

Real Measurements Lead to Real Understandings and Better Operating Control of the Recovery Liquor Cycle

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Abstract

Black liquor is a complex fuel of water, lignin fragments, hemicellulose, inorganic salts, sugars, starches, organic sulfur compounds and tall oil soaps. In contrast to the other fuels of the world, the properties of black liquor are poorly understood. It changes from species to species, from mill to mill, and from day to day. It is consistently inconsistent. Because of the changing properties of this fuel, the recovery boiler experiences operating problems associated with fouling, loss of thermal efficiency, environmental discharges, and corrosion.

Many of the earliest measurements of black liquor were inferential. These included temperature and density. The first attempts at providing online data occurred approximately 50 years ago and employed the use of auto titration which took advantage of the fact that mills were accustomed to tests based on titration. In 1996 Paprican (Pulp and Paper Research Institute of Canada) now FPInnovations, introduced the use of the FT-NIR (Fourier Transform Near Infrared) spectrometer to determine actual liquor parameters, online, at a Northern Ontario kraft mill. This approach did not use chemicals like the auto titration process. In molecular spectroscopy, the scan of the spectral frequency range allows for the individual components to be determined from their unique features. In 50 seconds, 128 scans are co-added to yield a spectrum of the liquor sample. In as little as a few minutes, including sampling time, information on numerous online black liquor parameters can be provided. Many of these parameters such as lignin, inorganic/organic solids and soap determination are not presently available from other measurement approaches. Additional samples to determine other parameters can be handled at the same sampling station. The spectrometer, in turn, can receive information from several sampling stations using fiberoptic cables. In 2023 this technology can no longer be considered new. It is, however, an evolving system, as new applications, developed in collaboration with partners offer new approaches of control to the kraft liquor cycle by measuring the actual (real) components of black liquor. This paper will summarize the benefits of spectroscopy-based measurement systems and demonstrate the potential use of this new information to improve the understanding and control of the chemical recovery and energy process of the Kraft mill.

Introduction

The Tomlinson recovery boiler is approximately 90 years old. (1) The original Tomlinson boiler design included the combination of drying, combustion, and chemical recovery within a water-cooled unit. There have been numerous improvements to this boiler design: increased spacing in tubes, the addition of retractable sootblowers, the conversion of economizers from a horizontal style to a vertical long flow, increased pressure and temperature, the switch to a single drum to allow for the building of larger units, at least 5 generations of air modifications and finally improved liquor delivery (2). Boiler vendors have done a remarkable job. The new recovery boilers being built today are the largest biorefinery units in the world. A recently built recovery boiler in Indonesia (2016) was sized to handle 11,600 tons of black liquor solids a day (later revised to 12,000 tons) and was stated to provide enough energy to meet the demands of a European city of 1,000,000 people (3). However, the average age of recovery boilers in the U.S. is presently just over 44 years old and the average age of a recovery boiler in Canada is almost 47 years old (4) (5). The majority of these boilers are small, overloaded, and encounter problems of plugging, corrosion and in some instances environmental upsets. Although upgrades are possible, they are expensive and require significant downtime for the conversions. The upgrades are also limited by available space in the mill setting.

Very little has been done with regards to improving the variability of the fuel (black liquor) to the recovery boiler. This is primarily due to the fact that the measurements of key components of the liquor have been limited. Many of the measurements are inferential (temperature and density for example). Other components are measured in a lab on

a limited basis. Reduction efficiencies, for example, might only be measured once a week. Other measurements such as REA (residual effective alkali) are done differently in different locations in the world and from one mill to another (6). Other measurements are not done at all in the majority of mills. These measurements include lignin, inorganic/organic content, and soap. However, lignin is the principal component of the BTU of black liquor which determines the steaming rate of the boiler, and it is also a prime determinant of black liquor viscosity, which potentially impacts droplet formation. A change in inorganic content can result in evaporator fouling. REA content can impact both black liquor viscosity (7) and soap solubility (8). A variance in soap content can result in evaporator carryover, excessive steaming rates of the boiler and the possibility of burning out the bed which in turn can impact the reduction efficiency and the settling of green liquor due to char entrainment. Operators need to have more information about the fuel they are burning in the recovery boiler if the industry wishes to improve the operation of recovery boilers and evaporators. This increase in knowledge of the fuel being burned in the recovery boiler is a potential solution that does not require extensive modifications to existing equipment with associated downtime and lost pulp production. It is an overdue need. The knowledge that chlorides and potassium impact recovery boiler fouling, a concept proposed in the 1980's, led to a significant improvement in recovery boiler performance, as presented by Hiner and Blair, at the 2000 Engineering Conference (9). These improvements were made possible due to numerous papers presented by Tran and the University of Toronto over many years. An expansion of the knowledge of the fuel to the recovery boiler by providing real measurements should lead to additional improvements.

Online measurement is obviously more advantageous than sporadic testing in a lab. This is primarily due to the increased frequency of testing results and the reduction of errors due to manual testing or a change in liquor properties created by time delays in testing or exposure to air. Black liquor at higher solids also changes from a Newtonian fluid (acts like water) to a non-Newtonian fluid (pseudo plastic) which complicates testing and the combustion process. The first online measurements were created approximately 50 years ago with online titration. This was an obvious first step because most lab tests involved titration. The advances of auto titration have continued with a paper presented just last year at PEERS on the use of auto titration for online reduction efficiency (10).

An online FT-NIR system was created by Paprican (Pulp and Paper Research Institute of Canada) and installed at a digester in 1996 at a Canadian mill. This system has been improved with numerous design changes at more than 90 installations throughout the world by Fitnir Analyzers Inc. (a licensee of FPIInnovations) so that it can supply, dependent upon the desired goal, accurate information to a kraft mill pertaining to the white, green, and black liquors of the Kraft mill cycle, along with necessary information needed for the improved production of chlorine dioxide. From a black liquor perspective, the REA of black liquor has been available for more than 25 years while inorganic and organic content, and lignin values have been available on a continual basis from a FT-NIR spectrometer since 2008. However, the acceptance of this type of data has been slow. Black liquor has been recognized as an extremely complex and variable fuel for a long time. As late as February of 2003 the AF&PA stated that "There is no analytical methodology available to characterize the composition of spent pulping liquor" (11). However, if we wish to improve recovery boiler and evaporator operations, we need to have a better understanding of the liquor parameters that make up the inorganic and organic content of black liquor. The worldwide use of the FT-NIR spectrometer in other industries such as the petrochemical industry, the food industry, and the pharmaceutical industry show the potential to provide this information. The development of the use of FT-NIR for the pulp and paper industry will be an ongoing process due to the complexity of black liquor. The AF&PA stated in 2003 that there are over 100 inorganic and organic components of black liquor that should be looked at (11).

The System

The liquor to be analyzed is first sent into a cell and given a short amount of time for settling to occur, as shown in figure below.



Figure 1: The sample cell of an online analyzer system. Sample flows in from bottom and returns to process. The fiber optic cable brings light to and through the cell and returns to the detector on a second fiber optic cable.

NIR (Near Infrared) light is delivered to a flow cell via fiber optic cable and passes through the sample and returns to the detector with another fiber optic cable. The broadband light is absorbed by the molecules in the sample, creating molecular vibrations. The frequency of these vibrations and corresponding absorption in the near infrared portion of the spectrum (800-2500 nm) allows for identifying different liquor chemical compositions and their quantity by the characteristic absorption associated with their chemical bonds, in the same way that a fingerprint can identify an individual. The combination band region has sharper features while the 1st and 2nd overtone bands are broader. In an aqueous sample, perturbation of the water band also provides unique information associated with water structure, referred to as aquaphotomics. Furthermore, the ability to see into the 1st and 2nd overtone bands provides the opportunity to use larger optical pathlengths, which is more appropriate for industrial process applications. The spectrometer is usually housed within a safe environment such as an MCC room. No chemicals are used. No sample preparation is required outside of settling time. It is fast, safe, and reliable. It is a non-destructive testing method. Multiple liquor parameters can be analyzed with a single sample. One sampling station can sample numerous samples. The spectrometer can handle up to 8 sample stations. A typical setup is provided in the figure below, comprising of an SRS (spectrometer rack system) and a FSS (field sample station), connected through fiber optic cables, both for measurements and communications to open and close valves as well as other digital and analogue inputs and outputs.

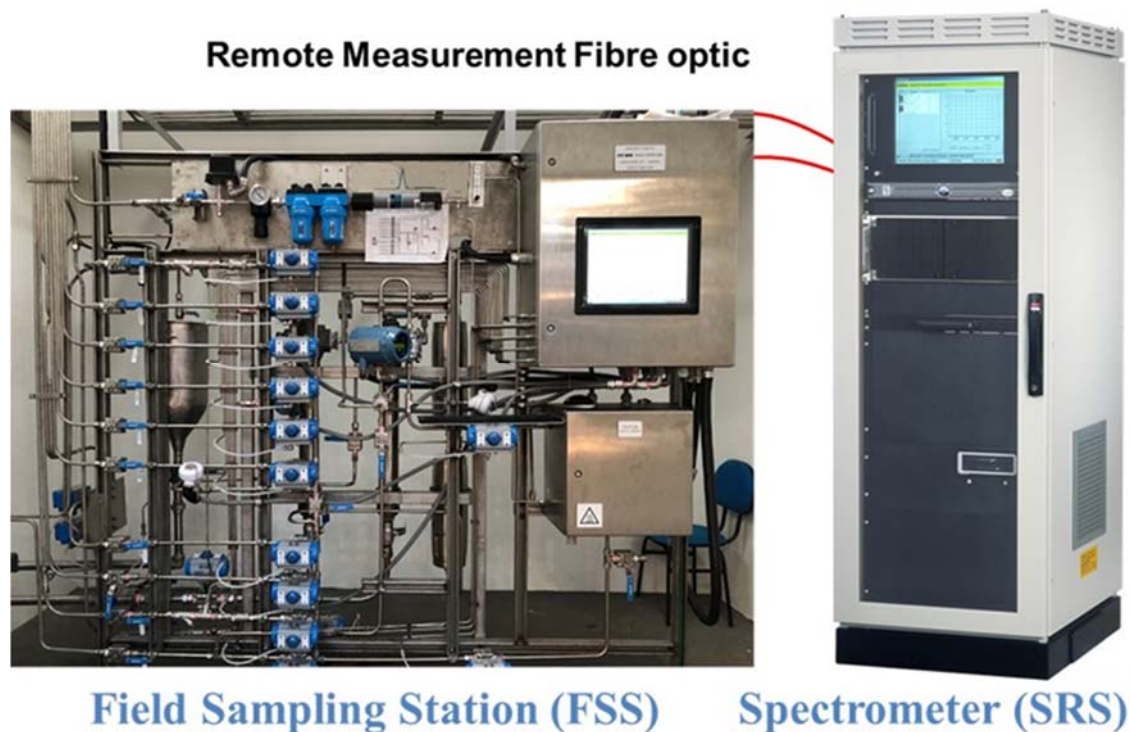


Figure 2: A sampling station connected to a spectrometer via fiber optic cable. Distance between the two units can be upwards of 1000ft.

As previously stated, most of the boilers in the world still encounters numerous problems. These include plugging, loss of thermal efficiency, environmental upsets, and corrosion. These operating issues are primarily due to the variability of the fuel, black liquor. Some of the potential costs to a mill will be first presented and then it will be shown how real measurements using the FT-NIR can reduce the variability and allow for better operating evaporators and recovery boilers.

Costs of Variability and Poor Operations: Plugging, Corrosion, Loss of Thermal Efficiency and Environmental Upset

Plugging

Recovery boiler plugging, one of the more serious problems, can easily cost a 1000 ton-a-day pulp mill over \$1,000,000 dollars per day when a water wash is required for the boiler due to fouling. The 3-month average selling price of NBSK (Northern Bleached Kraft Softwood) on June 21st, 2023, was \$1583 US a ton in the U.S., \$1292 a ton in Europe and \$763 a ton in China according to NRCAN (12). The loss of revenue for a 1000-ton mill, while on softwood, would be \$1,583,000 U.S. per day for a water wash if the pulp was destined for the U.S. If the pulp was being sold to China, the value would be less than ½ that amount. The only cost that can be reasonably subtracted when a mill is down for a water wash is the cost of the wood which in the 4th quarter of 2022 was \$104.79 /BDMT for softwood according to the Global Fiber Price Index (13). In order to safely water wash a recovery boiler, the boiler has to be significantly cooled to prevent a smelt water explosion. This cool down time varies from mill to mill and adds significantly to the downtime associated with a water wash. A water wash can easily take one and a half to two days when a proper start up curve is followed. It is possible that a water wash for a recovery boiler supporting a 1000-ton mill can cost a mill 2 million dollars U.S.

Corrosion

Corrosion, when encountered, can result in a bill of several million dollars on an annual shutdown due to expensive repairs and loss of pulp production. This corrosion in a recovery boiler can take the form of primary air port cracking, cut line corrosion and superheater corrosion to list a few. In N. America 45% of recovery boiler failures occur in the economizer. Superheater failures have been reduced due to a better understanding of the causes of corrosion in this area of the boiler (14). Variability in recovery boiler operation is a significant cause of corrosion or cracking. This is particularly true in older boilers with cascade evaporators that usually operate between 65 and 68% solids. This is explained, very well, in a paper entitled “The effect of H₂O on acidic sulfate corrosion in kraft recovery boilers” by Tran, Mapara, and Barham state the following; “Acidic sulfates, mainly sodium bisulphate (NaHSO₄) and sodium pyrosulfate (Na₂S₂O₇) are thought to be the main cause of fireside fouling and severe tube wastage in the generating bank and economizer regions of kraft recovery boilers”, and “Solid Na₂S₂O₇ which is non corrosive may revert to the corrosive liquid NaHSO₄ if the H₂O in the flue gas exceeds a critical value”. The critical value suggested by Tran was 33% (15). When water from sootblower steam is added to the high water content of black liquor fed to recovery boilers with cascade evaporators, this value can easily be reached. In older two drum boilers one source of corrosion discussed, as early as 1981, was near drum corrosion where the water from sootblower steam combined with water associated with low solids created corrosion where the tubes entered the mud drum in the area of the sootblower lanes (16). One of the principal reasons for the lower solids associated with cascade evaporator boilers is that operators often operate to the amps of the cascade evaporators which are determined by the viscosity of the liquor.

Loss of Thermal Efficiency

Loss of thermal efficiency from the recovery boiler is another potential cost to a mill. Black liquor solids measurement has always been an important measurement for recovery boilers because it is actually a measure of water in the fuel to the boiler. The water in the black liquor greatly impacts the thermal efficiency of the boiler as shown in Figure 3. With every lb of water entering the boiler as a part of the fuel, 970.3 Btu per lb (2260 kJ/KG) of energy has to be expended to vaporize it and then additional heat is further added before the water component of the fuel is exhausted to the stack. The steam generation of a boiler is significantly impacted by the operating black liquor solids.

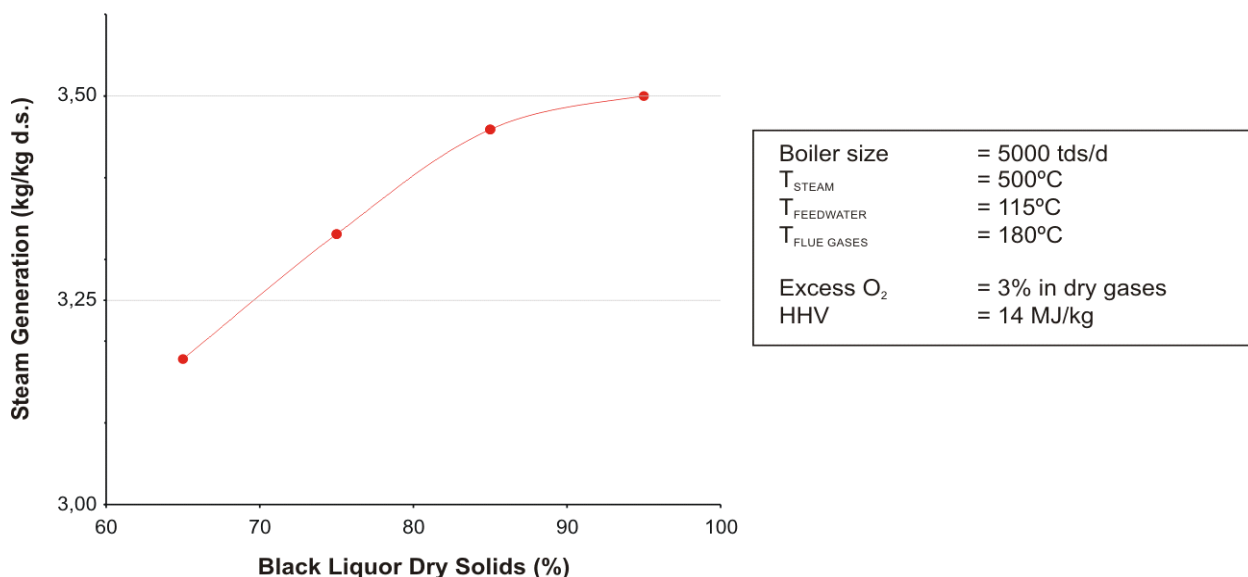
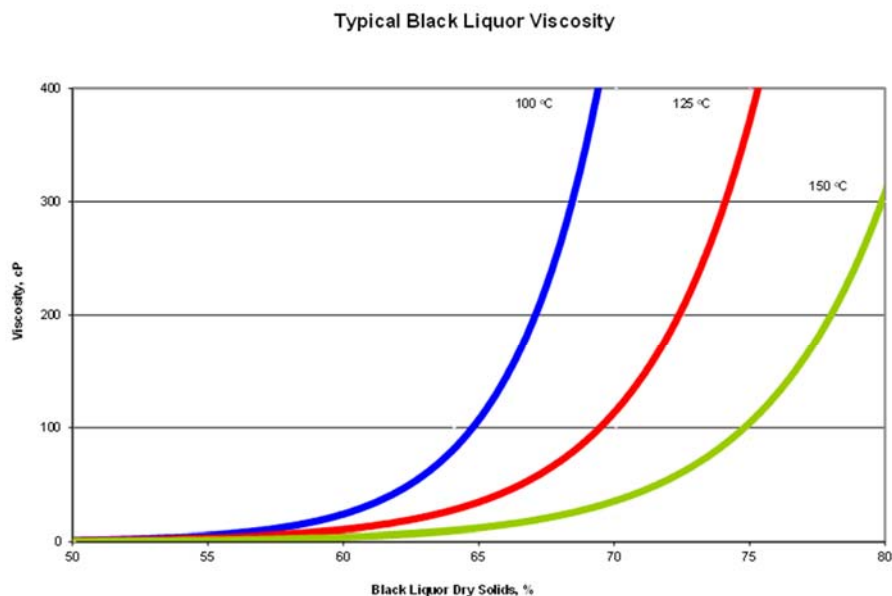


Figure 3. Black liquor solids impact steam generation, courtesy of Andritz (McKeough and Saviharju)

The immediate question that comes to mind with the information contained in the above graph is “Why don’t mills just operate at much higher solids?” The simple answer is viscosity. As the % solids are increased, the viscosity increases significantly making the pumping and handling of black liquor more difficult (Figure 4). In a paper by

Dutka, Crisalle, and Fricke entitled “Evaluation of a Capillary-Coriolis Instrument for On-Line Viscosity and Density Measurements of Kraft Black Liquor” published in 1997, they stated that if all the recovery boilers in N. America were able to raise the solids from 70 to 75% the energy savings per year would be 3.1×10^{13} Btu or 32,706,731 GJ. (17). Obviously things have changed since 1997. There are fewer recovery boilers today and many of the remaining boilers can operate at 75% solids. However, the number provided by Fricke suggests a significant loss of potential. Using a value of \$8.936 US per GJ (a natural gas price in July of 2022) and the number provided by Fricke, the potential energy savings for N. America would have been \$292 million dollars US last year. This year, the value of natural gas has dropped significantly. On June 27th, 2023, the Henry Hub spot price for natural gas was \$2.68 U.S. At this value of natural gas, the savings would only be \$88 million U.S. for N. America. Although many mills are now operating at 75% solids, the graph in Figure 3, clearly shows that additional increases in efficiencies and savings can still be obtained when the solids are further increased into the mid-80s or higher. Black liquor viscosity has been, and remains, a hurdle in the way of obtaining higher thermal efficiencies for recovery boilers. Operating at higher solids by controlling the liquor parameters, such as REA and lignin, that impact viscosity is still a viable approach to improve the thermal efficiencies of recovery boilers. This is a bigger opportunity in N. America where the boilers are older and smaller than other parts of the world. It should be noted that North America still has the most recovery boilers in the world with Canada having 40 and the U.S. having 148, as of 2018. The world total in 2018 was approximately 600 (18).



A typical black liquor solids / viscosity / temperature relationship (Reproduced from a slide by Marr and Adams)

Figure 4: Once black liquor reaches a % solids of roughly 70%, with a temperature of 125 degrees C, the viscosity curve is extremely steep.

Environmental Upsets

Similar to the critical solids for corrosion, there is a critical solids that can result in high sulfur emissions. This again applies mostly to older boilers that typically operate with lower solids than modern boilers. In 1992 Vakkilainen stated in a paper on long term fouling: “Long term fouling of a recovery boiler operating at 66 to 68% solids has been studied previously. At this solids the sulfur emissions are 100 to 500 ppm at 3% O₂. In high solids operation the outlet flue gas SO₂ can be continuously kept close to zero.” (19). Salmenoja provides a similar observation in a paper on the development of recovery boilers, “Both the sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) were practically zero when high dry solids firing was in operation.” (20). Andy Jones also presented this relationship between higher solids

and SO₂ emissions in 1993 when evaluating a mill's move towards high solids (21). Although newer boilers operating at higher solids can pretty much avoid sulfur emissions by operating at solids above 75% solids, many older boilers have not been able to achieve this, either because of evaporator performance or boiler capability. In many cases this is due to changing liquor parameters that impact the viscosity of the liquor and the potential to operate at higher solids.

Real Measurements can Lead to Better Control

It has already been stated that boilers in N. America are older. They are also significantly smaller than the new boilers being built in other parts of the world. The average size of a recovery boiler, in 2018, was 1300 tds/d in the U.S. and 1410 tds/d in Canada. The largest recovery boiler in the U.S. was 3400 tons per day (18). The majority of these older boilers operate above their original design and in many cases are the bottle neck of the kraft mill. One significant potential, in particular for older recovery boiler optimization, is to reduce the variability of the operation. As expressed earlier, black liquor is a variable fuel with respect to lignin content, REA, soap content, inorganic and organic content, and viscosity. This variability can be due to wood species, digester operation, recausticizing operation, recovery boiler operation, seasonality, and additions or subtraction from/or to the black liquor. The next segment of this paper will discuss how the measurement of these properties, using an on line FT-NIR system installed in a mill, combined with typical mill measurements such as % solids, temperature and pressure, can add to an operator's knowledge of the black liquor to be handled. This knowledge, in turn, can lead to reduction of operational variability of the evaporators and the recovery boiler. It should be noted that the monthly graphs provided below are from an operating mill and there are over 700 points of measurement per liquor property shown for hourly readings or over 2800 points made available when 15 minute intervals are used. As Lord Kelvin once stated, "if you don't measure something you can't improve on it".

REA of Black Liquor

From a black liquor perspective, REA has been successfully measured online with an FT-NIR analyzer system since 1996. It was measured initially to improve the operation of the digester. However, REA is important to evaporator and recovery operations because it impacts both black liquor viscosity and soap solubility.

Unfortunately, the testing of REA has not always been consistent. In a private correspondence with Roxare Thompson in 2009 she stated, "Many mills have used old procedures developed by PAPTAC (J15P) and TAPPI (625 cm-85) based on acidimetric titration. However, these methods overestimate the true concentration of alkali due to interference from dissolved organic compounds. The SCAN method (SCAN-N 33:94) provides a more accurate measure of the alkali content of a black liquor. In this method, potentiometric titration with 1M HCl to the first inflection point is used for black liquors with an initial pH of at least 11 and concentrations not exceeding 20% solids. If the first inflection point is not visible, the volume of HCl at a pH of 11.5 is used instead. A correction factor is applied to obtain the true value of the REA." (22). Both the PAPTAC (J15P) and the TAPPI (625cm-85) titrate to an 8.3pH end point and depend on barium chloride to avoid the interference of organics (6). In 1994, Milanova, after Paprican had introduced the Mortimer test to counter the over estimation of alkali in the existing REA tests in N. America, stated that 10.5pH as an end point for titration (the Mortimer test) was too low and could result in errors of 25% when the residual effective alkali was high and up to 260% when the residual alkali was low (23). This caused Milanova and Dorris to promote another method – the Milanova-Dorris method. In 2007, Radiotis tested the 4 methods used by mills and laboratories against capillary electrophoresis. He concluded that the Milanova-Dorris method and the Scan method were the most accurate (24). When FT-NIR analysis is used to measure REA, it has to be calibrated against known methods. In 1996, it was originally calibrated to the PAPTAC (J15P) which led to an overestimation of REA. It is presently calibrated against capillary electrophoresis. Once the calibration has been made it does not have to be continually redone.

Paprican showed in 2007 that there is a narrow range of REA in black liquor to maintain the lowest possible associated black liquor viscosity with the respective solids (7). In older recovery boilers, with cascade evaporators, the risk of obtaining a high viscosity liquor usually was because the REA was too low. In addition to the oxidation process, depletion of REA can be the result of hot storage and by acidic flue gases passing over the cascade evaporator and wet bottom precipitators. This can result in some cases, in extremely high viscosity liquor, even when the % solids

were quite low (6). Low odour boilers are not immune to low REA levels. Digester operation and hot liquor storage can deplete REA. In low odour boilers a higher viscosity could also occur if the REA was too high. Because of this relationship between viscosity and REA, REA needs to be measured. This might be even more necessary in mills that have additional sources of acid returning to the weak liquor, such as in a dissolving pulp mill or a mill that has undertaken lignin precipitation to add increased pulp production and to acquire a new product.

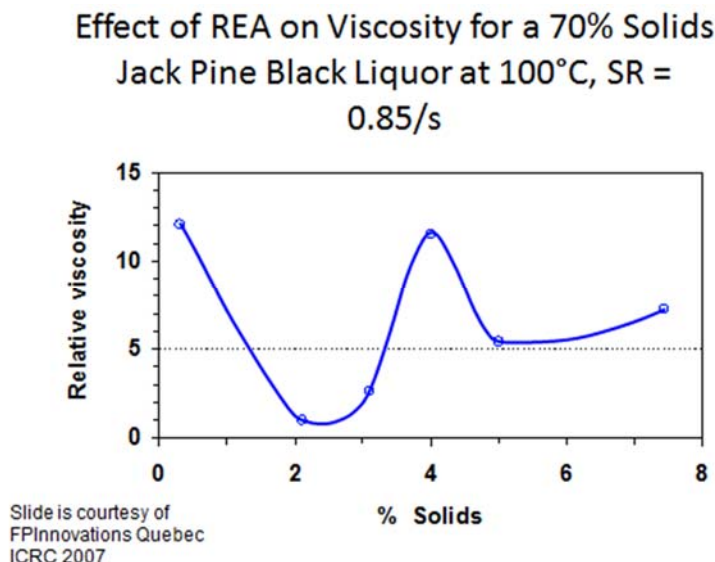


Figure 5: FPInnovations research shows a narrow window of REA for optimum black liquor viscosity.

REA has also been reported to impact soap solubility. Doug Foran states in his presentation at the Tappi Recovery short course that for the best soap removal and the lowest solubility of soap in black liquor, the REA should be above 6 grams per liter at 20% solids (8). If soap stays soluble, this might pose problems for the evaporators and will cause steaming issues in the recovery boiler due to a higher Btu. Soap has traditionally been viewed as a bad actor in evaporators because of the foaming and carryover it creates in lower % solids evaporators. However, some recent work suggests that soap or tall oil brine might help prevent fouling in concentrators (25) (26).

More work is required. Usually, the REA measurements during softwood runs are well above the solubility line of 6 grams per liter. However, during hardwood runs the REA is very often below the solubility line. Usually, it is assumed that there is no soap in hardwood, so this shouldn't matter. However, one source has stated that hardwood liquor contains less than 4% of the total % solids as extractives while softwood contains less than 5% of the total solids in the form of extractives. Extractives are primarily soap. The major difference is that hardwood extractives are mainly in the form of free fatty acids and fatty acid esters while softwood liquor contains a significant amount of resin acids as well as, to a lesser amount, of free fatty acid and esters of fatty acids (27). Regardless, it can be seen during the second softwood run, as shown in Figure 8, that numerous REA readings are below the suggested solubility line. Recent work by Fitnir Analyzer Inc. (28) on soap determination in black liquor and recent % solids work by FPInnovations on intermediate liquors in the 40 to 50% solids range (29) may improve our understandings of soap solubilities, especially in mills that switch between softwood and hardwood. The presence of soap is of particular interest to boilers that are overloaded from a steaming perspective. Soap has an average HHV of 21.8 MJ/kg or 9370 Btu (30) which is approximately 30% higher than the Btu of black liquor. Soap has also been reported to significantly impact the viscosity of black liquor (31). Soluble soap might at least partially explain the variability of steam flow per lb. of liquor. This is more dramatic between species but also occurs within single specie operations as shown in Figure 7.

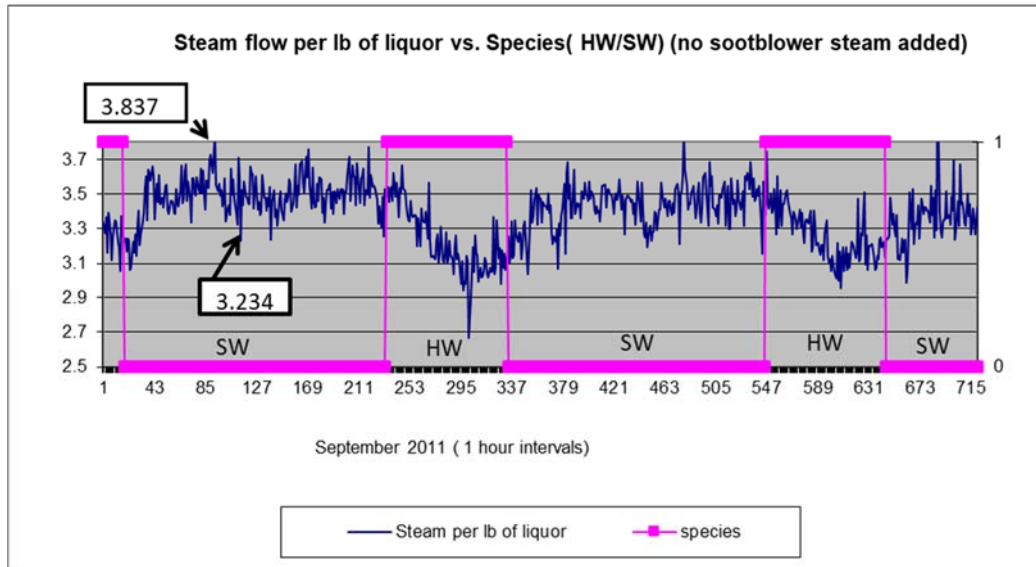


Figure 6: Although the steam flow per lb. of liquor variance is greatest between species there are still variances within single species operation, likely due to variances in digester operation or the presence of soap.

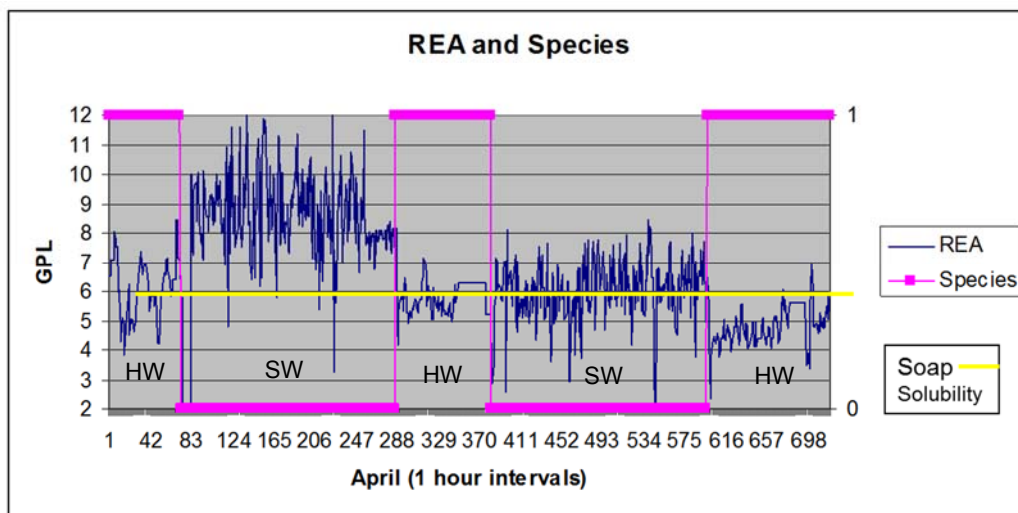


Figure 7: REA measurements in an operating mill during both hardwood and softwood with a soap solubility line based on REA.

Online REA determinations of black liquor can be supplied by both the auto titrator and the FT-NIR spectrometer. However, the FT-NIR can supply information on other liquor parameters with the same sample. One of these is the inorganic/organic content.

Inorganic/Organic Content

The inorganic content measurement of the solids in black liquor provides numerous possibilities to improve the operation of evaporators, recovery boilers, and recausticizing plants.

The inorganic content of black liquor will influence the amount of water required for transport, and hence the evaporation requirements of the evaporators. The inorganics will also influence the boiling point rise in the evaporators, the fouling of the evaporators, concentrators, and boiler, and will influence the smelt quantities, and the BTU of the liquor going to the furnace.

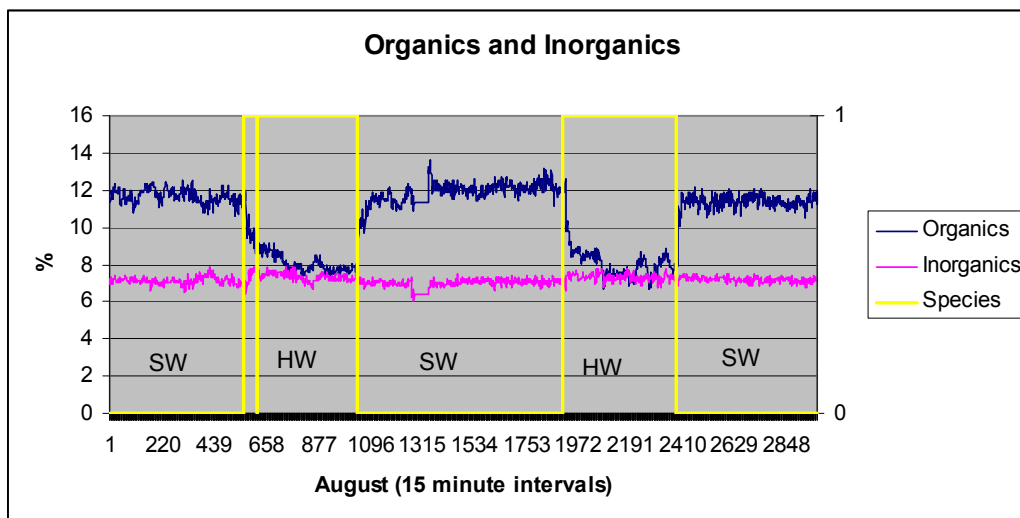


Figure 8: Online inorganic /organic measurements for a month at 15-minute intervals

Figure 8 shows a significant variation between species with regard to the measured organics. The organics are significantly higher on softwood runs compared to hardwood runs. The inorganic readings, in contrast, appear quite consistent for both softwood and hardwood, but from a ratio perspective (organic-to-inorganic), are higher on hardwood. This increase in inorganics compared to the organic content from a ratio perspective appears to play a factor in fouling of the concentrators. In Figure 9, the % of inorganics compared to the total solids in the liquor rises during each hardwood run.

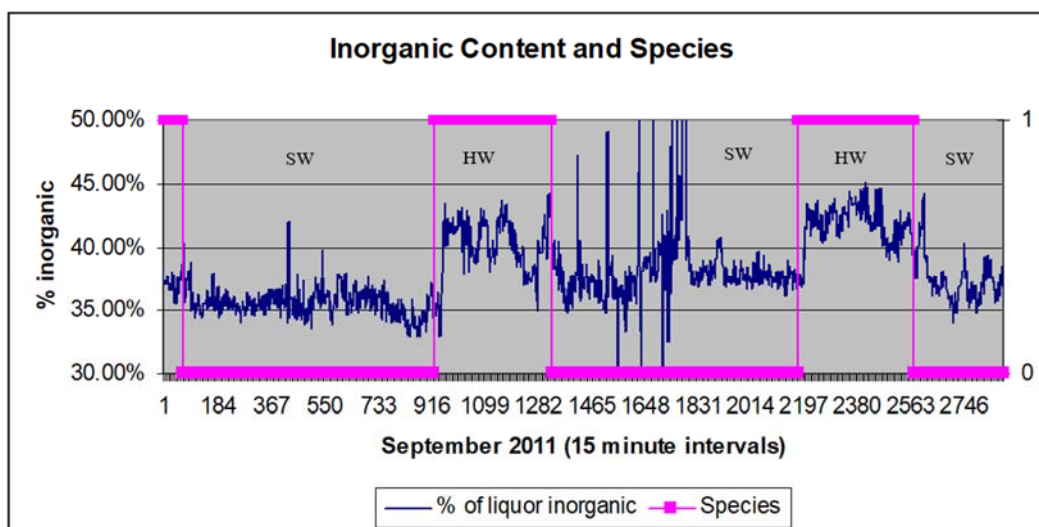


Figure 9: The % of inorganics in the liquor is always higher during hardwood runs because the organics are lower.

This higher % of inorganics could result in fouling during each hardwood run, as indicated by the need for increased steam flow as shown in Figure 10. Additional work is required using online measurements to determine why this fouling occurs during hardwood runs and how it might be reduced. Online knowledge of the inorganic content should aid this endeavour. The future breakdown of the inorganics into its component parts by spectroscopy would again further the understanding of evaporator fouling.

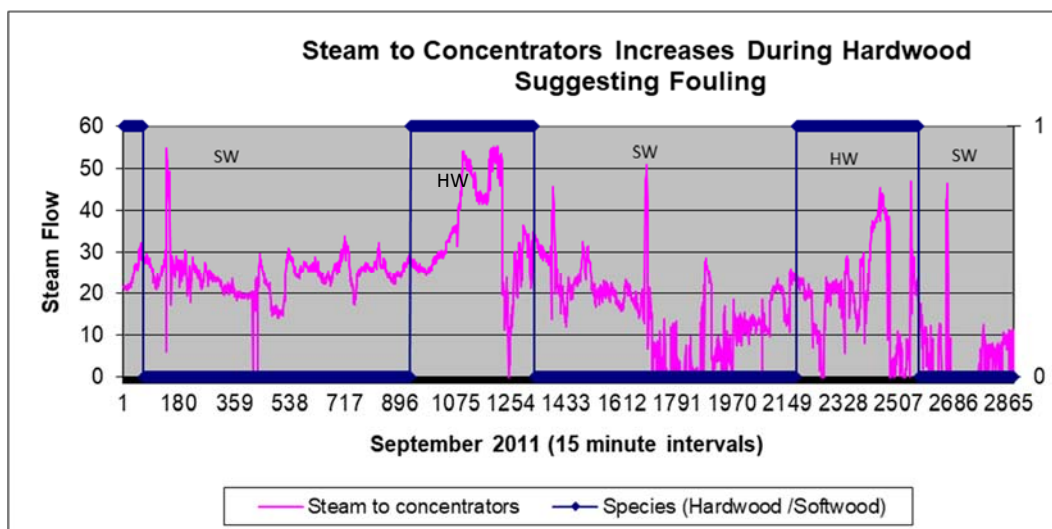


Figure 10: When the digester switches to hardwood fouling usually occurs shortly thereafter in the concentrators as indicated by a need for more steam.

When researchers discuss evaporator fouling, they usually mention burkeite and dicarbonate formation which are double salt components of sodium carbonate and sodium sulfate. They differ only by their concentrations. Burkeite is sulfate rich while dicarbonate is carbon rich. They sometimes also mention critical solids. Operators are told, for instance, that fouling from burkeite could occur at 50% solids in their mill so they should keep the output of the sextuple evaporators below that solids point to reduce the potential of fouling the 1st effect. However, the solids they are considering is a total solids determination of both organics and inorganics. Fouling is usually associated with inorganics content. Wouldn't it be useful to have a measure of the inorganic solids rather than the total solids at the point in the evaporators that fouling is most likely to occur? Although evaporator fouling is less costly than having to perform a water wash on a boiler downtime, evaporator performance can reduce pulp mill production and cost a mill money.

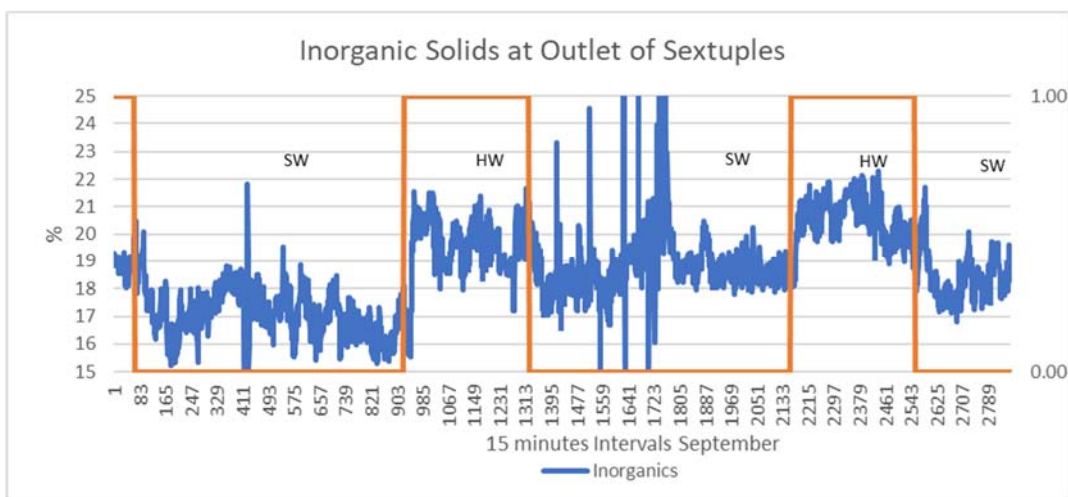


Figure 11: This graph shows the total inorganics ranging from 16 % on softwood to 22% on hardwood based upon the initial inorganic/organic content at the exit of the digester and the solids determination of the liquor exiting the sextuple evaporators.

Inorganics are the chemicals being recovered by the recovery boiler to be reused in the digester. Dead load chemicals, a component of the recovered chemicals, are the inorganic chemicals that do not participate in the pulping process. Although non-participants, they have the ability to circulate through the Kraft liquor cycle, thereby requiring additional

handling capacity and energy. This results in additional costs to the kraft liquor cycle and the mill. The largest and most commonly dead load chemicals are sodium carbonate, sodium sulfate and sodium thiosulfate. FT-NIR measurements have been able to provide online reduction efficiencies and causticizing efficiencies (indicators of deadload) since the mid 2000's (see Figure 12 and 13). The online reduction efficiencies determined by FT-NIR have the potential to also include thiosulphate, thus, providing a truer indication of oxidized sulfur deadload. Although thiosulphate is a form of dead load, it is usually not measured because of the difficulty of the test. The difference between a RE, with or without thiosulphate, is shown in Figure 12. Figure 13 shows that two means of determining CEs have been used in mills. In one case, the CE does not include the EA of the green liquor because the recausticizing department has not created it, while in the other, it is included. Additional information on dead load can be obtained from Grace and Tran's paper "The effect of dead load chemicals in the kraft pulping and recovery systems" (32) and Porter's paper entitled "Dead Load Determination Using Online Measurements (Using online FT-NIR measurements to evaluate the impact of dead load on the Kraft liquor cycle)" (33).

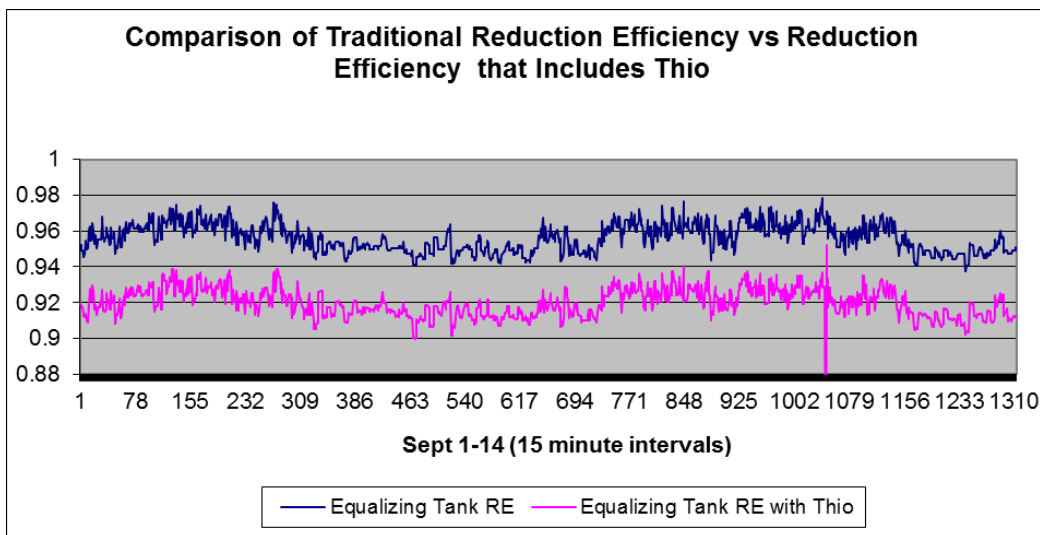


Figure 12: A comparison of the traditional means of reduction efficiency versus a method that includes thiosulfate in a modern well operating boiler.

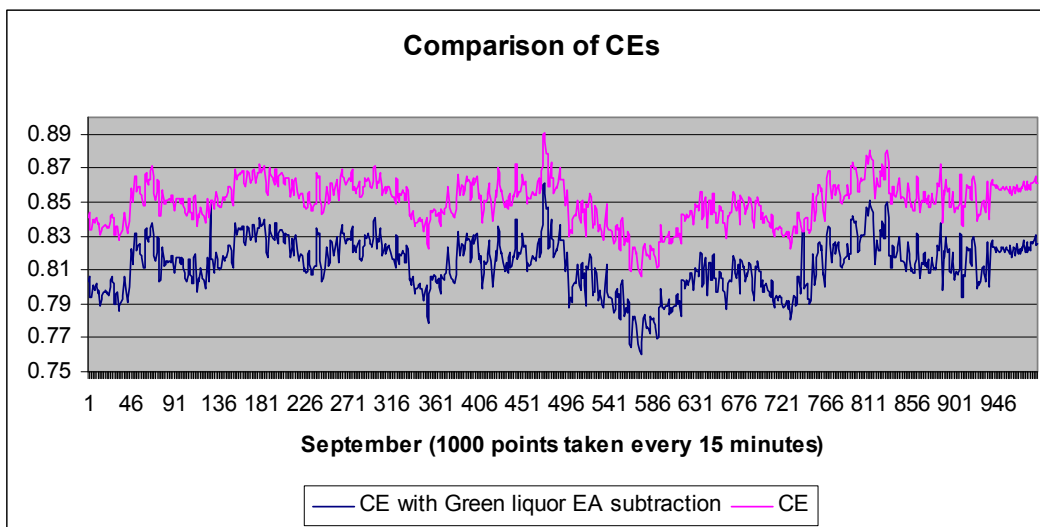


Figure 13: When the EA in green is subtracted from the CE formula (because it already exists in the green liquor prior to recausticizing) the result is a lower measured CE.

Lignin

Probably the most important liquor parameter, that is at presently only measured online by the FT-NIR analyzer, is lignin. The measurement of lignin online has been available since 2008. Lignin determines black liquor viscosity, calorific value, and can possibly impact environmental discharges, corrosion, and fouling. At a time when many mills are considering removing lignin to allow more pulp production, based on a lower steaming rate, the question has to be asked “How do you improve recovery operations when you don’t know the lignin content before or after lignin removal?”

Most researchers in the last 25 to 30 years have decided that lignin is a prime determinant on black liquor viscosity (34) (35). The online use of the FT-NIR to measure lignin supports this conclusion, as shown in Figure 14. It should be noted that the calibration for lignin was done by UV visible analysis. This is the same approach used by Fricke and Zaman (36) because it includes both high molecular weight (HMW) lignin and soluble lignin. Although HMW lignin is of the most interest because it can be precipitated for other purposes, soluble lignin was described as a possible plasticizer by Fricke (37), so it shouldn’t be ignored, as it could possibly play a part in the viscosity of strong black liquor.

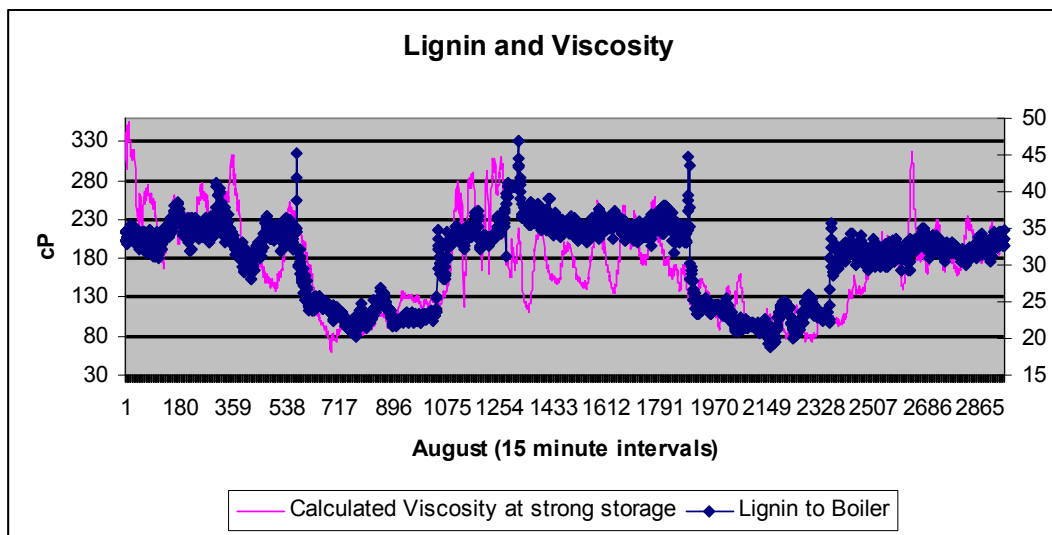


Figure 14: Viscosity of black liquor tracks very well with lignin content.

The black liquor viscosity shown in Figure 14 might very well be the most important parameter which significantly contributes to boiler variabilities, leading to reduced efficiencies, boiler fouling and lower revenues. Researchers have been looking at black liquor spray for years to try and come up with a nozzle that will provide the proper spray into the furnace, without creating droplets too fine to create carryover, but still create droplets that will combust properly, to form a uniform char bed. However, at high solids, black liquor is essentially a non-Newtonian fluid. This means that, unlike water, its viscosity is influenced by both shear and temperature. When the black liquor is sprayed into the furnace, shear is reduced; the liquor changes from a Newtonian fluid (because of high temperature and pressure) to a non-Newtonian fluid. Figure 15 is a graph that shows a steep climb in viscosity when the shear rate is lowered.

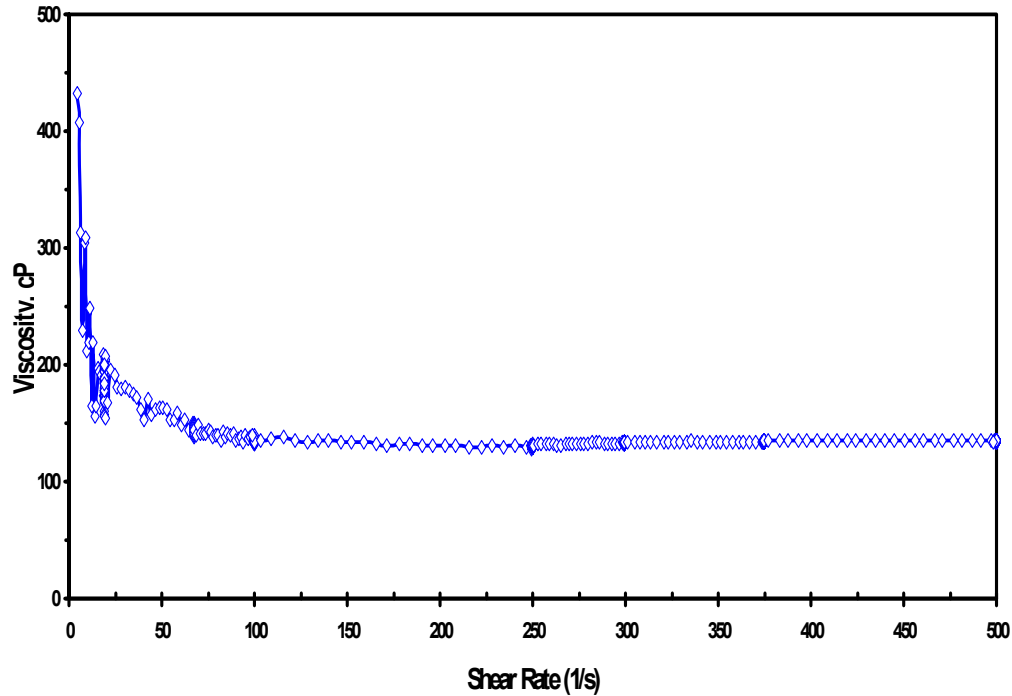


Figure 15: Graph showing the effect of viscosity as a function of shear rate (courtesy of Pak Wong, Steam and Power Fall Meeting December 2007)

The questions that have to be answered are: “Does the best droplet formation occur somewhere on the steep portion of the curve? Is this steep rise because the shear force has been reduced as the liquor is sprayed into the furnace? Is this why operators typically operate with “too high of a firing temperature”? Do they want to stay away from the potential of a high bed by keeping the droplets so fine that they risk upper furnace fouling? Do they fear high beds that are possible due to operating too high up on a shear curve that they can’t see?

If any of this is true, then we need to incorporate viscosity measurements with firing temperature and gun pressure in order to get the best spray pattern. Irving Paper essentially did this with a “poor man’s” viscometer derived from a relationship between pump amps of their strong tank recirculation pump to viscosity. They allowed the firing temperature to be changed with respect to a change in viscosity. The result was that they reduced the thermal spikes associated with primary air port cracking that they had been experiencing and they were able to increase their solids back to their previous levels that they had achieved prior to their discovery of primary air port cracking (38). As a point of interest, a similar graph to Figure 15 was provided in a paper by Andritz at the ICRC in 2014 (39) and by Esa Vakkilainen in 2022 during a virtual session of a small group of papers originally intended for the 2020 ICRC (40). Additional information on this point of discussion is available in a paper by Porter entitled “Optimizing the Other Half of the Log, Using online measurements to understand the properties of black liquor” (41).

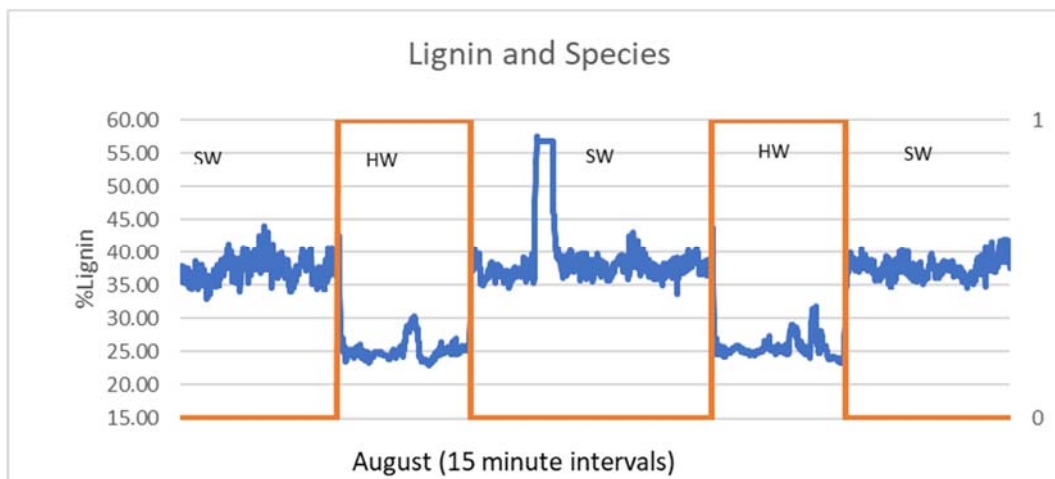


Figure 16: The % Lignin numbers of softwood and hardwood correlates fairly well with Fricke and Zaman’s numbers in “A Comprehensive Program to Develop Correlations for the Physical Properties for Kraft Black Liquor 1998.” (36)

The variability of lignin content between softwood (primarily jack pine and spruce) and hardwood (primarily aspen) is a major distinguishing difference between hardwood and softwood liquors. This difference in lignin could be able to track the progress in a change of species in the black liquor as it moves from the digester towards the recovery boiler. Combining it with viscosity, obtained either from online viscometers or through the observation of pump amps, one would further validate the location in the process of the changing liquor.

Recent work by FPIInnovations comparing FT-NIR and refractometer results for intermediate black liquor % solids is very encouraging. One of the hurdles for spectroscopy was to shine a light through very dark materials. It appears that with cell modifications, liquors in the range of 40 to 50% can now be scanned to provide good results of %solids. This means that lignin determinations in the 40 to 50% solids range can also be made available along with REA and inorganics and organics content. With measurements closer to the concentrators and recovery boiler the time lag between the digester and the recovery boiler will be reduced and time lags associated with the large tankage capacities of the weak tanks will be minimized. This in turn will allow for better predictive control, and a means to track liquor changes through the process. The major difference between softwood and hardwood liquors is the lignin content as shown in Figure 16. If we wish to track the process of the change of liquors based upon species, it makes sense to track the lignin content, which is the largest single variable between hardwood and softwood liquors. This would be an important predictor as to when to make changes to the operation of the evaporators and recovery boiler to reduce negative and costly upsets. More information on this concept is contained within Porter’s paper “What goes around comes around” presented at Peers 2014 (42). In this paper, it is shown how a change in lignin content at the digester, combined with a lack of recovery boiler operator response to the change led to a smelt run off, a potentially very dangerous situation due to controlled smelt flow entering the dissolving tank.

Summary

The majority of mills in the world have extensive data collection systems that incorporate measurements such as flows, temperature, pressure, and % solids. Some mills have online REA determination of black liquor obtained by auto titrators. Less than a handful of mills have online data such as lignin, and inorganic/organic content and viscosity. Although, there are approximately 90 installed FT-NIR systems installed around the world, the majority of them have been installed to improve the operation of the digester, the recausticizing plant, and/or the chemical plant. Fortunately, a significant amount of data has been collected from one mill that includes lignin, inorganic/organic content, REA,

and viscosity. Using this data numerous papers have been presented over the last 15 years that describe the potentials of improved operation by better understanding the parameters of black liquor and how these parameters impact the operation of the evaporators and the recovery boiler. In 1993 Rolf Ryham presented a paper entitled “Black Liquor, An Impossible Fuel” (43). Numerous researchers since that time have shown that there are narrow windows of REA that can lead to the lowest possible viscosity of black liquor and for the best recovery of black liquor soap. Significant research has been undertaken to develop better testing approaches to the compositions of this very difficult “impossible fuel”. Boiler vendors have done a remarkable job in making new boilers more efficient in every way. The use of FT-NIR spectroscopy has shown, through mill data, that a better understanding of the operation of the evaporators and the recovery boiler is possible with real measurements. This technology has been used in other industries to measure the octanes of fuel, the alcoholic content of beer, the freshness of food, and has been employed in the new James Webb telescope to look at the farthest reaches of the universe. Many years of mill data has shown the potential for new measured liquor parameters to provide the necessary information for kraft mills to move away from the descriptor of black liquor as an “impossible fuel”. These “real measurements” can be obtained through molecular spectroscopy, using the absorption features, which are then calibrated using the “best” available reference techniques provided by the researchers within the industry. They are fast, non-destructive, use no chemicals, and have little sample preparation. In the case of lignin, REA, % solids, inorganic and organic content, and soap, one sample can analyze them all at the same time.

The next step is for this information to be incorporated into an AI and/or a machine learning system to provide a new tool to operators to improve the operation of the Kraft liquor cycle. The recovery liquor system is a dynamic process and many of the problems that a mill encounters are due to the changing nature of black liquor. Real measurements of the changing properties of black liquor should allow dynamic modelling rather than static modelling. At some point, an operator should be able to say “Enki” (Sumerian god of knowledge and a name that isn’t commonly used) “When can I expect the hardwood liquor to arrive at the recovery boiler?”

“If you want to find the secrets of the Universe, think in terms of energy, frequency and vibration.”

Nicolai Tesla

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