Effects of variability of wood chip composition on recovery cycle operation

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ABSTRACT: Fluctuations in wood chip properties in kraft pulp mills, which often follow seasonal patterns, can lead to changes or disruptions in the operation of the recovery cycle whereby the root causes are not immediately obvious. In some cases, these changes are attributed to operational adjustments in the digester or brownstock washing areas resulting from the variability in wood characteristics. Varying wood chip characteristics that have the most significant impact on the recovery cycle operation include the content of non-process elements (NPEs), extractives, and properties influenced by chip storage conditions. Elevated levels of NPEs, often associated with a higher influx of wood bark into the digester, can negatively affect the entire recovery cycle. Increased levels of chlorine and potassium can lead to severe fouling and corrosion in the recovery boiler. Higher concentrations of silicon, aluminum, phosphorus, magnesium and calcium in the chips may accelerate scaling in the evaporation plant, impair dregs and lime mud settling and filtering, reduce lime mud solids content and lime availability, and increase the amounts of dregs, grits, and purged lime mud.

This technical review provides an overview of the most significant effects that changes in wood chip quality can potentially exert on various processes within the kraft recovery cycle.

Application: This technical review presents insights into the associations between wood chip quality and recovery cycle operation, relationships that are often not immediately apparent. It may therefore assist mills aiming to identify the root cause(s) of process deterioration.

The composition of wood chips used in pulping varies and often follows seasonal patterns. However, these changes are often overlooked when investigating the underlying causes of process instabilities, and the relationships between wood chip composition and recovery cycle processes may not be immediately apparent. Chip properties can vary based on factors such as climate (including temperature and humidity), soil properties, and tree age, as well as the storage time and conditions of the logs or chips. Throughout the year, the harvesting location of trees can vary, resulting in a seasonal impact of their provenance. For instance, a mill might receive wood chips from trees harvested in moist lowland areas during the drier summer months, while obtaining chips from trees in upland areas harvested during the wetter season or the spring snowmelt. The composition of the wood sourced from these different regions can exhibit significant variations.

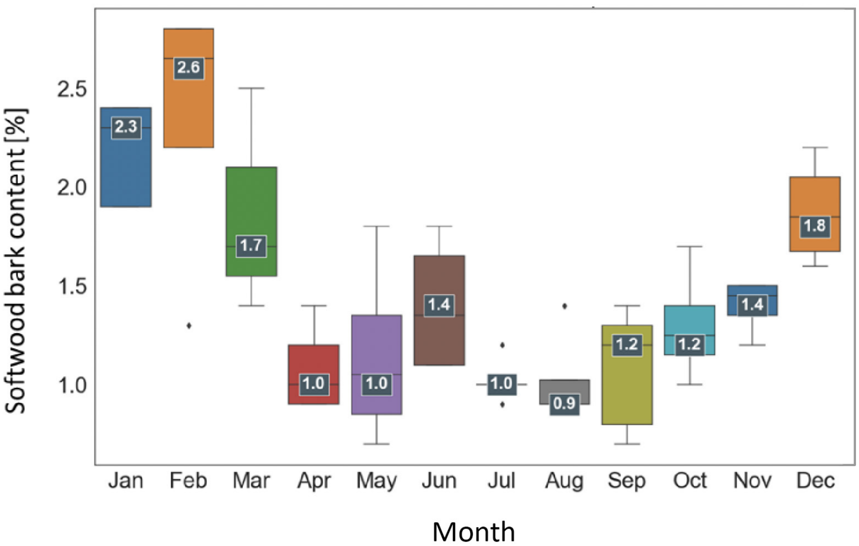
The impact of these varying wood properties on pulp yield and pulping costs is substantial and has been detailed in the study by Hart [1]. For instance, in a 1000 tons/day mill, the amount of wood required per ton of pulp can vary by 0.5 green tons throughout the year, resulting in a cost variation of almost US$600,000 per month, assuming a nominal cost of US$45 per green ton. The effects of wood variability on the recovery cycle operation have received less scrutiny. However, the potential costs associated with shutdowns and maintenance due to this variability can be high, particularly when considering the impact of chlorine- and potassium-induced corrosion and plugging in the recovery boiler, as well as sodium-salt or silicon/aluminum-related scaling in the evaporators.

Therefore, this study aims to bridge this knowledge gap by identifying the connections between chip quality and various processes within the recovery cycle. This review is based on results from the literature, as well as new results from the author.

NON-PROCESS ELEMENTS IN CHIPS

Large variations in NPE concentrations in chips can be caused by the varying bark content in the digester feed. At colder temperatures during the winter months, debarking becomes more challenging, resulting in higher bark content. In regions like North America and Scandinavia, the bark content in chips can more than double. Research has linked the increased difficulty of debarking in winter, especially below freezing temperatures, to a stronger bond between the bark and wood [2 and references therein].

In winter, the diameter of logs used for pulping tends to be smaller compared to the summer due to wood scarcity and longer hauling distances. These thinner logs have a higher ratio of bark to wood, leading to a higher bark content in the chips [1]. **Figure 1** illustrates the trend of bark content in softwood chips used for pulping in a Canadian kraft pulp mill. It begins to rise in the fall, reaches its peak in February, and then experiences a rapid decline thereafter.



1. Bark content in the digester feed of a Canadian kraft mill, covering a period of three years. The bars in the box plots show the range between the 25th and 75th percentile, including the median value. Whiskers show the range between minimum and maximum values, and dots are outliers (data compiled by the author of this study).

Silicon and aluminum

The silicon content in chips exhibits notable variations mainly due to varying bark content. At the same time, silicon is one of the most problematic NPEs in the recovery system. The majority of silicon input into the mill usually comes from wood, while other sources can be the makeup lime, defoamers used in brownstock washing [3], and biosludge [4] if processed with black liquor. Aluminum content in chips also displays variations due to the varying bark content. Most of the aluminum introduced into the mill originates from wood and makeup lime. Due to their solubility in alkaline solutions, a large fraction of the silicon and aluminum from the incoming wood is diverted into the recovery cycle via the black liquor [4,5]. Silicon and aluminum are responsible for the formation of tough aluminosilicate deposits in the evaporation plant. Silicon is also responsible for poor settling and filtering of dregs and lime mud, reduced lime mud solids content, and limited availability of lime (**Table I**).

The concentration of silicon in bark varies widely and is often more than an order of magnitude higher than in wood [6-9]. Silicon concentrations can also vary substantially among trees from different harvesting locations. Hogan et al. [10] reported silicon concentrations in bark ranging from 380 to 5,500 mg/kg dry wood among spruce seedlings in Ireland, which were to some extent linked to the soil pH conditions and the tree growth rate. Aluminum levels in bark may exceed that in wood chips by a range spanning from a few to more than hundred times [7,9,11,12]. Assuming an increase in bark content in the chip mixture from 1% during the summer to 2.5% in the winter, the influx of aluminum into the mill may occasionally increase by more than half. These variations may have a notable impact on the processes within the evaporation and recausticizing plants.

Chlorine and potassium

Most of the potassium and chlorine in the recovery cycle originate from wood. However, a significant amount of chlorine can also come from makeup and bleaching chemicals, process water, biosludge, and spent acid [13].

Both elements play a critical role in corrosion and fouling, particularly in the superheater and generating bank of the recovery boiler. Chlorine and potassium contribute to lowering the ash's melting point and increasing deposition in heat recovery sections [14]. Additionally, potassium in the deposit covering the tube surface lowers its first melting temperature, which can accelerate corrosion in the superheater area [15] (Table I).

Changes in chlorine and potassium levels in pulp chips are correlated with changes in precipitator dust composition [16]. If not properly balanced through purging, these changes in the chips can directly impact recovery boiler operation. The variations in pulp chip composition largely stem from differences in tree concentrations at various harvesting locations. Saarela et al. [17] measured multiple elements in stem wood of pine and spruce trees from different sites across Finland within a ~200 km radius (**Fig. 2**). Their findings showed that average chlorine concentrations varied by a factor of 7 in pine and 1.5 in spruce between the locations, while potassium concentrations varied by factors of 1.7 and 1.9, respectively. Furthermore, individual trees within the same site can also exhibit significant variation [11,17].

Chip Characteristics and Main Causes for Variability	Digester and Brownstock Area	Evaporation Plant	Recovery Boiler	Recausticizing Area
NPEs				
Silicon Bark content; harvesting location		Aluminosilicate deposit		Poor dregs and lime mud settling/filtering; low mud solids content, and lime availability
Aluminum Bark content		Aluminosilicate deposit		
Chlorine Harvesting location			Corrosion; fouling	
Potassium Harvesting location			Corrosion; fouling	
Phosphorus Bark content; harvesting location				Low lime availability; increased lime purging
Magnesium Harvesting location				Poor dregs, lime mud settling/filtering; lime cycle deadload (in case of poor purging with dregs)
Calcium Harvesting location		Scaling		
Manganese Bark content	Scaling	Scaling		
Wood extractives Chip storage; bark content; seasonal variations	Foaming; reduced washing efficiency	Foaming; liquor carryover and condensate contamination; fouling	Changes in liquor heating value; combustion behavior	
Lignin Lignin content and composition at different locations	Change in cooking requirements	Black liquor viscosity affecting heat transfer	Black liquor heating value and viscosity affecting combustion behavior and throughput	
Fines and pins Seasonal variability	Partial depletion of cooking chemicals		Increased liquor solids load	
Moisture content Seasonal variability	Dilution of cooking liquor	Black liquor properties		
Aged chips Storage time, temperature	Change in cooking requirements	Black liquor viscosity affecting heat transfer		

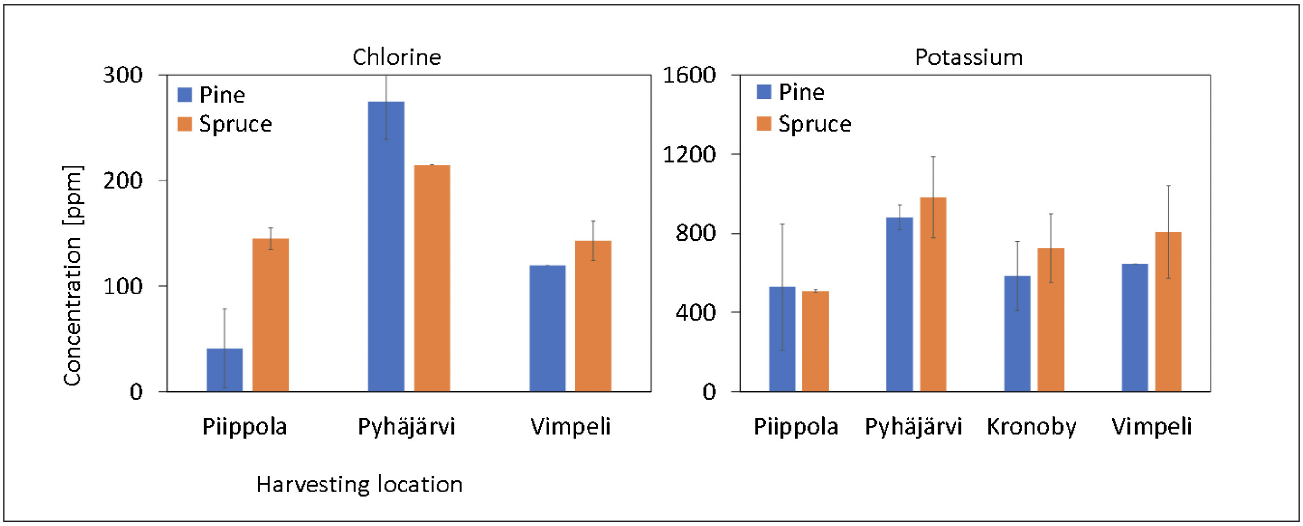
I. Wood chip characteristics and potential effects of their variability on different areas within the recovery cycle.

Also, and similar to other NPEs, potassium and chlorine concentrations can be several times higher in bark than in wood [6,11,18,19].

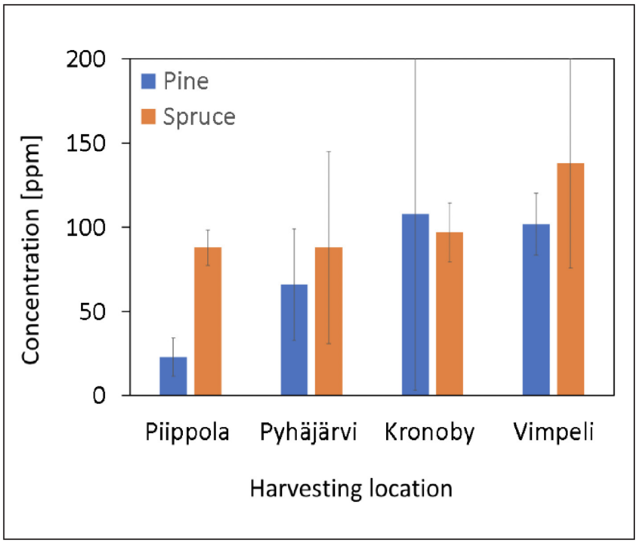
Phosphorus

The primary source of phosphorus in the recovery cycle is wood, except in cases where biosludge from wastewater treatment is added to black liquor. In the study by Salmenoja et al. [20], biosludge accounted for approximately one-third of the phosphorus intake. While most phosphorus from wood enters the recovery cycle, a notable portion ends up in the pulp and in the wastewater [4,20,21].

The phosphorus content in the digester feed varies based on harvesting location and bark content. Bark can contain more than ten times the phosphorus concentration of wood [9,11,18,22,23], which may lead to somewhat higher phosphorus intake during winter. However, variations among trees from different harvesting sites may cause larg-



2. Concentrations of chlorine and potassium in pine and spruce stem wood in Northern Finland within a 200km radius. Adapted from Saarela et al. [17].



3. Concentrations of phosphorus in pine and spruce stemwood in Northern Finland within a 200-km radius. Adapted from Saarela et al. [17].

er fluctuations in phosphorus levels, as shown by the concentration differences and large error bars in **Fig. 3**.

Excess phosphorus in the recovery cycle can have detrimental effects, including reduced lime availability and increased lime and energy consumption in the lime cycle (Table I).

Magnesium and calcium

Wood is a major source of magnesium and calcium for the mill, while both elements can also originate from makeup lime and biosludge [20]. Additionally, magnesium sulfate ($MgSO_4$) used during oxygen delignification can contribute significantly to magnesium intake. A substantial portion of both magnesium and calcium is directed to the fiber line [4,20,21].

The calcium content in spent liquor from the digester can vary depending on carbonate levels. Higher carbonate concentrations in the digester promote calcium precipitation as calcium carbonate, reducing its concentration in the liquor [24]. Magnesium can negatively impact process efficiency by contributing to poor dregs settling and filtering, lime mud filtration issues, and a high dead load in the lime cycle [13,25]. Calcium can be a key contributor to scaling in evaporators [13] (Table I).

Magnesium and calcium concentrations in bark can be an order of magnitude higher than in wood [11,23]. Their concentrations also vary significantly among trees from different harvesting locations, although the variability of magnesium seems to be higher than that of calcium [11,17].

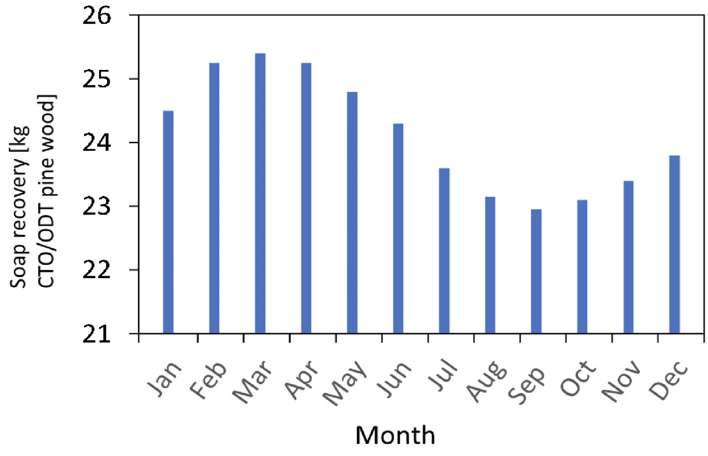
Manganese

Manganese enters the mill primarily through wood, with smaller contributions from process water and makeup lime. Its concentration in bark can be several times higher than in pulpwood. Manganese can contribute to scaling in the digester, brownstock washers, and evaporators but can be effectively purged with green liquor dregs [26].

EXTRACTIVES

Variations in extractives content can be attributed to several factors. Firstly, similar to NPEs, the content of extractives is higher in bark compared to wood [22]. Secondly, the concentration of some types of extractives and the extractives composition in wood exhibits seasonal variations [27,28 and references therein]. Thirdly, the storage conditions (e.g., duration, temperature) of the roundwood and chips have a significant impact on the extractives content.

The aging process of wood chips in piles can have an important purpose by reducing the presence of pitch-like compounds, including triglycerides, sterol esters, waxes, fatty acids, and resin acids [29]. These compounds can



4. Seasonal variation in soap recovery (kgCTO/ODT: kilograms of crude tall oil per oven-dried ton). Adapted from Foran [35].

cause various issues during pulping and papermaking. As a result of microbial activity, exothermic reactions occur within the wood chip piles, creating a hot environment ranging from 50°C to 80°C. This elevated temperature facilitates the degradation of extractives through processes such as oxidation of fatty acids, enzymatic hydrolysis of fats, consumption of fatty compounds by microorganisms, and potentially the evaporation of volatile extractives from the wood [30].

While seasoning of chips of some tree species can be beneficial to several mill processes [31], prolonged storage can have adverse effects, such as wood decay and pulp darkening [32].

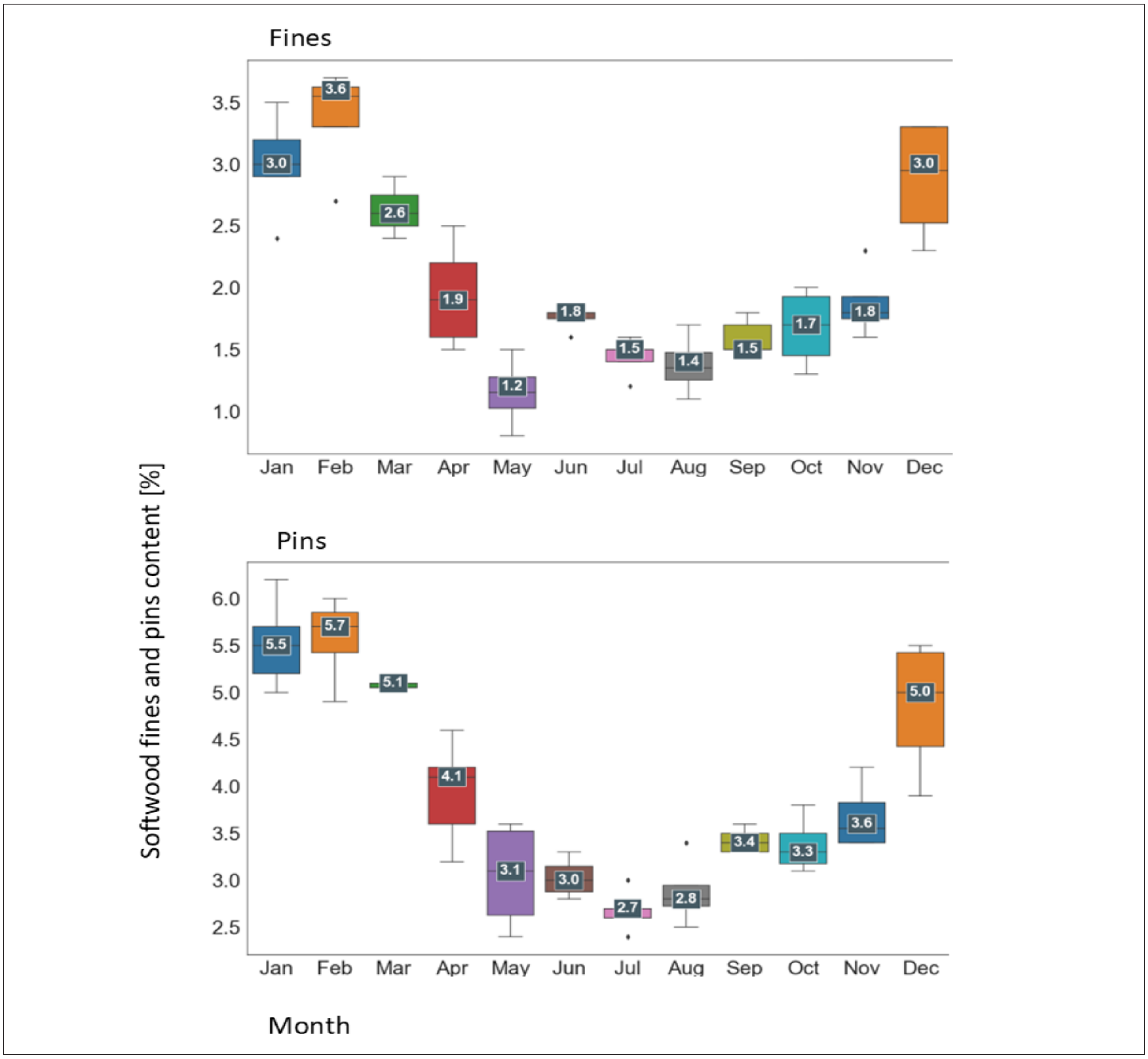
No consistent trend has been identified in the relative degradation rates of resin and fatty acids during chip storage, whereas triglycerides degrade notably faster. Their hydrolysis leads to increased fatty acid concentrations [33 and references therein], potentially enhancing soap separation from black liquor [34]. Consistent with variations in temperature and the extent of degradation during chip storage is the quantity of soap recovered from the black liquor. **Figure 4** illustrates the average seasonal variation in tall oil soap recovery based on data obtained from two Southeastern U.S. mills [35]. Degradation can proceed rapidly during the initial phase of chip storage. In as little as two months of chip storage, the tall oil loss may reach up to 65% [35].

Elevated concentrations of extractives entering the digester have various effects on the recovery cycle (Table I). The presence of extractives leads to foaming in the brownstock washing system, resulting in increased filtration resistance and reduced washing efficiency. Foaming in the evaporator can cause carryover of black liquor droplets into the condensate, which can lead to sodium and sulfur losses and operational problems in the stripper [36]. The utilization of contaminated condensate for pulp washing can have a similar detrimental effect on the pulp as an enhanced washing loss during brownstock washing [37]. The formation of organic deposits in foul condensate stripping systems, likely enhanced by liquor carryover, can result in the deposition of tar-like blobs in the pulp that was washed with the condensate [38]. Additionally, the buildup of soap layers in black liquor tanks can reduce storage capacity and impair tank management [37].

Soap contributes to fouling on heat exchanger surfaces in evaporators by carrying high levels of fiber and soluble calcium, which can also increase the fouling rates of other scales [39,40]. Efficient soap skimming is therefore considered a suitable method to limit soap-related scaling. However, in an evaporator survey, Grace [41] observed that a small amount of tall oil soap in black liquor had a beneficial effect, reducing the frequency of water washing and acid cleaning. More recently, it has been observed that resin and fatty acids, tall oil soap, and tall oil brine can reduce sodium salt scaling [42,43].

Fluctuations in soap concentration within as-fired black liquor can present challenges to recovery boiler operation, including variances in sulfate reduction [44]. Laboratory experiments have shown that adding tall oil soap to black liquor at concentrations typical of mill operations (<5%) slightly reduces liquor swelling, resulting in prolonged droplet combustion times [45-47]. However, mill experience, including findings by Niemi et al. [44], suggests that soap addition can intensify overall combustion and potentially burn down the char bed, likely due to the high heating value of soap, which is more than twice that of black liquor [48,49]. Additionally, increasing soap content in the liquor can reduce throughput in recovery boilers operated based on consumed air, potentially diminishing pulp production.

When the extractives content in the incoming wood is high, operators often increase the addition of silicon-based defoamer and/or drainage aid during brownstock washing, which in turn elevates the silicon input into the recovery cycle.



5. Seasonal variation of fines and pins in softwood chips at a Canadian kraft mill.

LIGNIN

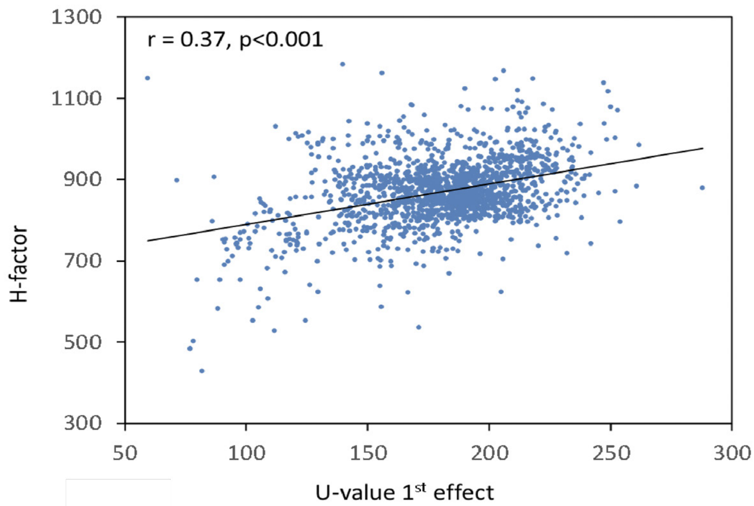
Lignin is a major constituent of pulp wood, with hardwood typically containing 18%–25% lignin and softwood containing 25%–32% lignin [50]. However, the content, composition, and molecular mass of lignin can vary significantly among trees, even within the same growing location [51]. Differences in microbial composition and activity have been correlated with seasonal variations in wood components within pulp chips, including lignin, as well as with differences among locations within a wood chip pile [52]. Since the heating value of lignin is double that of carbohydrates, an increasing proportion of lignin in black liquor can increase its heating value, potentially affecting the combustion process.

Moreover, varying molecular mass and chemical structure of lignin observed among aspen clones have been shown to affect pulping yield and residual lignin content [51]. Variations in the syringyl-guaiacyl ratio of lignin correlate with the ease of pulping [51], potentially affecting the required H-factor and liquor properties.

Another seasonal effect that can impact the lignin content is the partial replacement of wood species at certain times of the year. For instance, in some mills, due to limited availability of spruce logs in winter, a temporary shift towards using fir logs in the softwood mixture may occur. Fir tends to have a higher lignin content and lower cellulose content compared to spruce [53].

OTHER CHIP PROPERTIES

The presence of fines and pins in the digester feed shows seasonal variability, with higher levels observed during the



6. H-factor during cooking vs. U-value in the first effect of a Canadian kraft mill over the course of 7.5 years (r: correlation coefficient; p: p-value). All H-factor outliers with z-scores > 2 were removed.

winter months [1]. During winter chipping, wood tends to fracture and splinter, which may lead to a doubling of fines and pins concentration compared to summer (**Fig. 5**). Increasing levels of fines and pins can deplete cooking chemicals, as these particles dissolve and become part of the black liquor instead of the pulp [1], and their accumulation can create pockets within the digester where liquor depletion leads to localized undercooking [1,54]. Excessive amounts may also increase the liquor solids load on the recovery boiler, potentially leading to production losses for a recovery-constrained mill [55].

The moisture content of the chips exhibits significant seasonal fluctuations, with higher moisture levels during winter. Elevated moisture content can dilute the concentration of active chemicals in the cooking liquor [56].

The composition of organic compounds in the liquor significantly impacts its corrosivity towards carbon and stainless steel in digesters and black liquor tanks. Black liquor derived from softwood species tends to be more corrosive than that from hardwood species. Interestingly, the corrosion rate in black liquor does not correlate with the composition of inorganic compounds. Various organic compounds in black liquor, such as thujaplicins, catechols, pyrogallol, pinene, taxifolin, and others, have been identified as corrosive agents [57 and references therein]. However, due to the complex nature of the organic composition of black liquor, predicting the corrosivity of individual black liquors remains challenging.

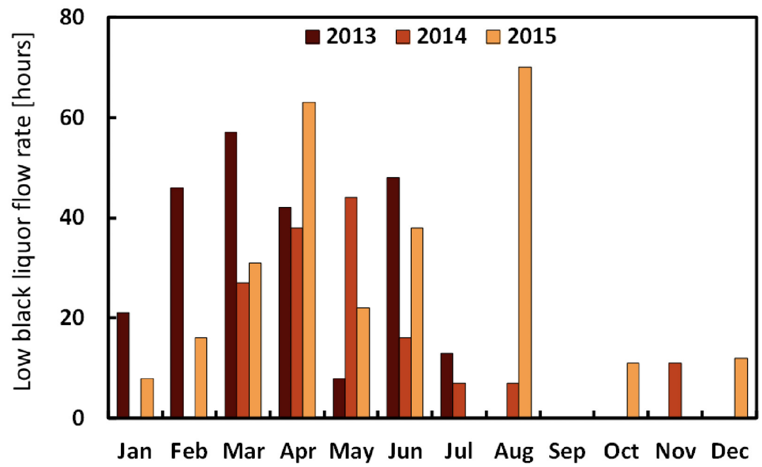
INDIRECT EFFECTS OF WOOD CHIP VARIABILITY ON RECOVERY CYCLE OPERATION

Wood chip variability can have indirect impacts on recovery cycle operation. In these cases, changes in digester or brownstock washing operation that are made in response to wood variability may affect recovery cycle operations. One such example is the influence on black liquor evaporation caused by an annual chip pile inventory. Towards the end of winter, some mills face a shortage of wood chips as the chip inventory approaches zero [1]. During the process of depleting the chip pile, some of the chips used for digestion have been stored in the pile for up to a year. These aged chips often undergo significant degradation, become acidic, and exhibit lower bulk density compared to regular chips. Moreover, due to their lower density and increased solubility in the cooking liquor, they require a smaller H-factor to achieve the desired kappa number after cooking.

To address this issue, operators reduce the H-factor and the degree of cooking for these aged chips. Within the kappa number range (after cooking) of approximately 20 to 50, reducing the extent of cooking may cause a reduced degradation of the extracted lignin, leading to a higher molecular weight of these compounds. A higher molecular weight of lignin in the black liquor causes an increased viscosity [48,58]. Consequently, the elevated viscosity adversely affects the efficiency of heat transfer in the evaporator, leading to reduced performance [48,59]. An associated temporary reduction in liquor solids content may cause a temperature drop in the lower furnace, higher SO_2 emission, and lower reduction efficiency.

The molecular weight of lignin in black liquor is influenced by various factors such as residual effective alkali (REA) and wood chip composition. However, in analyzing data from the Canadian kraft pulp mill, a weak but statistically significant correlation between reduced heat transfer in the first evaporator effect and a lower H-factor in the digester was found (**Fig. 6**). Numerous mills face similar evaporation challenges during periods when strongly aged chips are being cooked.

In another case, the variation in wood quality at a dis-



7. Number of hours per month during which the black liquor flow rate was lowered as a response to a rising boiler bed. Figure from Meyer et al. [60,61].

solving pulp mill likely had an indirect impact on the ability to burn black liquor effectively in the recovery boiler [60]. On multiple occasions, the presence of a high pitch content in the wood chips coincided with difficulties in efficiently burning the black liquor (**Fig. 7**). Although the pitch content was not directly measured, the quantities of defoamer and drainage aid used during the brownstock washing process served as an indicator of the pitch content. A strong correlation was observed between the increased usage of defoamer and a time-lagged expansion of the recovery boiler bed volume. To address the issue during each incident, the operators reduced the black liquor firing load until normal operation was restored. Although the exact mechanism behind this correlation is not completely clear, the occurrence of seasonal problems with liquor burning, which coincided with periods of high pitch content, implies a link between these issues and the variability in wood quality.

In general, to identify potential links between the varying wood composition and compromised processes or instabilities within certain stages of the recovery cycle, the presence of a seasonal pattern in these process-related problems could suggest that the wood itself is the root cause of the issue.

CONCLUSIONS

Wood chip properties such as the composition and content of NPEs, extractives, and lignin vary, and these variations can notably impact recovery cycle operation. Fluctuations in NPE content entering the digester can affect the degree of deposition in the evaporators and corrosion/deposition in the recovery boiler, as well as dregs and lime mud settling and filtering. Enhanced concentrations of extractives fed to the digester can lead to ineffective brownstock washing, foaming, and instabilities in the liquor combustion process. Foaming in the evaporators exacerbates black liquor carryover into the condensate, leading to washing issues in other parts of the mill. Lignin variations can change the viscosity and the heating value of the black liquor, which in turn may affect evaporation and combustion. In some cases, adverse effects in the recovery cycle may be due to operational changes in the digester or brownstock washing areas in response to wood variability. Therefore, the effects that the changing wood chip composition has are often not obvious. This technical review may help operators identify the root causes of issues located in recovery cycle departments. **TJ**

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ABOUT THE AUTHORS

I chose this topic because many recovery issues seem to link back to the variability in wood chip composition, which isn't well understood but can play a large role in the process. This research is similar to earlier studies that looked into the causes of process disturbances in the recovery cycle. What is different with the research here is that it focuses on how changes in wood chip composition may be linked to those disturbances.

The most challenging aspect of this research was finding enough reliable information on how wood composition affects the recovery cycle. There is not too much research on this, and some past findings don't fully agree with each other. That made the work more challenging, but also more interesting. One surprising discovery was how much the wood chip composition can vary. It was also interesting to realize that this is one of the hardest things to control in a kraft pulp mill.

This study may help mills identify links between wood chip composition and recovery issues, potentially making troubleshooting easier. While the manuscript may not cover every possible connection, it highlights key patterns that could guide further investigation.

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