

Understanding the Kraft Liquor Cycle: A need for online measurement and control

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ABSTRACT

The Kraft digester has two products – pulp and black liquor. Approximately 50% of the log that enters a Kraft mill goes to the Kraft recovery boiler as black liquor. The value of this black liquor varies with the value of oil and natural gas. At times of high oil prices the energy value of black liquor can rival that of pulp. Even at low oil prices however black liquor is a valuable “green” energy source that when optimized can determine the economic viability of the mill. Every dollar of energy savings associated with the efficient combustion of black liquor goes to the bottom line. There is a need for a more complete understanding of the black liquor going to the recovery boiler to allow for this optimization.

To optimize the Kraft pulping process, mills also need to more fully understand and control the green and white liquors of the Kraft liquor cycle, which directly impact on the quality and volume of the pulp exported from the mill. An important consideration in this control is to reduce a negative variation in one part of the cycle that results in downstream unit operations disturbances which in turn can create further variations, causing a downward spiral effect. Traditional manual testing procedures performed by the operators associated with the Kraft liquor cycle do not provide a full spectrum of the needed properties of the black, green and white liquors to optimize the cycle. The infrequency of the tests accompanied by time lags in the process do not allow for corrective actions to mitigate process upsets. In many cases operators respond to upset conditions without ever knowing the originating cause or possibly even induce upsets when acting on erroneous information. They simply state that “the liquor has changed.”

The FT-NIR (Fourier Transform-Near Infrared), a vibrational spectroscopy technique, is an optical measurement based on absorption of infrared light by chemical constituents in a sample. Its application as a process analyzer in the pulp and paper industry was developed by FPInnovations – Paprican in the early 90s and has been implemented in Kraft mills as fully automated and self calibrated process analysers since 1996. It has been proven to be accurate and precise with measurement frequency that far exceeds traditional testing. The maintenance required is minimal. It has allowed for the online determination of reduction efficiencies, effective alkali, sodium carbonate, sodium sulphate, sodium sulphide, and sodium thiosulphate in the green liquor and white liquor. It has allowed for on line residual effective alkali, lignin content and an organic/ inorganic content determination of the black liquor.

This paper will present actual online data from FT-NIR installations along with thoughts as to how this new knowledge can lead to new understandings which eventually will improve the control of the Kraft liquor cycle. Present participants in this exercise include: FPInnovations, the Institute of Paper Science and Technology and the University of Toronto.

INTRODUCTION

The Kraft digester has two products –pulp and black liquor. This is an important statement because it recognizes black liquor as a product of value rather than a waste product that has to be processed to allow the digester to produce pulp. When a process material is viewed as a waste then there is little incentive to know its properties. Without knowing the process material properties it is difficult to optimize the processing. As Lord Kelvin has stated that, “To measure is to know,” and, “If you cannot measure it you cannot improve it.” For years, operators of recovery boilers have been operating with a very incomplete knowledge of their fuel, black liquor. Typically they operate using % solids, firing temperature and gun pressure as their tools of control. If they run into problems such as a high bed, a smelt run off, and/or a poor liquor spray, their response is usually, “the liquor has changed.” They

do not know what has changed – they just know that the liquor is different and that their tools of control are not working.

The rest of the Kraft liquor cycle is also not fully understood or properly controlled. Automatic titrators, though somewhat limited due to presence of solids, has improved the control of the green and white liquor segment of the Kraft liquor cycle in mills where it has been applied but there are still chemical properties that are not measured. The autotitrator has not been successfully implemented for recovery dissolver tank green liquor analyses and is not able to provide liquor digester black liquor properties such as organic, inorganic, and solids content. Time lags are not fully appreciated so a recovery boiler operator may make a poor operating change to sampling information from the recausticizing department.

The FT-NIR (Fourier Transform-Near Infrared), a vibrational spectroscopy, is an optical measurement technique relying on fundamental absorptions of light by the chemical constituents in a sample. Its application as a process analyzer in the pulp and paper industry was developed by FPIInnovations – Paprican in the early 90s and has been implemented in Kraft mills as fully automated and self calibrated process analysers since 1996 with the first one being at mill in northern, ON, Canada. It has been proven to be accurate and precise with a measurement frequency that far exceeds traditional manual testing. The maintenance required is minimal.

In a mill in Ontario, two FT-NIR-based systems have been installed to analyze the liquors of the Kraft liquor cycle. Green liquor from the dissolving tank and, the green liquor stabilization tank are sampled in the recovery boiler area. Green liquor at the green liquor clarifier and slaker along with white liquor at the outlet of number one causticizers, the outlet of number two causticizers, the outlet of the pressure filter, and from the white liquor storage tanks are analyzed with a second cell and sampling station, connected to a common spectrometer via fibre optic cable,. Black liquor is analyzed at the digester with a third sampling station, measuring liquor properties at upper circulating zones, lower circulation zones, and extraction zones, and hopefully in the future from the evaporators. In total there are two separate FT-NIR spectrometers and 4 sampling stations. The information from all of these collection points is extensive. It includes the online determination of reduction efficiencies, effective alkali, sodium carbonate, sodium sulphate, sodium sulphide, and sodium thiosulphate in the green liquor. The white is measured for many of these same liquor parameters with the addition of causticizing efficiencies. The digester black liquor is tested for residual effective alkali, lignin content and an organic/ inorganic content. Much of this information has been provided to FPIInnovations, the University of Toronto and the IPST (Institute of Paper Science Technology) to further their particular explorations into better control of the Kraft liquor cycle. Process control strategy using these fundamental chemical signals has been developed for some of these areas and have shown to be extremely beneficial to mill operations. We are at the *beginning* of the maximization of the liquor cycle from an energy, quality and operation perspective.

This paper will describe some of the information and results acquired to date and some of the potentials of tomorrow. It will look at the “needs” of the Kraft liquor cycle and show how the FT-NIR technology, and potentially other process analyser, can satisfy these needs.

The Needs of the Kraft Liquor Cycle

Although the modern Kraft liquor cycle that includes the Tomlinson recovery boiler is roughly 80 years old [1], the properties of the liquors within the cycle are not fully understood and the information provided to the operators for control is limited. A recovery boiler operator does not know the BTU value of his fuel. He does not know the lignin content. He does not know the inorganic/organic ratio of the liquor. If he is supplied a REA (residual effective alkali) number it is usually from a manual test performed once or twice a shift. All of these liquor parameters have been shown by researchers to influence the viscosity or thermal characteristics of black liquor but the operator has little idea of what they are or if they are changing.

In order to optimize the recovery boiler from an efficiency, operations and environmental perspective, the operator needs consistent black liquor and stable properties. This consistent and stable liquor properties requirement follows through to the recausticizing department and to the Kraft digester. However the black liquor that the recovery boiler operator handles is not consistent and varies with wood species, age and season, along with other cooking conditions. The green liquor supplied to the recausticizing department is also not usually consistent. Upsets in the recovery boiler and/or poor TTA (Total Titratable Alkali) can influence the strength and quality of the green liquor

that the recausticizing department has to convert to white liquor. This usually results in operational issues in the recausticizing department that in turn generates a poor quality or low strength white liquor for the digester. The inconsistency of the cycle prevails. In order to work towards consistency there needs to be measurement and the measurement has to be reliable and frequent. Additionally, the data has to be integrated with feed-forward or feed-backward for better control. This requires the process analyser to be on line and automatic.

The Use of the FT-NIR Spectrometer as an on line Analyzer of Liquor Properties

The FT-NIR (Fourier Transform Near Infrared) technology has been discussed in numerous papers and the specifics are best left to the experts. From a layman's perspective, FT-NIR spectrometer is able to acquire spectra which are capable of providing both chemical identifications and quantification. Since different molecules absorb at different regions within the spectrum, multiple chemistry can be detected with the same spectral data. In Kraft liquor, spectral features can be assigned to EA (OH-band), sulfide (HS- band), carbonate (CO₃), as well as other features which are dependent on the sample matrix. As such, multi-constituents can be measured from the same spectrometer. Since one spectrometer can handle multiple detectors, multiple liquor streams can be utilized the same equipment. From an operations perspective it consists of a sampling station in the field (Figure 1) combined with a flow through cell (Figure 2). Fiber optics then transmits the incident light from the spectrometer, through the fibre optic cable, through the cell, and back to the spectrometer located in a rack room or MCC room. A computer, with the aid of PLC and DCS to manipulate valves, records and processes the spectral data predicts the liquor properties, using a pre-determined calibration model and send this information to the control rooms. A schematic of the recovery boiler and the recausticizing installation in Northern Ontario is provided in Figure 3.



Figure 1: Sampling station



Figure 2: FT-NIR Cell

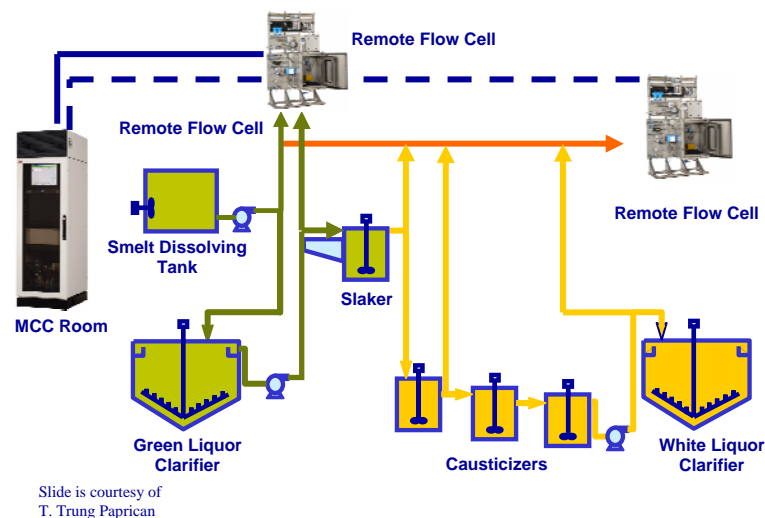


Figure 3: FT-NIR Schematic Arrangement

The Value of Black Liquor

Although there are potential gains with a better understanding of the properties for all liquors associated with the Kraft liquor cycle, the largest gains are probably associated with the black liquor sector of the cycle. For this reason the majority of this paper will deal with the black liquor portion of the cycle. It is also the least previously discussed.

When a log enters a Kraft mill approximately one half of the log finds its way to the recovery boiler as a mixture of organic components which has been liberated from the wood and the inorganic component associated with the liquor. This point has been reiterated to stress the magnitude of the value of black liquor. The organics contained within black liquor are the principal energy source of a Kraft mill. In a world of fluctuating energy prices the energy from black liquor can rival the value of pulp. In an article by Rolf Ryham in 2001, he states that the hourly energy value of black liquor for the world was \$1.6 million dollars based upon an equivalent energy value of 52,300 barrels of oil. The world hourly value of pulp in 2001 was stated as being \$8.5 million [2]. In 2001 the selling price for oil was \$30 a barrel. In 2008, oil reached \$147 a barrel. If the value of black liquor is extrapolated from this high value of oil then the black liquor in June 2008 had a world value of over \$7 million an hour. Looking at the energy value of black liquor from an individual mill and natural gas perspective, a 3.5 million lb black liquor solids recovery boiler would have a steaming rate of approximately 550,000 lbs of steam per hour. If this quantity of steam were obtained by burning natural gas the daily cost would be \$150,000 a day at \$8.00 a GJ or \$75,000 a day at \$4.00 a GJ (author's calculations). Like oil, natural gas has been extremely variable over the last few years.

What makes the energy from black liquor even more valuable is that it is considered to be “green” energy. Black liquor is one of the original biofuels. No matter what the price of oil happens to be it is environmentally responsible to maximize the energy from black liquor.

For many years it has been acknowledged that firing at higher solids will improve the thermal efficiency of the recovery boiler. This is simply due to the fact that every lb. of water entering the furnace has to have energy applied to it so it will evaporate and pass through the boiler and out the stack as a vapour and unfortunately as heat lost. The following graph in Figure 4 (courtesy of FPIInnovations - Paprican) shows the increase in thermal efficiency as water is eliminated from black liquor and % solids are increased. It has been modified to show the potential savings of a 3.5 million lb boiler with a 5% increase in solids. It should be noted that this savings is solely based upon the energy released to the stack.

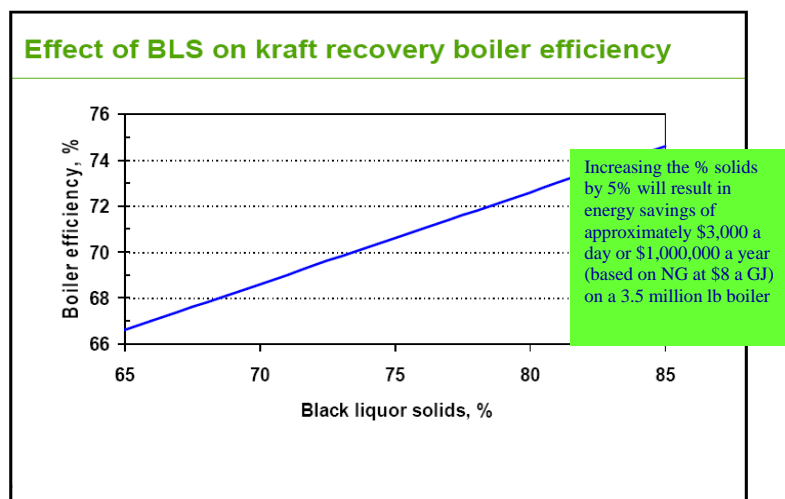


Figure 4: The Impact of % Solids on Thermal Efficiency

There are operating issues however when operating at high solids. Over 72% solids black liquor viscosity starts to increase quite dramatically as shown by the following slide in Figure 5. The operator is operating on the steep slope of the viscosity curve in order to achieve a higher thermal efficiency from the boiler. If the viscosity becomes too

great as determined by the black liquor spray or the bed formation the operator will add temperature. The temperature line of 257 degrees can reach 263 or even 265 degrees for viscosity control. If liquor conditions then change (species, % solids etc.) and the viscosity drops the operator has to react and lower the firing temperature. If the liquor temperature is not lowered, the result will typically be a finer spray, higher carryover, burning out of the bed, and possibly a smelt run off.

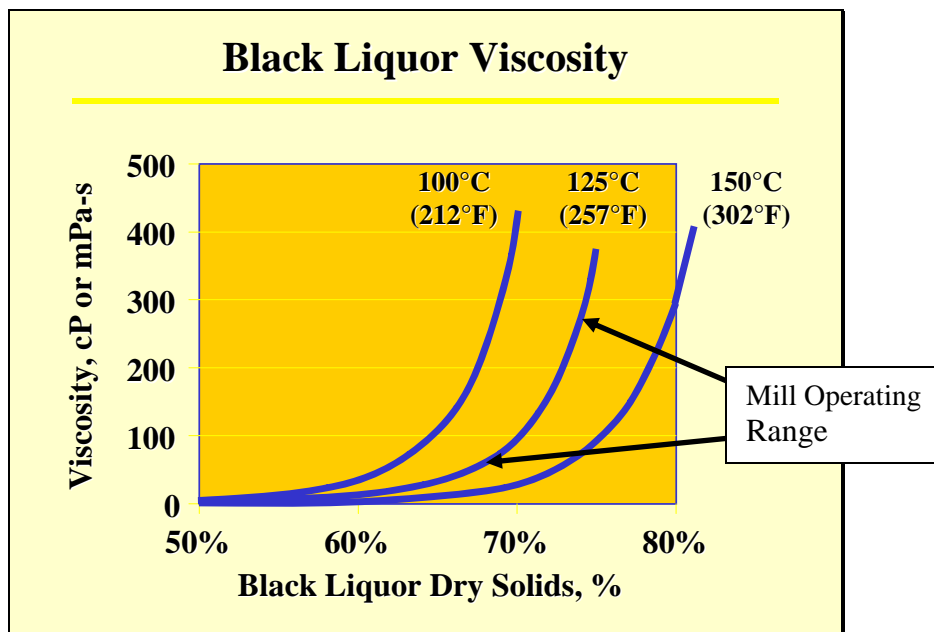


Figure 5: Original slide is from Terry Adams and Richard Marr- It was modified to show a mill operating range of % solids over 6 months

Conversely, other changes in the liquor can increase the viscosity of the liquor over and above the impact of operating at higher solids. The operator may not be able to counter these viscosity changes by increasing firing temperature and he will probably lower the % solids. In most instances this operating change is left far longer than the conditions warrant and thermal efficiency is lost. Liquor changes that can increase viscosity include: a variation in REA (residual effective alkali), a change in lignin content, and/or a change in the inorganic/organic ratio. All of these components can be measured with the FT-NIR. The majority of mills would only know their lignin content or inorganic/organic content from isolated liquor tests that have been sent to an external lab. REA is usually determined by manual titration tests a few times a day. Yet at times of digester or recausticizing upset these liquor properties can have a dramatic impact on recovery boiler operation.

High mass molar lignin has been suggested by numerous researchers to be a cause of higher viscosity liquor, particularly in softwood liquor [3-5]. The FT-NIR in the Northern Ontario mill has been configured to measure lignin in weak black liquor as shown in Figure 6.

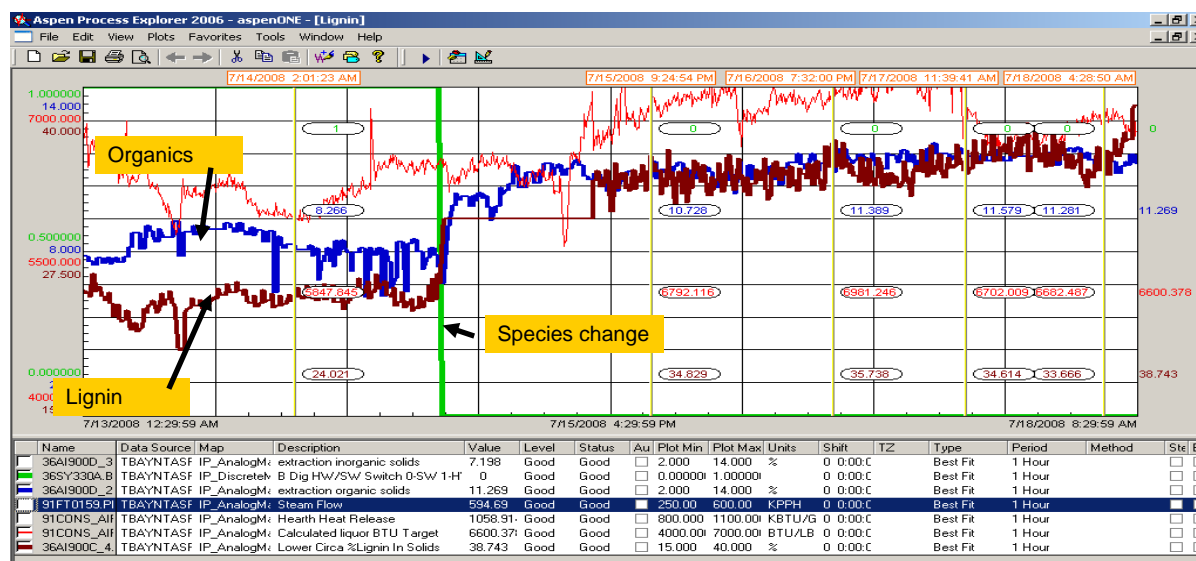


Figure 6: Graph from Mill Data Showing Lignin Change with Species Change

Fricke states that softwood liquor contains 35% to 44 % lignin [6]. As can be seen in Figure 6, there is a rough agreement to these numbers from a real time, online perspective. Other lignin numbers obtained from the FT-NIR and supplied through the mill's Aspen system shows lignin content as high as 50%. It can also be seen from the graph that hardwood has less lignin than softwood. This is again in agreement with Fricke's lab results.

Fricke also states in "A Comprehensive Program to Develop Correlations for the Physical Properties of Kraft Black Liquors" that 23.1% to 29.9% of total liquor solids is high mass molar lignin and that high mass molar lignin is the lignin that can be precipitated with acid [7].

Lignin precipitation using CO₂ is now a commercial process with Lignoboost. The lignin product is being considered for alternate energy uses, a binder for wood pellets and for use as an animal feed. Lignin is also being looked at as a replacement for carbon black in tires by Goodyear, Lakehead University and AbitibiBowater. With the ability to measure lignin on-line, a next step might be to control the content to manipulate the viscosity and thermal properties of the liquor to desirable targets. Difficult liquor such as that from Eucalyptus pulping might benefit from improved viscosity control with an approach such as this because of their high lignin content. The lower molecular weight of the lignin however might make precipitation more difficult [8]. Information on lignin content and other liquor properties could also be used to offload recovery boilers that are operating above their design capacity.

REA (residual effective alkali) has been shown to have an impact on black liquor viscosity. Too little REA can result in a steep viscosity rise while too much REA can also result in increased viscosities. Figure 7 (courtesy of FPInnovations – Paprican) shows the effect of REA for a given solids content liquor.

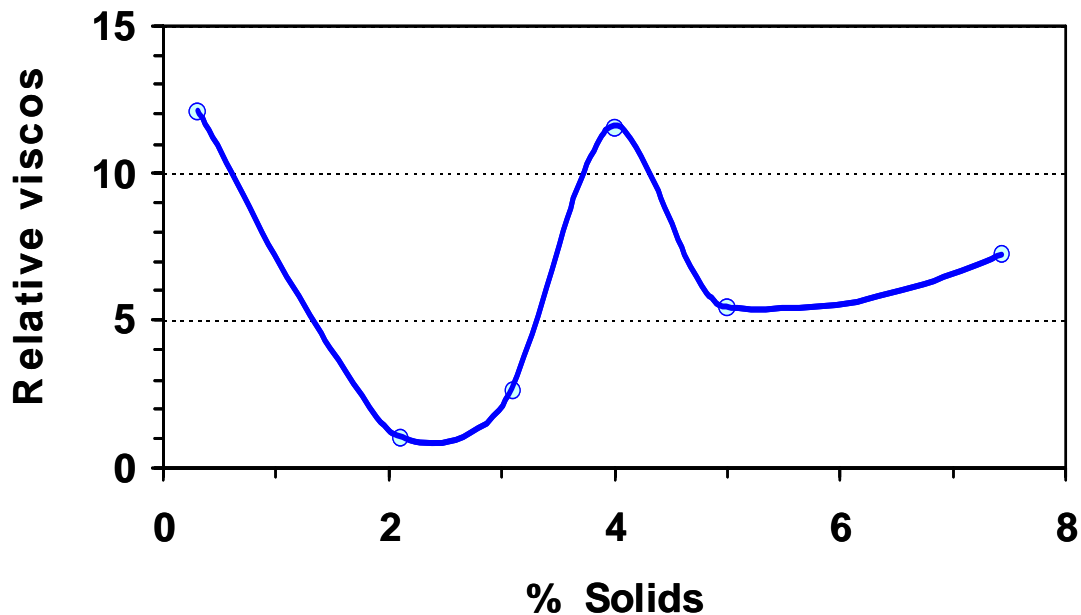


Figure 7: Graph from FPInnovations showing Relationship between REA and Viscosity

Currently, black liquor REAs are available on weak black liquor from the described mill system. The intent was to also have REAs from intermediate and strong black liquors to allow for timely information on the decline of this important liquor property process due to hot storage or various acid additions as the liquor moves from the digester extraction to the liquor guns of the recovery boiler [9]. However, a difficulty with the ability of the light source to see through the liquor at higher solids has prevented this from happening to date. Work is continuing on this by FPInnovations - Paprican.

REA is also important in that it can impact the soap content and hence the BTU of the “as fired” liquor. Foran, in a presentation at a TAPPI Recovery boiler short, has stated that REA has a marked effect on the minimum solubility of soap in black liquor. For good soap recovery the REA should be kept above 6 g/l in 17-20% solids liquor [10]. The author further shows that there appears to be an optimum window for REA to achieve good soap recovery just as there is for viscosity control. However, most mills do not monitor REA for this purpose. If mills use the TAPPI rather than the SCAN method for REA determination in black liquor, they are likely to not even have an accurate measurement of REA from the manual tests that are performed [11].

Evaporator performance is also impacted by soap. Reliable online measurement of REA could enable consistent soap solubility; this would address and improve one of the variables of evaporator performance. This is of particular importance in evaporator sets that have falling film units encountering low solids liquor and are prone to foaming.

Another need of evaporators and concentrators is to know the critical solids of burkeite and dicarbonate which are both recognized fouling double salt compounds of sodium carbonate and sodium sulfate. They differ only in their percentage makeup. Burkeite is sulfate rich while dicarbonate is carbonate rich [12]. Burkeite is difficult to handle in long tube rising film evaporators but can be controlled by staying under the critical solids of burkeite [13]. However, if the % solids target selected for operating the multiple effect evaporators is too low then a penalty will be paid in evaporator efficiency. This is due to the fact that any solids increase not picked up in the multiple effect evaporators with a steam economy of approximately 5 to 1 will have to be picked up in a set of concentrators with a steam economy of around 1.8 to 1 [14].

The Institute of Paper Science Technology is a recognized leader in this type of evaporator fouling. Mill data from both FT-NIR spectrometers has been provided to IPST to attempt to gain a better understanding of the mechanism from a real time perspective. Online causticizing efficiency, reduction efficiency and the inorganic/organic content of black liquor provide new information to help better understand the dynamics of crystallization and fouling. The capacity of the FT-NIR to determine inorganic/organic ratio is shown in Figure 8. The organic content changes with the species change while the inorganic content stays relatively the same. The viscosity of the liquor increases with the higher organic content. The ultimate goal is to create a control strategy in which crystallization occurs in the most optimum part of the process and not on the evaporator or concentrator heat transfer surfaces. An online critical solids determination calculation would be advantageous to an operator.

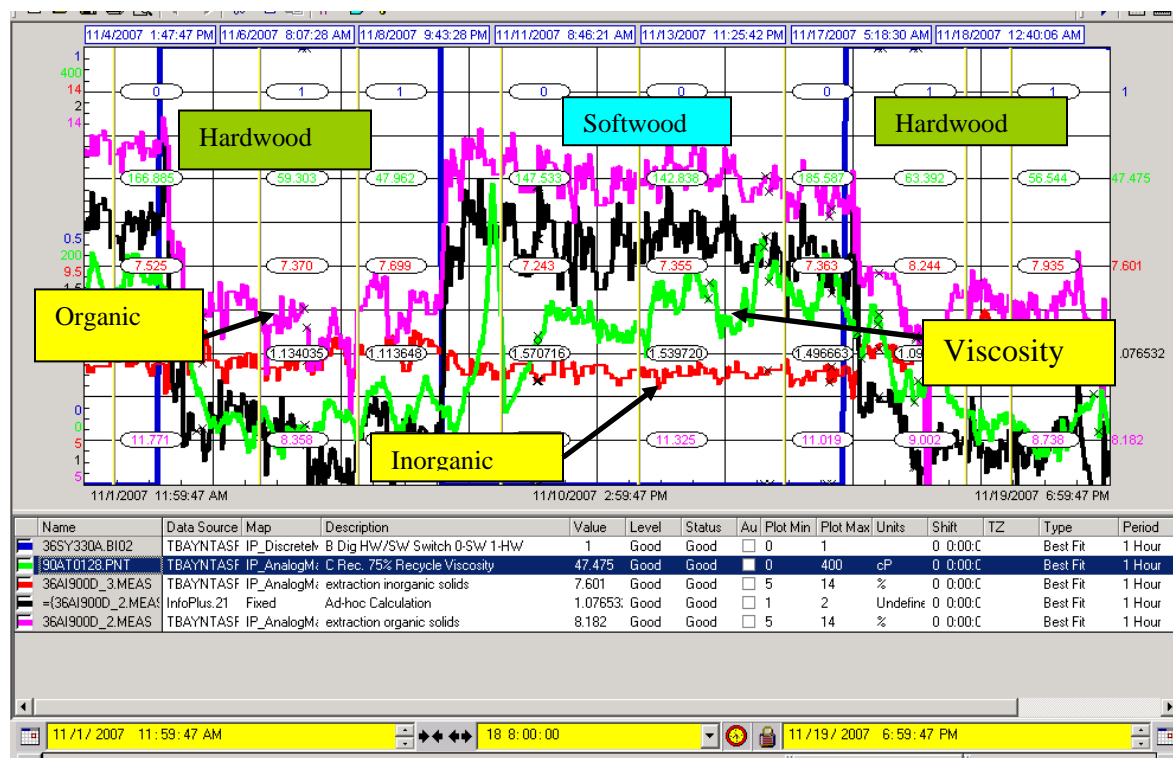


Figure 8: Mill graph showing organic and inorganic content of liquor with species change

Green Liquor Control

Dissolving tank control begins with the operation of the recovery boiler and more specifically the liquor spray that enters into the boiler. If a boiler operator has used firing temperature to control the spray of fairly viscous softwood liquor at reasonably high solids and there is a species change to hardwood then there is a need to drop the firing temperature to correspond with lower viscosity liquor. A failure to do so can result in bed burn out and a smelt runoff as shown in Figure 9. High smelt run off definitely impacts dissolving tank control and has even been linked to dissolver tank explosions by Grace [15]. However, there is a significant time lag between the digester and the recovery boiler. Depending upon tank size, inventory and boiler operating rate this can easily be 10 or 12 hours. Without online measurements operators sometimes do not make the correct operating changes to counter changes in liquor properties.



Figure 9: Mill graph showing operating conditions that led to a smelt run off

The typical dissolving tank control is based upon the density of the liquor. By controlling the density the operator also controls the TTA (Total Titratable Alkali). Although they are not the same the two properties usually track one another quite well. Figure 10 shows one of the earliest indications of how well the FT-NIT determines the TTA of green liquor.

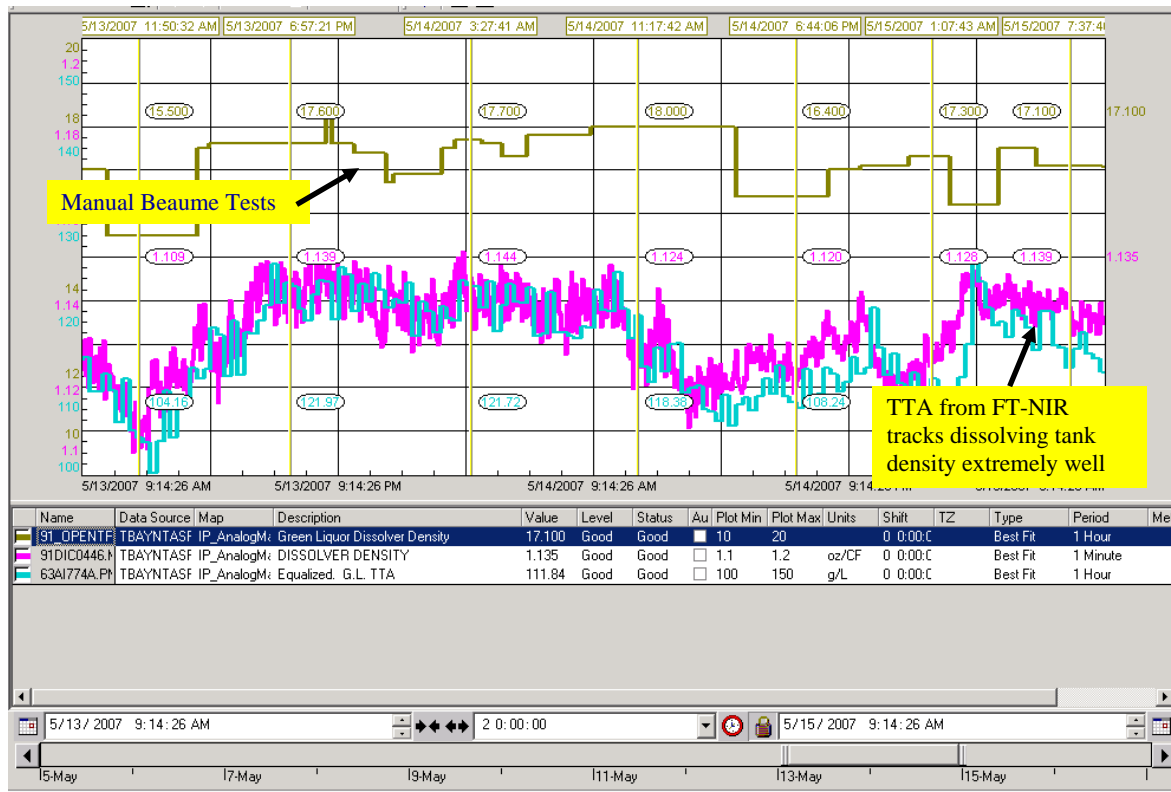


Figure 10: Mill graph showing the correlation between density and TTA (supplied by FT-NIR)

The manual beaume tests are sporadic and only provide a general determination of this important property. In contrast the TTA derived from the FT-NIR tracks the dissolving tank density very well. Both appear to be good means of density control. However, at times the density measurement will drift due to pirssonite formation. During instances when this occurs, the green liquor control is compromised, as shown in Figure 11. The swings in the process are still observed, but the absolute match is no longer observed.

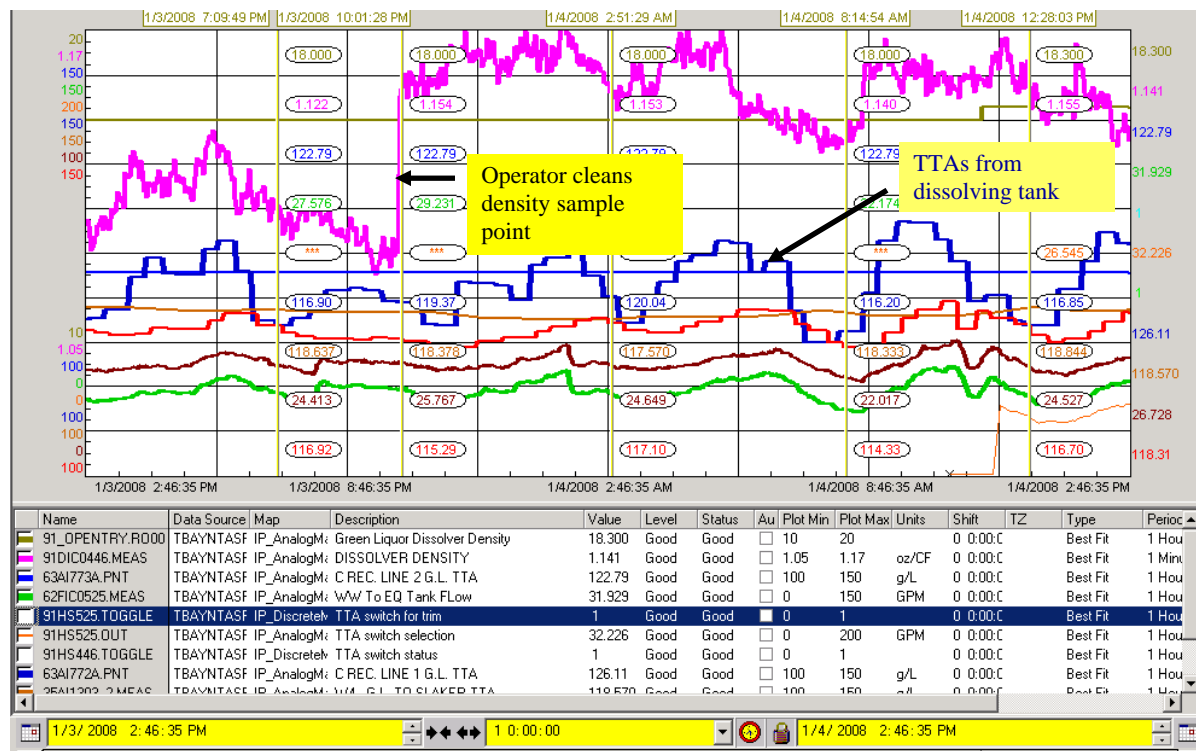


Figure 11: Mill graph showing a density drift as the sample point became plugged with presumably pirssonite

Reduction efficiency of green liquor is another important property that is measured by mills but on an infrequent basis. Poor reduction efficiency can increase the dead load of the liquor cycle. Chandra and Empie have suggested that the black liquor heating value of black liquor can be increased by 1.1% by reducing the inorganic content of black liquor by reducing the dead load associated with poor reduction efficiency and poor causticizing efficiency. [16] Figure 12 shows how an air change impacts the reduction efficiency. If reduction efficiency is only taken once or twice a week the operator has very little feedback on how boiler operation changes impact this liquor parameter. The FT-NIR also has the ability to measure thiosulphate, which is a difficult test for mill operations. There is a thought that thiosulphate should be made a part of the reduction efficiency calculation in that it is the sulphide that is required for efficient digester operation.

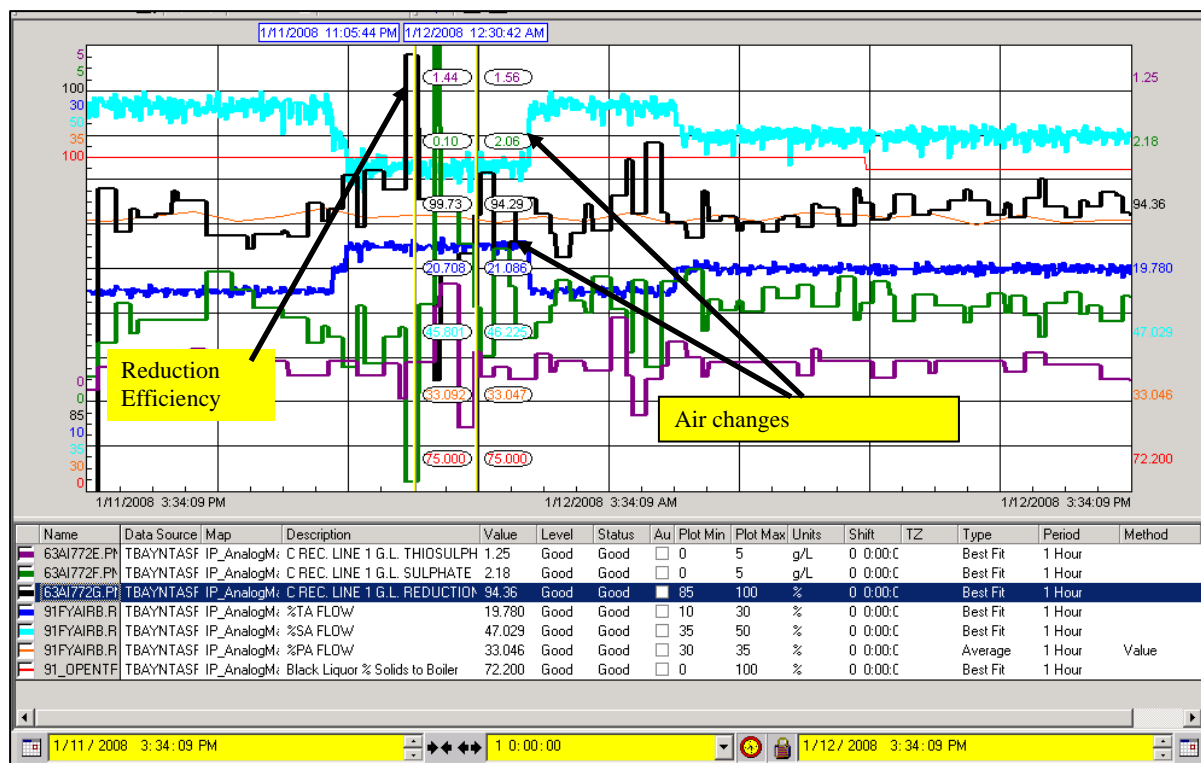


Figure 12: Mill Graph showing how recovery boiler operating changes can impact reduction efficiency

The original FT-NIR spectrometer installed in the Northern Ontario mill was installed in 1996 for the primary purpose of creating better white liquor for the digester. This FT-NIR spectrometer was replaced in the last couple of years with a new unit. Recent reports from the mill indicate that the consistency of the white liquor to the digester has greatly improved. This is in all probability due to the fact that the entire cycle is now being examined with a greater consistency. Operators of the recovery boiler and the recausticizing department are receiving feedback from their operational changes. The result is an improvement in their area of operation and a more consistent liquor to be sent to the next department. The old adage “What goes around comes around” is totally true for the Kraft liquor cycle. To better manage the liquor cycle all parts of the cycle have to be understood and controlled. The FT-NIR has allowed a reliable, maintenance friendly, online measurement of the recognized important liquor parameters to be controlled. Perhaps more importantly it has allowed for the measurement of new parameters such as lignin, inorganic/organic ratio, REA, and thiosulphate. As we start to understand how these liquor parameters impact operations an even better control of the cycle is possible. As Lord Kelvin stated, “If you cannot measure it you cannot improve it”. After almost 80 years of operation the Kraft liquor cycle has new and reliable on line measurements of important liquor parameters. The FT-NIR technology has made this possible. We now have the potential to improve the Kraft liquor cycle.

References

1. Kitto J.B., and Stulz S.C., "Steam, its generation and use" Babcock and Wilcox, edition 41 2005. 28-10.
2. Ryham, B.C., "Black Liquor a Man- Made Fuel", 2001 International Chemical Recovery Conference. P.449
3. Zaman A., and Fricke A., "Effects of pulping conditions and black liquor on viscosity of softwood kraft black liquors: predictive models" Tappi Journal October 1995. p. 117
4. Soderhjelm L., "Viscosity of strong black liquor "Paperji ja Puu-Papper och Tra 9/1986. p 652
5. Louhelainen, J., Alen, R., and Zielinski, J., "Effects of Oxidative and Non-Oxidative Thermal Treatment of the Viscosity and Chemical Composition of softwood Kraft Black Liquor" ,Journal of Pulp and Paper science: Vol 28 No.9 September 2002 p.290
6. Fricke A., and Zaman A., "A Comprehensive Program to Develop Correlations for the Physical Properties for Kraft Black Liquor" - Final Report May 1998 p 110.
7. Fricke A., and Zaman A., "A Comprehensive Program to Develop Correlations for the Physical Properties for Kraft Black Liquor" - Final Report May 1998 p 59.
8. Goncalves,C., Cardoso, M., "Analysis of Composition Characteristics of "Kraft" Black Liquor From Brazilian Pulp and Paper Industries" unknown.
9. Grbich, M., and Porter, J. "New Information on How Process affects Black liquor – a residual effective alkali profile from the digester to the recovery boiler" 1999 presentation at the Midwest Branch of Paptac
10. Foran C.D. , "Tall Oil Soap Recovery" 2006 Kraft Recovery Operation Short Course. 3.7-5
11. Porter J., Maki K., and Dokis R., "REA and Recovery Boiler Operations: (The "other" liquor parameter)"2004 International Chemical Recovery Conference.
12. Soemardji, A.P. ,Verril,C., Frederick, W.J., and Theliander,H., "Predictions of crystal species transitions in aqueous solutions of Na_2CO_3 and Na_2SO_4 and kraft black liquor"Vol.3:No.11p.27
13. Adams T.N., "Sodium Salt Scaling in Black Liquor Evaporators and Concentrators" Tappi Journal June 2001 p.3
14. Marr R.Y., Adams T.N., "Black Liquor Evaporator Basics" 1994 Kraft Recovery Boiler Short Course 3.1-13-14
15. Grace,T., Tran H., "Dissolving Tank Issues and Research Needs" presented at University of Toronto 2008 Annual Research Review Meeting
16. Chandra,Y., Empie,H.J., "Impact of deadload reduction in the kraft chemical recovery system" Tappi Journal June 2007 p.24