodium Tallate are salts of Tall Oil Acid" [6].

I. Typical properties of black liquor soap skimmings.

gives a general comparison of lower quality vs. higher quality soaps. Options for disposition of recovered soap include:

1. Acidulate the soap onsite to produce crude tall oil (CTO). At mills with high quality soap in sufficient quantity, a tall oil plant might be built to allow acidulation of the mill's soap, resulting in a marketable CTO, which is typically produced at about 50% yield from soap. Crude tall oil is the organic phase resulting from this acidulation process, followed by phase separation. The aqueous phase is a low pH brine, usually at 10%–15% concentration of sodium sulfate. After neutralization with caustic soda, the brine can be returned to the liquor cycle, allowing the sodium to be recovered via the recovery boiler.

2. Load soap to railcars or trucks for processing at other locations. If the mill does not have an onsite tall oil plant, the soap can be transported by truck or rail to another intra-company location or sold to another party for soap acidulation for CTO production. This option depends on: (1) production of high-quality soap amenable to CTO production; and (2) availability of economical truck or rail transportation from the mill site to locations where it can be used.

3. Blend with heavy liquor (firing liquor) to the recovery boiler. If soap quality is not sufficiently high to justify its use for acidulation (CTO production), or if economical transportation options are not available, it may be necessary to recover the soap in the mill and then gradually pump it into the firing liquor for (1) recovery of its fuel value; and for (2) recovery of the sodium content as smelt.

SOAP RECOVERY CONSIDERATIONS

Rationale for soap recovery in kraft mills

Mills should ensure effective soap recovery for the potential revenue and efficiency benefits and to mitigate process, environmental, and safety issues.

1. Increases mill revenue.

The recovery and sale of soap and/or CTO is a valuable supplementary source of revenue for mills. Demand for this byproduct of the kraft process has increased in recent years, making this limited resource even more valuable. In addition, removal of soap from black liquor debottlenecks recovery boilers (running at solids limit or steaming limit), potentially allowing more pulp production if upstream equipment has capacity.

2. Improves operational efficiency.

a. ***Removing soap reduces liquor carryover and evaporator scaling.*** As noted by Foran [3], "…removal of the soap prior to evaporation will dramatically reduce the average bubble life and reduce liquor carryover permitting increased evaporator throughput." Concerning scaling, Uloth [7] notes that "soap which remains after skimming can precipitate on evaporator tube walls, and soap has been reported to be a significant component of evaporator and concentrator scale samples, particularly soluble sulphate carbonate scales."

b. ***Removing soap increases recovery boiler solids burning capacity and reduction efficiency.*** Uloth [7] states that "the major disadvantage of burning soap is that it reduces the capacity to process black liquor in a recovery furnace that is limited either by plugging or steam production capacity." In addition, he indicates the following:

   i. There is sometimes a connection with liquor soap content and the occurrence of blackouts in kraft recovery furnaces.

   ii. Burning soap, even at low concentrations, has been observed in some mills to increase total reduced sulfur (TRS) emissions.

c. ***Unrecovered soap accumulates in tanks.*** As noted earlier, in kraft mills using a high percentage of softwood (for example, linerboard mills and fluff pulp mills), soap will naturally separate from the black liquor in the 15%–40% solids range, especially if the liquor remains stagnant in any portion of a vessel. Unless the soap is purposely removed at the most convenient locations, it may become necessary to handle it anyway in undesirable locations that may be disruptive to normal operations.

3. Improves mill environmental and safety performance.

a. Black liquor and soap components are toxic to marine wildlife (and detrimental to wastewater treatment "bugs").

b. Proper handling of soap helps to avoid slips and falls due to tank overflows and spills.

Soap recovery potential

In the southeastern United States, mills processing loblolly or slash pine can potentially recover soap at a benchmark yield of 80–90 lb soap/ovendry (o.d.) ton (40–45 kg soap o.d. metric ton) softwood digested, or about 40–45 lb CTO/o.d. ton (20–22.5 kg CTO/o.d. metric ton) softwood, based on typical 50% yield of CTO from soap.

Actual results depend on the availability of the extractive components in the wood supply, which is somewhat seasonal and also highly dependent on the freshness of the pine chips. Loss of extractives through oxidation, volatilization, and microbiological activity occurs quickly after the chips are made. With fresh chips (less than two weeks old), 60–70 lb CTO/o.d. ton (30–35 kg/o.d. metric ton) pine chips may be available at the time of digestion. Recovery of about 65%–75% of the available CTO is considered near-ideal performance. These figures would correspond with the above benchmarks.

As an example, a 2000 tons/day (1814 metric tons/day) linerboard mill feeding 3700 o.d. tons/day (3357 o.d. metric tons/day) pine chips could produce 52,000 tons/year (47,200 metric tons/year) of soap at the benchmark 80 lb soap/o.d. ton (40 kg soap/o.d. metric ton) of pine.

EVALUATING SOAP RECOVERY PERFORMANCE WITH AVAILABLE MILL DATA

Various sources of mill data can provide valuable insight into soap production vs. industry benchmarks.

Monthly mill production data

Reviewing monthly production accounting figures for comparison of monthly or seasonal results against previous years may reveal a trend of declining soap production. A year-to-date comparison is even better, as it allows for some rise and fall of monthly results as the year progresses but also reveals if the mill is generally achieving expected production. Better yet is an ongoing look at annual performance on a rolling 12-month basis, as it provides a constant comparison against many years of previous data.

Calculate soap yield from digested softwood

Another important data set from mill accounting is the monthly tons of softwood digested or tons of softwood pulp produced. Whichever of these is available should be used, along with the monthly soap production data, to calculate soap yield on a monthly basis, as well as on a rolling quarter or rolling 12-month basis. Yields are typically reported as lb soap/o.d. ton pine chips digested or lb soap/o.d. ton pine pulp produced, or equivalent SI units. Monitoring soap yield on a rolling time frame smooths out some of the month-to-month variations, while giving an accurate view of current performance as compared to long term results. Soap yield for the particular mill can also be compared to industry benchmark performance of 80–90 lb soap/o.d. ton (40–45 kg soap/o.d metric ton) of pine.

If a decline in soap yield vs. previous performance becomes noticeable, this would lead to a more detailed evaluation of each location where soap is recovered in the mill.

Evaluate energy value of firing liquor to the recovery boiler

The fuel value of BLSS is typically in the range 8500–10,300 Btu/lb (19,771–23,958 kJ/kg) as-received; a fuel value of 12,500 Btu/lb (29,075 kJ/kg) dry solids is also reported [8]. Black liquor, as fired to recovery boilers, has varying fuel value ranging from 5600–6700 Btu/lb (13,026–15,584 kJ/kg) black liquor solids, depending on many variables; some of the important ones are wood furnish, pulp kappa number, residual alkali, and efficiency of soap recovery [9].

The effects of poor soap recovery can be noticeable in recovery boiler operation, as the flame will be hotter and brighter due to the higher soap content in the firing liquor. Also, considering the previously mentioned figures, additional soap in the firing liquor results in higher energy content, which would result in higher steam production for a given mass flow of firing liquor. A calculation in the distributed control system (DCS) or data historian may be available to show the average energy value of the firing liquor (based on steam production and firing liquor flow). If other variables have remained constant, an increase of firing liquor energy measurements over time could indicate inefficient soap recovery (especially if considered along with a decline in soap tons or soap yield from softwood).

An example calculation by Frederick and Adams [9] gives a good idea of the extent of variation in heating value of the black liquor due to soap recovery. In their example, the base case has heating value of 6498 Btu/lb (15,114 kJ/kg) black liquor solids. With soap recovery ranging from 0 to 100% (maximum feasible), the heating value ranges from 6742 to 6358 Btu/lb (15,682–14,789 kJ/kg) black liquor solids.

EVALUATING PERFORMANCE OF SOAP RECOVERY EQUIPMENT

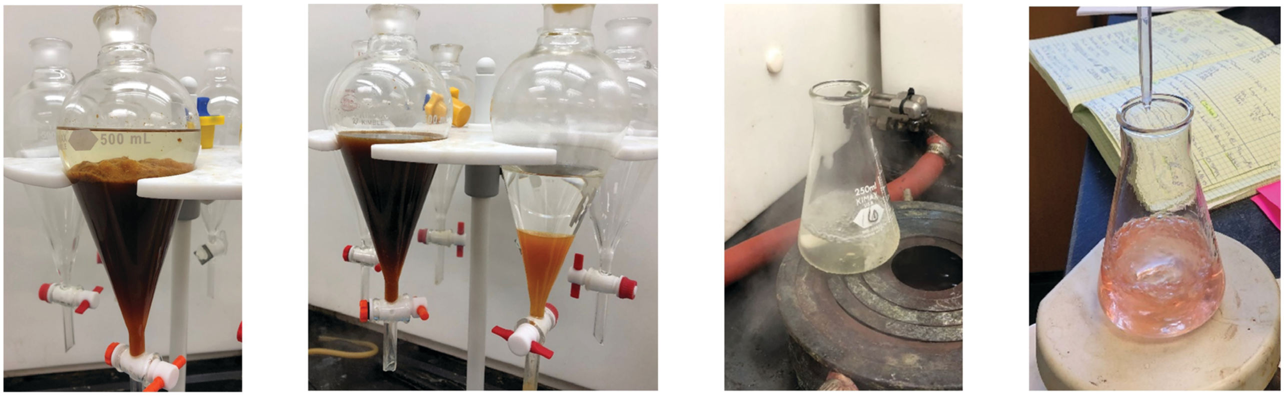
Ideally, mills should routinely monitor soap recovery performance of the key equipment in which soap is recovered. These locations would typically be in the weak liquor tanks and the soap skimmers located midway through evaporator sets. The key data needed is the soap content in black liquor around these soap recovery locations.

A traditional method (based on solvent extraction) and an alternate method (based on surface tension) for measuring soap content in black liquor will be compared in the following section. The two methods use the same type of black liquor samples, obtained at inlet and outlet of the soap separation equipment. Results of either test method can be used to determine soap separation efficiency.

Collect samples of black liquor

Both the traditional and alternate methods for measuring soap content start with obtaining samples for analysis, as described in the following:

1. Dilute each black liquor sample to ~5% solids at the time of sample collection by starting with a sample bottle pre-filled with distilled or deionized water, so that with careful addition of the black liquor into the bottle, the resulting mixture will be near the desired dilution. An approximation of % solids at the sample location is sufficient for determining the required dilution water, as the purpose is simply to ensure that soap does not separate from the sample before it is analyzed.
2. Record liquor flow data and approximate % solids for each sample location at the time of sample collection. The data will be useful in soap material balance calculations, if desired.
3. If an outside laboratory will do the analyses, the samples must be secured well to avoid leakage in well-labeled bottles for shipment.



Initial extraction.
Top phase: organics.
Bottom phase: aqueous

After multiple extractions, final organic phase (top right). Residual aqueous phase bottom both funnels.

Evaporating solvents from organic phase

Titration end point

3. Overview of key steps in PCTM-24 Test Method for estimating CTO in black liquor

Traditional method for testing soap in black liquor (PCTM-24)

The widely-used solvent extraction method for measuring soap in black liquor was developed over 60 years ago by W. Saltsman and K. Kuiken [10]. The method was modified in the 1990s by the Pine Chemicals Association, as Pine Chemicals Test Method (PCTM) 24 "Method of estimating crude tall oil (CTO) in black liquor." The PCTM-24 method uses a simpler potassium hydroxide (KOH) titration with phenolphthalein indicator for the endpoint; otherwise, the methods are the same.

A short description of the PCTM-24 method, as shown in **Fig. 3**, includes the following steps:

1. Measure the solids content of the diluted black liquor sample.
2. Mix 100 g of black liquor sample in a separatory funnel with 10 mL of 50% hydrochloric acid (HCl) solution to convert soap in solution to organic acids (tall oil).
3. Perform solvent extraction (multiple steps) with 80% acetone:20% methanol solution and petroleum ether, washing the organic phase with acetone:water:methanol solution.
4. Organic phases are combined and heated on a steam bath to evaporate volatile solvents.
5. Organic residue in the flask is dissolved in isopropyl alcohol, then titrated to a pink endpoint with 0.05 N KOH in methanol.
6. Results are reported as weight percent (wt%) of black liquor solids.

This multi-step method is complex, with about 1 h of direct analyst time required per sample, and 2–3 h total elapsed time (including time required to evaporate solvents). The solvent usage (methanol, acetone, isopropyl alcohol, and petroleum ether) amounts to 500–600 g for each sample tested.

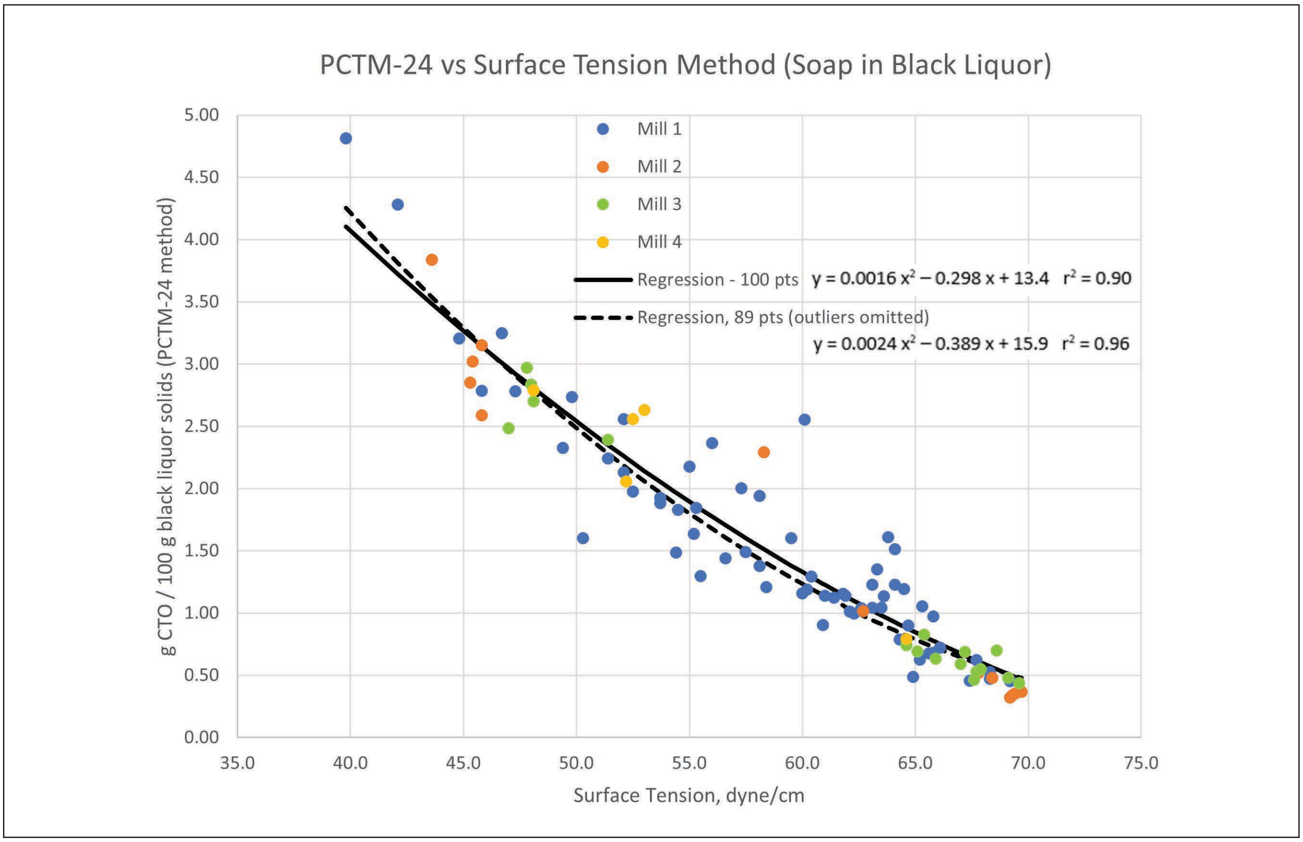
Due to the complexity of this solvent extraction test method, the laboratories in most mills do not conduct it themselves. Samples are usually sent to an outside laboratory for this test method, so that sample results are not available for days or weeks after the samples have been collected. The costs and delays with these tests limit the extent of their usage and somewhat diminish the value of the results due to the time lag.

Alternate test method: surface tension

A wide range of black liquor samples with varying soap content was tested by Ingevity (North Charleston, SC, USA) over a couple of years using the standard PCTM-24 (solvent extraction) test method. In parallel, we also tested surface tension of these samples (after further dilution to 0.5 wt% solids) and observed that surface tension of these diluted black liquor samples correlates directly with soap content determined by the PCTM-24 method.

<u>Background on using surface tension to measure soap in black liquor</u>

Ingevity (formerly MeadWestvaco) developed technology for lignin extraction from black liquor over 50 years ago and has produced a wide variety of lignin derivative products since then. The process for extracting and concentrating lignin from black liquor works best when the soap content in the black liquor stays below a certain defined maximum. The PCTM-24 test had been used for many years in our laboratory to measure soap content of 40% black liquor feeding the process. Since this test method was burdensome to use regularly, our chemists looked for a simpler test a few years ago and developed surface tension measurements of diluted black liquor samples as a suitable alternative, noting the strong correlation between surface tension readings and soap content in black liquor. As confidence in the method grew, surface tension



4. Full data set, with different options for regression equations (and trend lines).

was fully implemented as a replacement for the solvent extraction test; the reading is applied directly with comparison to a desired minimum surface tension as a pass/fail test. This history laid the groundwork for further development, as reported here, of surface tension measurements over a much wider range of soap content (from weak liquor to firing liquor).

<u>Overview of simplified surface tension procedure</u>

1. Start with the same type of black liquor sample (~ 5% solids) as collected for the PCTM-24 method.
2. In the laboratory, measure actual % solids of sample, as received.
3. Dilute the sample to 0.5% solids, using deionized (DI) water. Note that the diluted sample should be at room temperature (~ 25°C).
4. The surface tension measurement will be performed using a mobile bubble pressure tensiometer. Various models are available from different manufacturers at modest cost.
5. After cleaning and calibration, immerse the capillary of the surface tension meter into the diluted sample at room temperature. Our tests are based on surface tension readings using a bubble lifetime of 15 ms.
6. Surface tension results (dyne/cm) appear almost immediately on the meter.

For comparison with the PCTM-24 solvent extraction method, the surface tension method only requires about 10 min of direct analyst time per sample, with a total of only 20 min elapsed time (which includes the hold time for % solids measurement). No solvents or other chemicals are required. With the simplicity of this method and the speed of analysis, it should be easy to implement this method in the laboratories at most mills. The minimal cost and the quick turnaround of results should allow for regular onsite evaluation of soap recovery performance at most mills.

CORRELATION OF SOAP CONTENT IN BLACK LIQUOR WITH SURFACE TENSION

Over a couple of years, 100 black liquor samples were tested from four different mills in the southeastern United States. These samples were collected around weak liquor tanks, evaporator soap skimmers, or firing liquor to the recovery boilers, with 14%–70% solids content at these sampling points. Each sample was diluted to ~ 5% solids at the time of sample collection, as described previously. These samples were analyzed for soap content with the standard PCTM-24 solvent extraction method. A portion of each sample was also diluted further to 0.5% solids, as noted previously, after which the surface tension was measured. All the data points are shown in **Fig. 4**, along with a second-degree polynomial regression (with correlation coefficient of 0.90).

Mill ID	Surface Tension, dyne/cm	Soap in BL (g CTO/100 g BL solids)	Outlier	Mill ID	Surface Tension, dyne/cm	Soap in BL (g CTO/100 g BL solids)	Outlier
1	39.8	4.82		1	61.8	1.16	
1	42.1	4.28		1	61.9	1.14	
2	43.6	3.84		1	62.1	1.01	
1	44.8	3.21		1	62.3	1.00	
2	45.3	2.85		1	62.6	1.04	
2	45.4	3.02		2	62.7	1.01	
1	45.8	2.78		1	63.1	1.04	
2	45.8	2.59		1	63.1	1.23	
2	45.8	3.15		1	63.3	1.35	
1	46.7	3.25		1	63.5	1.04	
3	47.0	2.48		1	63.6	1.14	
1	47.3	2.78		1	63.8	1.61	yes
3	47.8	2.97		1	64.1	1.51	yes
3	48.0	2.84		1	64.1	1.23	
3	48.1	2.70		1	64.3	0.79	
4	48.1	2.79		1	64.5	1.19	
1	49.4	2.33		3	64.6	0.74	
1	49.8	2.74		4	64.6	0.79	
1	50.3	1.60	yes	1	64.7	0.90	
1	51.4	2.24		1	64.9	0.49	
3	51.4	2.39		3	65.1	0.69	
1	52.1	2.56	yes	1	65.2	0.63	
1	52.1	2.13		1	65.3	1.06	
4	52.2	2.06		3	65.4	0.83	
1	52.5	1.98		1	65.6	0.67	
4	52.5	2.56	yes	1	65.8	0.97	
4	53.0	2.63	yes	1	65.8	0.68	
1	53.7	1.88		3	65.9	0.63	
1	53.7	1.92		1	66.1	0.72	
1	54.4	1.49		3	67.0	0.59	
1	54.5	1.83		3	67.2	0.69	
1	55.0	2.17		1	67.4	0.46	
1	55.2	1.64		3	67.6	0.47	
1	55.3	1.84		1	67.7	0.62	
1	55.5	1.30	yes	3	67.7	0.53	
1	56.0	2.37	yes	2	67.8	0.52	
1	56.6	1.44		3	67.9	0.55	
1	57.3	2.00		1	68.3	0.47	
1	57.5	1.49		1	68.3	0.53	
1	58.1	1.94	yes	2	68.4	0.48	
1	58.1	1.38		3	68.6	0.70	
2	58.3	2.29	yes	3	69.1	0.48	
1	58.4	1.21		1	69.2	0.45	
1	59.5	1.60		1	69.2	0.46	
1	60.0	1.16		2	69.2	0.32	
1	60.1	2.55	yes	2	69.3	0.34	
1	60.2	1.19		2	69.4	0.35	
1	60.4	1.29		3	69.6	0.44	
1	60.9	0.90		2	69.7	0.37	
1	61.0	1.14					
1	61.4	1.12					

II. Full data set from four United States mills comparing PCTM-24 (solvent extraction analysis) vs. surface tension. (BL = black liquor; CTO = crude tall oil.)

After eliminating eleven of the most noticeable outliers, a slightly improved regression equation (correlation coefficient 0.96) was developed, as also shown in Fig. 4. This equation will be applied with several examples in the following sections to demonstrate the usefulness of surface tension as a surrogate for the more complex PCTM-24 analyses.

Though the data was not evaluated with a rigorous statistical approach, the simple regression equations developed in this initial study demonstrate that a strong correlation exists between surface tension measurements and soap content of black liquor (as traditionally determined with the PCTM-24 method). The sampling and laboratory methodology were all performed according to normal practice and procedures, without any consideration that the samples needed any extra attention (or redundant checks) for purposes of a study; the data analysis and presentation became more of an afterthought as the validity of the correlation became more evident. In addition, since the time of this study, the model has been tested at other mills where it was found to apply equally well. For readers interested in more detailed statistical evaluation, all the data points, generic mill identification, and selected outliers are presented in **Table II**.

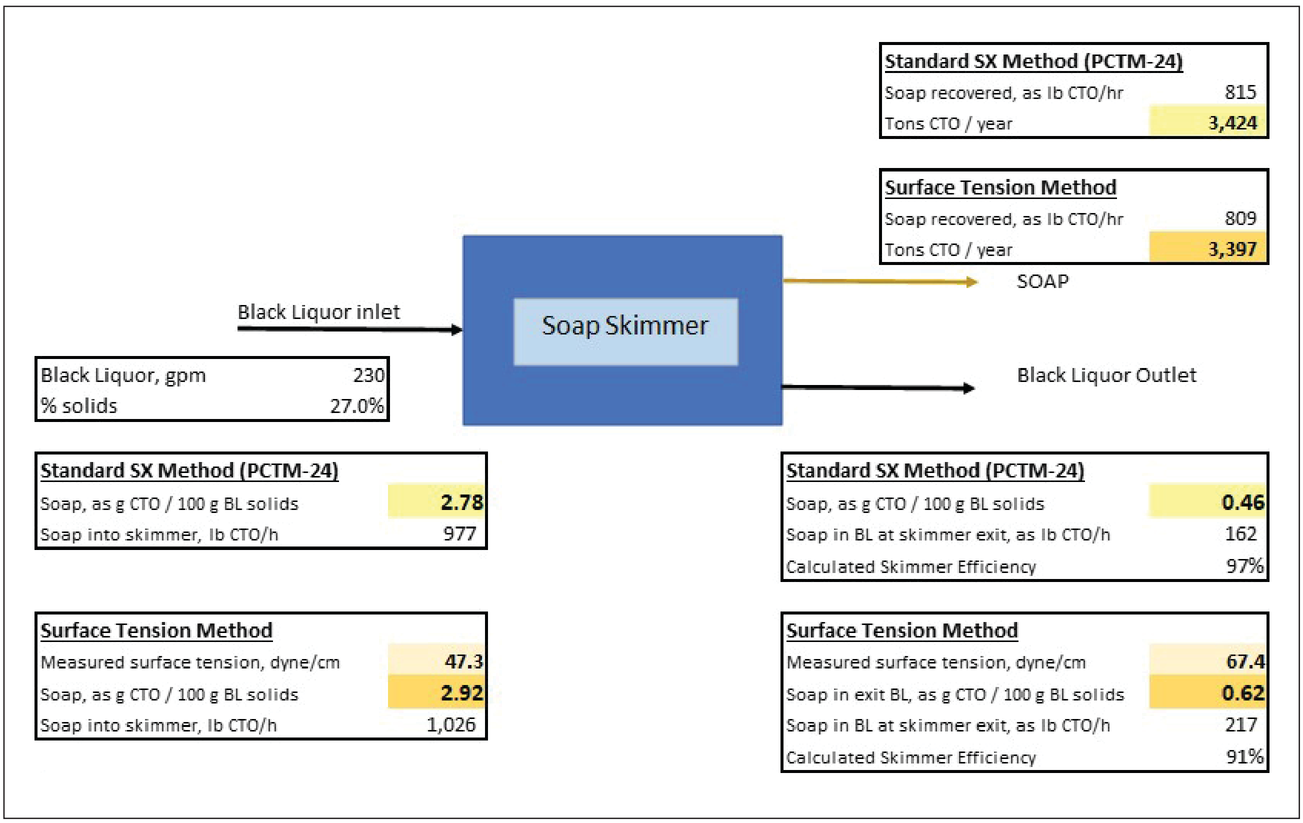
MILL EXAMPLES: SURFACE TENSION DATA AND CORRELATION VS. STANDARD PCTM-24

Example 1: Skimmer efficiency calculations — southern United States mill

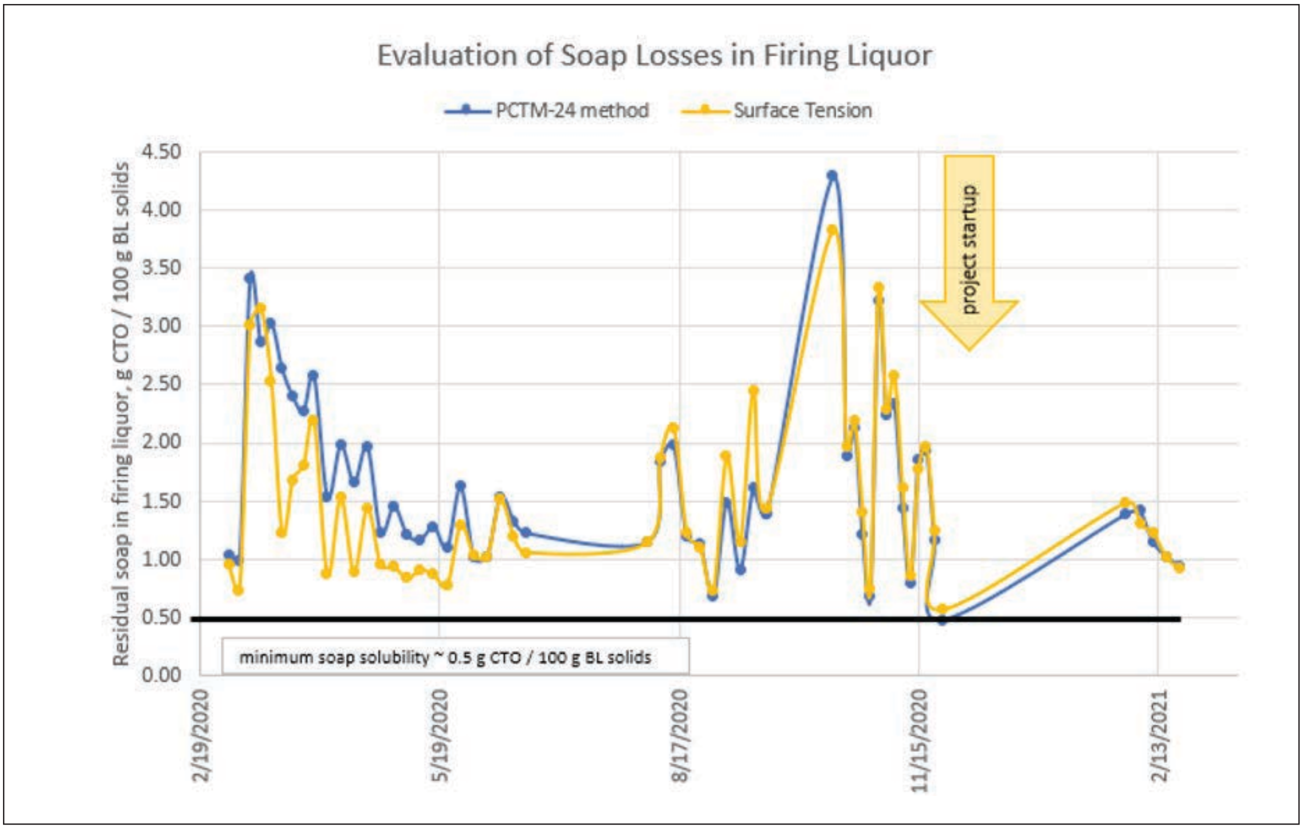
In this example, as shown in **Fig. 5**, data is shown from one of the mills included in the data development and correlation. Black liquor samples were collected at the skimmer inlet and outlet. The flow of liquor and its solids content were estimated at the time of sample collection at 230 gal/min (871 L/min) and 27% solids.

The inlet and outlet data are shown in separate boxes in Fig. 5 for the two methods: (1) standard PCTM-24 solvent extraction test results, and (2) corresponding surface tension readings of the sample, with calculated soap content, using the second-degree polynomial equation shown previously in Fig. 4. The data was also used to develop a material balance around the soap skimmer, showing a snapshot of soap recovery at that time, expressed as lb/h of CTO equivalent (assuming 50% yield from soap), also extending the calculation to full year results if this level of skimmer performance were achieved all year. Skimmer efficiency is also calculated using both types of data.

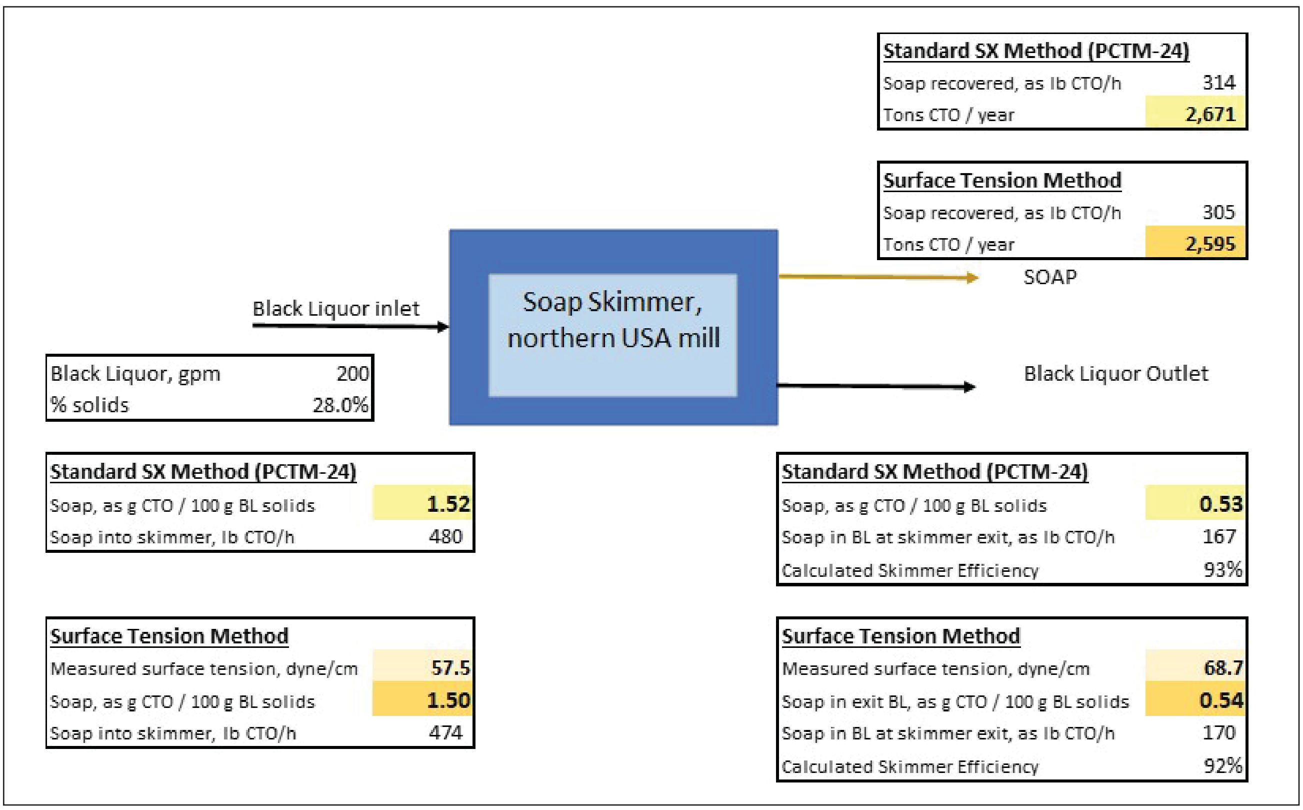
The calculated results using surface tension do not match perfectly with the PCTM-24 results, but they are very close, which indicates that estimating soap content using simplified surface tension measurements allows a very



5. Example 1: Soap skimmer performance evaluation, southern United States mill. Comparison of PCTM-24 analyses vs. surface tension tests.



6. Example 2: Evaluation of soap losses to firing liquor using surface tension analysis.



7. Example 3: Soap skimmer evaluation at a northern United States mill, comparing surface tension vs. PCTM-24 tests.

quick and useful assessment of soap skimmer performance, almost in real-time.

Example 2. Soap losses in firing liquor to recovery boiler

The data shown in **Fig. 6** was developed from frequent samples of firing liquor to a recovery boiler, collected over an extended time, as this mill was not recovering soap efficiently. A significant project at the mill was under development during this evaluation period. Losses of soap in the firing liquor improved slightly, leading up to the implementation of this project. A few post-project samples show significantly reduced losses to the recovery boiler.

Similar to Example 1, in this case, while the match between the PCTM-24 results and the surface tension results is not exact, the ability to collect frequent samples and get more immediate results at very low cost potentially provides a significant benefit to mills that implement the surface tension method.

Example 3. Northern United States mill — skimmer material balance

The final example, shown in **Fig. 7**, presents another skimmer material balance that is very similar to the one shown in Example 1. In this case, the surface tension test was used at a northern mill, not part of the data set used to develop the correlation between surface tension and soap content in black liquor. Despite the different geography and wood furnish between the regions, the method worked very successfully, as shown by the close match of results using PCTM-24 vs. calculated soap content with surface tension measurements.

CONCLUSIONS

The traditional solvent extraction method (PCTM-24) for measuring soap content in black liquor provides accurate and useful data. However, the method is complex, time-consuming (delayed results), costly, uses hazardous solvents, and usually requires an outside laboratory to complete the analyses.

An alternate method was developed using surface tension measurement of diluted black liquor samples. The results correlate strongly with standard PCTM-24 test results. Elapsed time from sampling to calculated results (soap content of black liquor) can be available in less than 1 h. The simplicity and low cost of this alternate method allows mills to frequently sample and evaluate soap content of black liquor in multiple locations, which will strongly support efforts to troubleshoot and to optimize soap recovery.

FUTURE WORK

Some next steps for additional development and improvement of this method might include: (1) test the method for sensitivity to sample conditions (% solids, testing temperature); (2) expand testing to a wider diversity of mills and consider in more detail if individual mill correlations are better; and (3) consider implementing an online surface tension instrument to provide continuous data to support mill operations. **TJ**

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ABOUT THE AUTHOR

Mills need timely data to support evaluation of soap recovery from black liquor, and the alternate test method developed with this project is a useful supplement to the traditional solvent extraction method. Its simplicity allows for much more frequent testing, and the results are available in real time.

One challenging aspect of this project was that it grew from an initial idea to a fairly large set of data over a couple of years. When the data was assembled together and evaluated, the usefulness of the method became even more evident.

As we learned that surface tension of dilute black liquor solutions correlates closely with soap content, it was interesting to discover that one equation for soap content as a function of surface tension applies well for multiple mills across a wide geography. Initially, we expected an individual correlation might be needed for each mill.

Mills that are seeking to evaluate and improve soap recovery need regular data to assess soap content in black liquor. The method presented here uses low-cost equipment, is simple to implement, and provides rapid results. Some of the next steps for consideration would include testing the method for sensitivity to sample conditions, expanding the testing to a wider diversity of mills, and considering use of an online surface tension instrument.

Bohannon

Bohannon is senior principal engineer and CTO technical manager at Ingevity in North Charleston, SC, USA. Email Bohannon at joseph.bohannon@ingevity.com.

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