

I. Introduction

Understanding black liquor rheology is very important to the pulping industry.

Combustion of black liquor is more efficient at higher solids contents due to the lower evaporation duty. However, the viscosity also increases dramatically with solids content as shown by numerous investigators and in Chapter 3 of *Kraft Recovery Boilers* (Frederick, 1997). The rheology of black liquor determines many important aspects including droplet size and formation, as well as drying characteristics and swelling characteristics during firing in the recovery boiler. In a mill, control of solids, viscosity and temperature are all extremely important. At the higher solids concentrations that are more efficient for burning, the liquor is quite unstable and can form a gel or even solidify with temperature decreases. This leads to hazardous clean-up and high costs.

Temperature is thus a very important control parameter. Another control parameter is alkali content. Several theories have been proposed for this control mechanism. One idea is that the lignin molecules should be seen as long chain polymers. On a macroscopic scale one could visualize these chains as strings of spaghetti. When alkali is present, these spaghetti strings ball up into tight coils (more like pasta shells) allowing them to move past each other since there are fewer interactions. Without the alkali, the negative charges on the chain repel each other, opening the chain. However, if too much alkali is present the chain reaches a minimum coil diameter with a maximum charge density. At this point the repulsion is no longer important and the molecule relaxes. When this occurs the effect is lost and the viscosity increases again. While this is a very nice picture, little research has been done to support it. The big question is what is the

right alkali level to maintain. Lowering the viscosity slightly should save money in pumping costs and potentially permit higher solids concentrations for firing, improving combustion.

Most mills maintain some level of residual alkali in their black liquor. The mill liquors used in these studies were from kraft mills using softwood (primarily Douglas Fir) for bleached or unbleached kraft. All three liquors showed an initial EA_r of 3-3.5 wt%. This means that this weight percent of sodium hydroxide is present in the black liquor on a dry basis. This study will seek to determine if this is an acceptable/desirable level to maintain, or if there might be some benefit to supplementing the residual alkali by adding caustic to the liquor. This study will also seek to determine if there are any obvious firing effects through the use of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). These two instruments are well regarded in a variety of industries for sample characterization.

II. Procedures and Methodology

Theory of Rheology

Rheology is defined as the study of the deformation of matter in response to an imposed stress. To test the viscosity of the black liquor, a rheometer was used. The theory behind a rheometer is quite simple. The black liquor sample is analyzed under the desired temperature conditions by applying a steady shear rate and measuring the stress generated. In the Couette (Cup and Bob) Geometry chosen for this study, the shear rate,

$\dot{\gamma}$, is chosen in the software package by the user. The rheometer then measures the stress, σ , using a torque gauge (producing measurement τ). Using the equipment chosen, the Bohlein CS Rheometer with v. 4.90 software or the Rheometrics RFR-7800, all of the calculations are transparent, and the computer generates viscosity, η , data using equations 1, 2, and 3.

$$\dot{\gamma} = \frac{2\omega_o R_o^2}{R_o^2 - R_i^2} \quad \text{Eqn. 1}$$

$$\sigma = \frac{\tau}{2\pi L R_i^2} \quad \text{Eqn. 2}$$

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad \text{Eqn. 3}$$

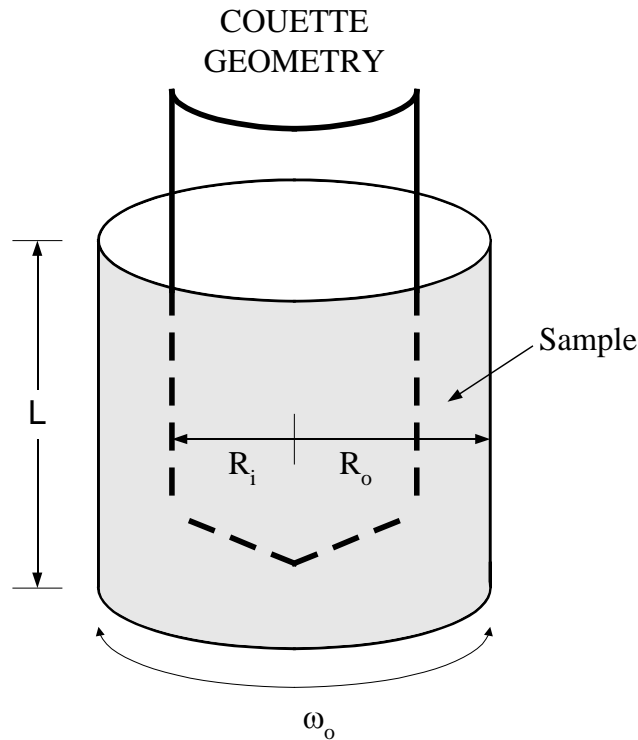


Figure 1: Couette Geometry for Rheometry
Relevance of Rheology to this Study

The rheometers used in this study provide the best data possible for the viscosity of the black liquor samples. Rheology is well regarded in all industries for the characterization of materials properties. The viscosity data may seem rather simple compared to the capabilities of the equipment, but this is the most important data since viscosity increases due to caustic addition will be counter productive to the mill. Any viscosity increase will lead to higher pumping costs as well as a greater likelihood of gelling. The opposite is true for a viscosity decrease. Due to this importance of viscosity to the black liquor and the ease of analysis using the rheometer, this equipment is most useful in a study of this nature.

Application of Rheology to this Study

Mill samples A and B (room temperature) were analyzed on a Rheometrics Fluids Rheometer (RFR-7800). The Couette (Cup and Bob) Geometry was used.

Approximately 30-ml of sample were used for each test. Before each test, the sample was gently stirred for uniformity. A syringe was used to draw a uniform sample and add it to the cup. The bob was lowered and the cup was rotated. The torque transducer measurement attached to the bob was used to calculate a viscosity by the system software. These samples were run at room temperature due to their low solids and correspondingly lower viscosities. Back to back runs were performed on each sample for comparison.

Mill sample C was run on a Bohlein CS Rheometer using software package v. 4.90. The Couette Geometry was again used for the experiment. However, only a 14-ml sample was necessary due to the precision of the instrument and size of the geometry. This instrument was used due to a new software package that became available (CS 4.90) which allowed for reproducible steady shear rate experimentation. The instrument also simplified temperature control (an extremely important parameter at elevated temperatures). Due to the elevated temperature and the likelihood of evaporation, a thin layer of DOW-Corning 710 fluid was applied to the surface to prevent evaporation. On a low solids sample run at room temperature, there was no indication of a viscosity change when the sample was left overnight in this condition. This indicates that the oil effectively prevented evaporation. Back to back runs were performed on each sample for comparison.

Differential Scanning Calorimetry Theory

Differential Scanning Calorimetry (DSC) is a widely accepted method for analyzing heating and cooling characteristics of substances. The DSC operates on a simple energy comparison. The equipment compares the energy required to raise the sample to a set temperature to the energy required to raise a blank pan to the same temperature. This difference is represented on a graph (see Figure 11 for an example). In this case, exothermic events require less energy than the blank sample and correspond to positive deviations on the graph. Events requiring energy, evaporation for example, shows strong

negative peaks since for an identical temperature change the sample requires more energy.

Relevance of DSC to this Study

DSC is an outstanding tool to use for observing the physical and chemical changes of a substance as the temperature is increased. In this study DSC provides excellent sample characterization. The DSC can provide important data on black liquor behavior as more caustic is added to the liquor. The data generated about heating effects is easily obtained from the DSC, and vital to the mill's operation. Mill's that are recovery boiler limited will be concerned about any impact, positive or negative, that caustic addition will have on firing of the liquor.

Application of DSC to this Study

By observing the DSC graph and recognizing where peaks are occurring at, the sample can be better characterized. For the project at hand this means indications of the effects of greater NaOH concentrations on the behavior of the liquor. Specifically, this project is looking for evaporative effects, but also of importance are the overall effects later on in the system. The reason non-evaporative effects are of interest is due to their effect on firing efficiency. DSC will provide useful data showing where thermal events occur. These events might include thermal decomposition, combustion and many others that are important for efficient recovery boiler operation. Several papers have been written

covering the application of DSC and its closely related cousin DTA (Differential Thermal Analysis where temperature differences are measured). Individual samples were taken from the center (presumably the most homogeneous sample point), weighed and then loaded in the DSC where computer software performed the testing on a TA Instruments DSC 2920 Modulated DSC.

Thermogravimetric Analysis Theory

The Thermogravimetric Analysis (TGA) is another widely accepted method of material characterization. In the TGA, after the sample is massed, and the temperature is slowly raised while the mass is measured. TGA gives a good indication of how the liquor behaves as a function of temperatures above its boiling point. TGA takes highly accurate masses giving an excellent indication of temperatures where events occur. By applying a software package, subtle slope changes can also be analyzed.

Relevance of TGA to this Study

Thermogravimetric Analysis is extremely useful as a tool to determine what is happening to the mass of a sample as the temperature is changed. By observing both the weight % curve and the derivative with temperature of this curve ($\delta \text{ wt \%} / \delta T$) the subtle changes of water evaporation and hydrocarbon breakdown can be observed. While DSC observes the heating requirements, TGA strictly looks at the mass decrease.

Application of TGA to this Study

In this project TGA will be used to compare four different points on the Weight % curve. Of interest is the wt % at which the greatest slope in the drying region is observed, this occurs at a lower temperature than each of the other interest points. The next point of interest is the radical slope change at the point where evaporation is complete. This point should correspond nicely with the liquor % solids, although due to some apparent hydrocarbon breakdown, this point may be slightly off. The third point of interest is the slope change when the majority of hydrocarbon breakdown (or combustion in an oxygen rich environment occurs). This is well documented in various sources and observed by Kubes et al. for spent kraft liquor as between 260 and 375°C (Kubes et al., 1982) For the purposes of data observation and comparison, the greatest slope in the region has been chosen to represent this point. The last point of interest is where the majority of hydrocarbons are gone and only ash remains. This last point will be chosen as the slope closest to zero. This point typically occurs on the TGA graphs between 500-500°C. These points can then be analyzed to determine if any correlation exists that might be best explained by caustic addition to the liquors. The TA Instruments Modulated TGA 2950 Thermogravimetric Analyzer used in this study requires the user to load a balance pan for tare weight, and then a tiny sample at which point the equipment weighs the sample and then begins to steadily increase the temperature while continuously weighing the sample.

Liquor Preparation and Analysis

The liquors were sampled, and tests run either in the lab at Oregon State University or by titration equipment at the mill to determine the liquor density, EA_r , and % solids. The tests run at Oregon State University were done using TAPPI Standard Methods T 625 cm-85 and T 650 om-89. All of the liquor specific gravity's were near 1.3-1.4. The Mill A and B samples were run at low solids concentrations, 49% and 41% respectively while Mill C was a high solids (71.5%) sample. All sample testing was run more than 24 hours after sampling, but all samples were kept sealed and maintained at room temperature for the duration of all testing except for brief initial heating for the 71.5% liquor sample run at elevated temperatures. Unfortunately due to mill policies, black liquor Kappa numbers were not provided.

In order to maintain the same percent total solids in the liquors while testing, the EA_r was increased by adding sodium hydroxide (NaOH), then the amount of water necessary to maintain the percent solids was also added. Based on the studies of Milanova and Dorris (1990), slight increases from the initial alkali residual were chosen. Once specific EA_r 's were chosen, individual calculations for the necessary water and NaOH to be added to each sample could be done.

Sample Repeatability and Error Analysis

Due to the complex nature of black liquor, sample error and difficulty in repeatability is naturally present. Several properties of the liquor are particularly troublesome. High Solids liquors have the tendency to absorb water from the air. This is most noticeable

when taking a small sample of a high solids liquor and allowing it to sit. It will develop a shiny gloss surface from this absorption in a few minutes. Similarly a low solids liquor will evaporate water leaving the surface a dull color and having a dry clotted appearance. Needless to say all of these have an impact on the sample repeatability and error.

Rheological Repeatability and Error

In the rheological studies sample temperature and solids content play a well documented role in the viscosity of the black liquor. So in order to truly evaluate the effect of the caustic addition these variables must be convincingly removed from the procedure. This is done as described above in the sample preparation portion by maintaining solids composition by adding the appropriate weight of solid sodium hydroxide and water to the sample and then heating the liquors in a sealed environment and mixing them well.

Temperature was controlled by a large temperature bath which was recycled through the rheometer. To analyze repeatability, two independent samples were taken from a Mill A, 66% solids black liquor and run at 100°C. each sample was run twice in an up/down manner where the shear rate is increased, then decreased. The results of this test are shown in Figure 2.

It is easy to see that the first run samples are not repeatable at least on the rate increase portion. However, the second run samples line up so well that they are nearly indistinguishable. There are several apparent reasons for the discrepancy. It should be noted that every single black liquor sample was run in a two run fashion (all of them for

the purposes of this study), showed this marked difference between the first run and the second run.

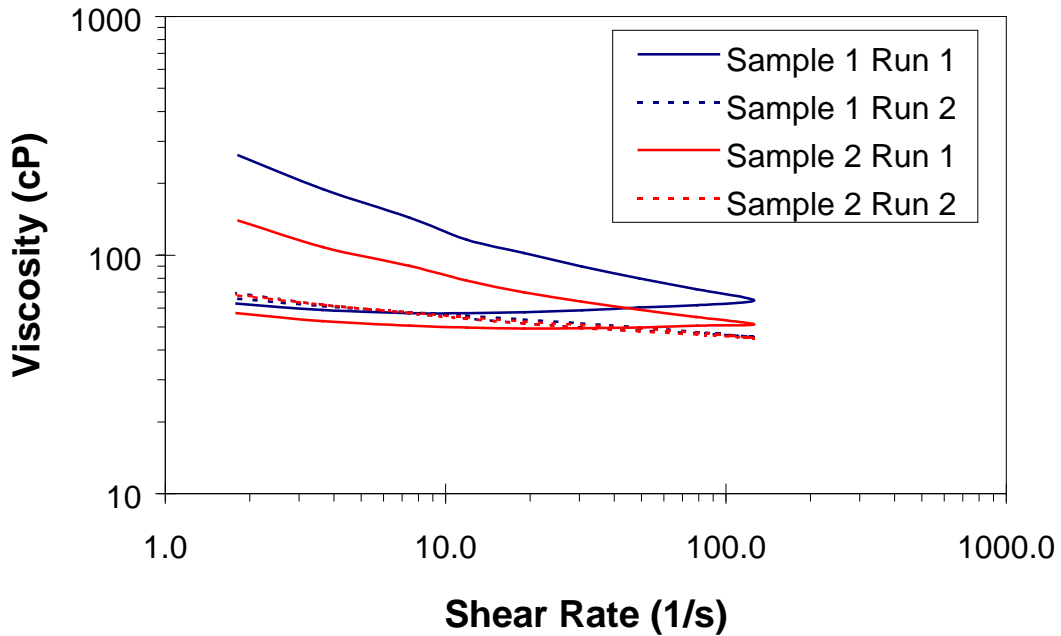


Figure 2: Mill A, 66% solids First and Second Run Repeatability at 100°C

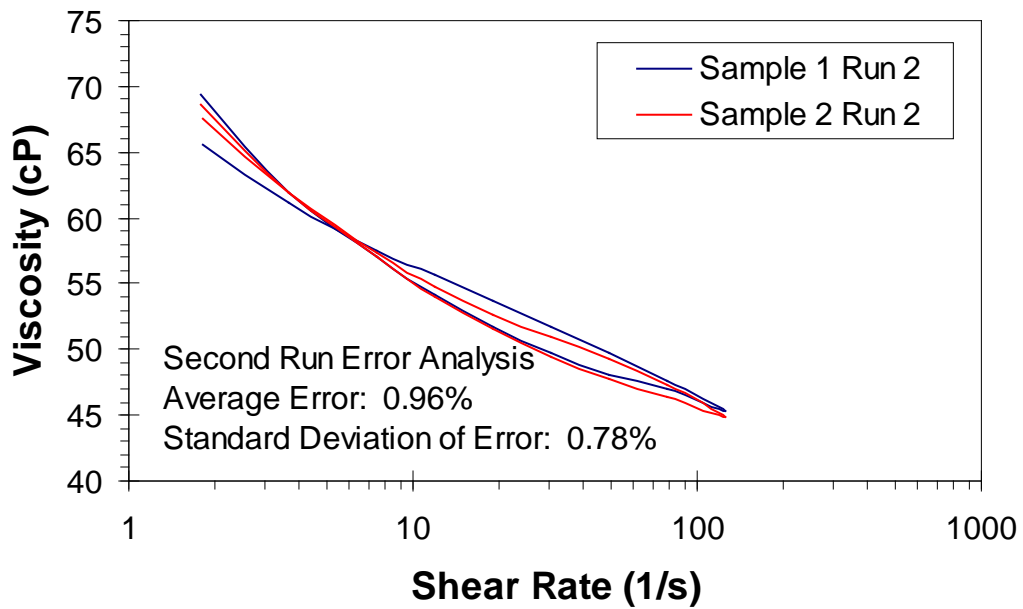


Figure 3: Mill A, 66% solids Second Run Repeatability at 100°C

Furthermore, while results for the first run were somewhat inconclusive, second run results show the effects distinctly. However, even though the graph shows that the results for the independent second run samples match up nicely, by expanding the scale in Figure 3, we can see that they are not perfect.

This leaves us to attempt to calculate their differences. Since the data points are easily comparable for the two curves, a simple Average and Difference method was applied to determine the error (Equation 4).

$$\% \text{Error} = \frac{(\text{Difference})}{(\text{Average})} \quad \text{Eqn. 4}$$

The average of this error for each point sampled produces an average % error of 0.96% with a standard deviation of 0.78%. This average error is under 1%, a very good result for black liquor. The implication of this is that the results obtained for the second run samples are quite reliable.

DSC Repeatability and Error

DSC repeatability is very difficult to accomplish. This is due to the small nature of the sample (5.0-5.6 mg). Since black liquor is such a complex mixture, any two tests of this small a sample will produce slightly different results. However, by looking for certain distinct peaks and valleys in the graph and smooth curves, the graph can be taken as reproducible. It is also important to note if any swelling has occurred which brings the

sample into contact with the surface of DSC cell. If this has occurred, then the sample should not be considered reproducible. For the purposes of an example, Figure 4 presents indications of a black liquor sample that represents reproducible data, and one that does not.

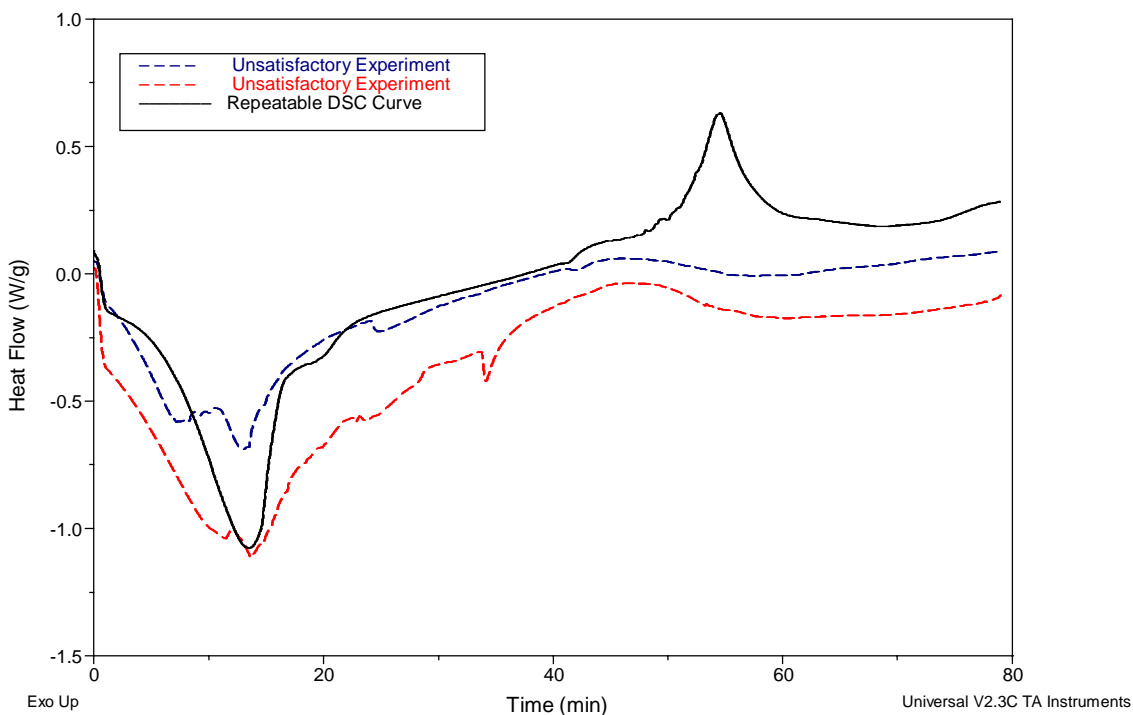


Figure 4: Mill C 71.5%, 6.0% EA_r, Reproducible and Non-Reproducible DSC

Note that the non-reproducible curve contains lots of sharp peaks and valleys at various points along the graph. This is a good indicator that the sample was not properly loaded, or unevenly balanced in the sample pan or some other problem that would lead to erroneous data. The data used in this study was reproducible to the limits of the equipment and the homogeneity of the sample.

TGA Repeatability and Error

The TGA by nature is more repeatable than the DSC. The TGA takes a sample of black liquor and simply heats it up recording the mass. It isn't looking at specific heating changes, only the increase of temperature as it corresponds to the sample mass. For this reason, if the sample taken is representative of the sample then the results should be very similar. Figure 5 presents two TGA curves and their corresponding derivative curves in order to compare and determine the repeatability.

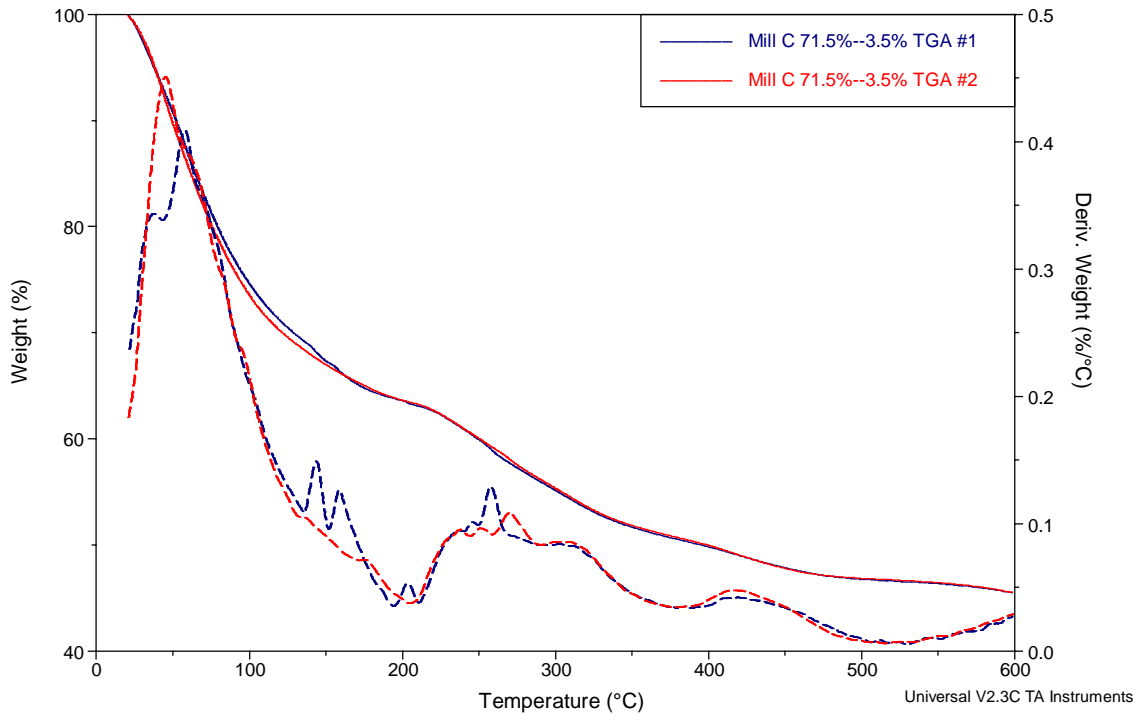


Figure 5: Mill C 71.5%, 6.0% EA_r, Reproducibility of TGA

The curves themselves are practically indistinguishable. However, when observing the derivative curves, slight differences in slopes can be observed. However, when looking at the four points of interest mentioned previously, all of these points are in very close

proximity for both samples. So, the TGA can also be pronounced reproducible and its data can be accepted as reliable.

III. Results

Rheological Results

All of the liquors show a shear thinning behavior (see Appendices A-C). At higher shear rates, they behave more Newtonian. They are also temperature thinning to a certain extent. At higher temperature, they show lower viscosities. Figure 6 shows the decreased viscosity with increasing residual alkali in the Mill A liquor. It also shows the characteristic viscosity decrease in the second run. Note that the bump in the middle shifts after the first run.

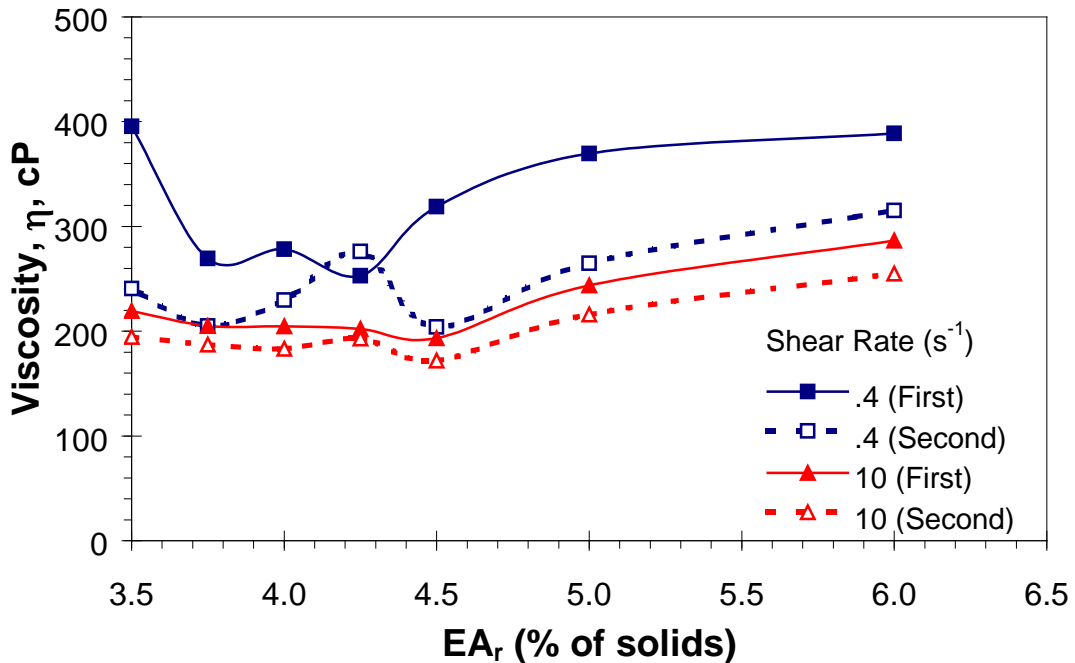


Figure 6: Mill A 49% Black Liquor Viscosity at Various EA_r at 27°C.

Also note that the viscosity begins to increase at higher EA_r . The data for the first run is not repeatable, but is presented in this case to show that the bump is not present due to a faulty sample, but is rather some property of the liquor as not yet understood.

Figure 7 shows the same decreased viscosity for the bleached kraft black liquor from Mill B. However, the increase at higher EA_r is not as evident. It is interesting to note that Mill B is the bleached kraft mill and might presumably be cooking to a higher Kappa number and so perhaps the effect is muted due to the difference in lignin breakdown unit size. It is possible that at a much higher EA_r , this sample would also show viscosity increases. However, over the practical range of achievable residuals, only a viscosity decline is observed.

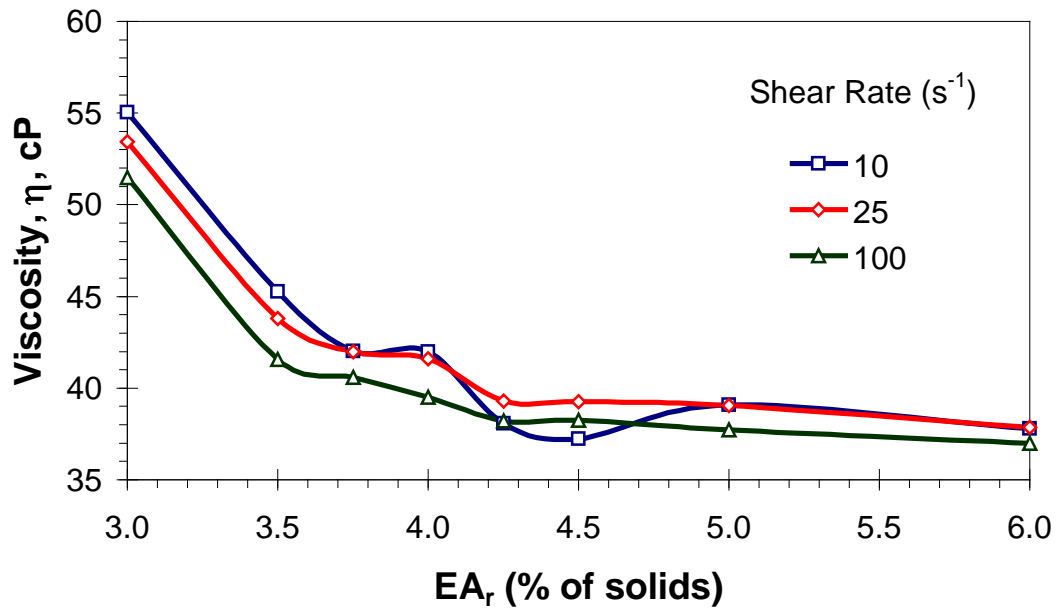


Figure 7: Mill B 41% Black Liquor Viscosity at Various EA_r at 27°C.

Figures 8 and 9 present the second run Mill C high solids data at elevated temperatures. It is notable that the viscosity decrease is present, but not to the same extent that it was previously. This is easily attributable to the fact that there is a greater concentration of solids, reducing the effect. Theoretically this makes sense due to the fact that a dry sample viscosity should not change regardless of the amount of dry sodium hydroxide added to it.

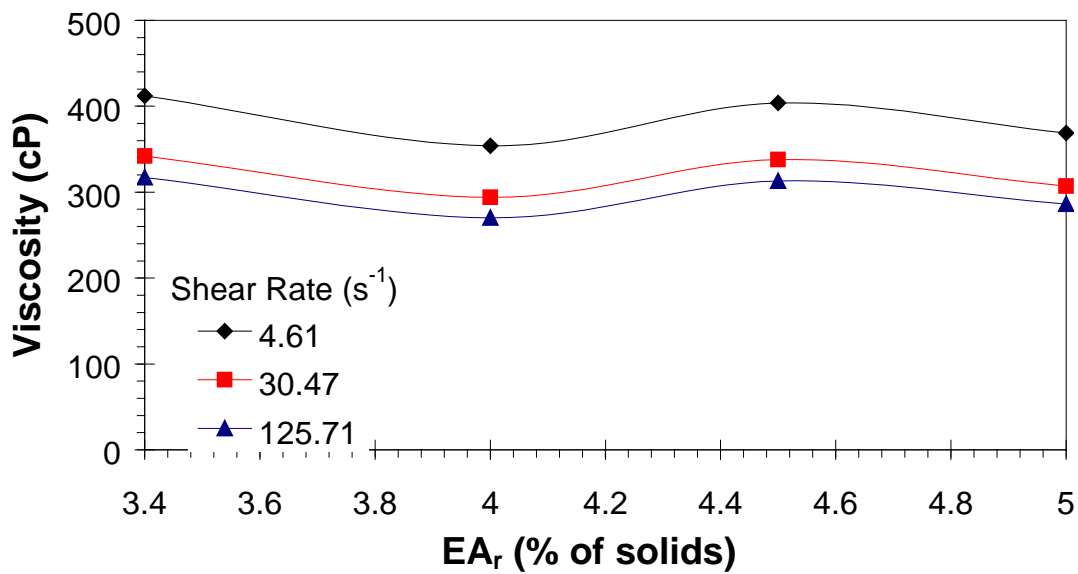


Figure 8: Mill C 71.5% Black Liquor Viscosity at Various EA_r at 100°C.

While this is obviously taking the argument to an extreme, this is the general reason for why the effect goes away. Without at least a small amount of water, the liquor won't flow. In light of this argument, it is then important to note that even at 115°C, the liquor still underwent nearly a 25% reduction in the viscosity (from ~170 cP to ~130 cP) for the highest shear rate tested.

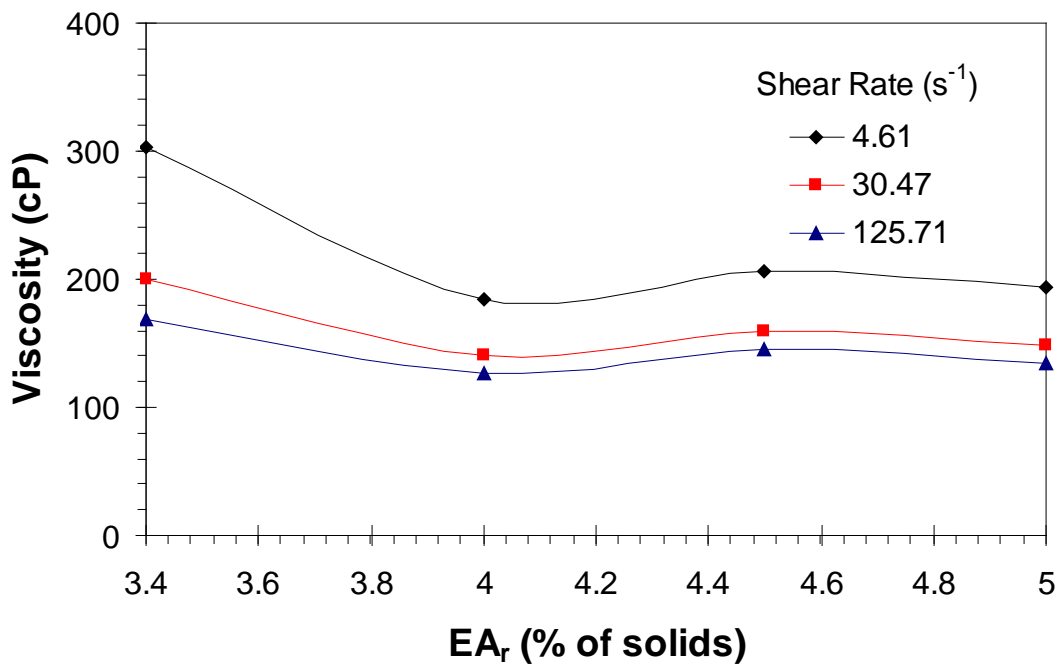


Figure 9: Mill C 71.5% Black Liquor Viscosity at Various EA_r at 115°C.

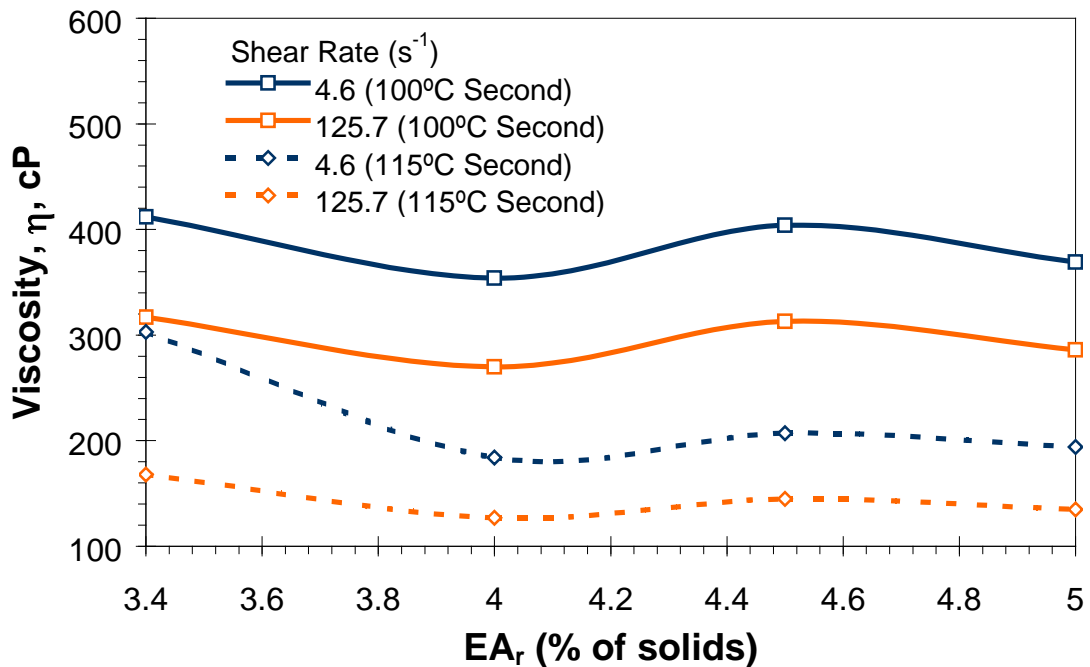


Figure 10: Mill C 71.5% Temperature Comparisons (100°C and 115°C).

Figure 10 presents the Mill C data at the two different temperatures to show any effects that might be present. It indicates that at the higher temperature, the effect is slightly stronger. This result indicates that as known, temperature does have an important impact of black liquor viscosity. It also indicates that instead of negating the previously described viscosity reduction from caustic addition it enhances it slightly.

Differential Scanning Calorimetry Results

The DSC results show that the addition of alkali to the liquors had little to no effect on their heating properties and behaviors. This is a good indicator that alkali addition might be a good treatment to reduce liquor viscosity in a mill environment. Since black liquor

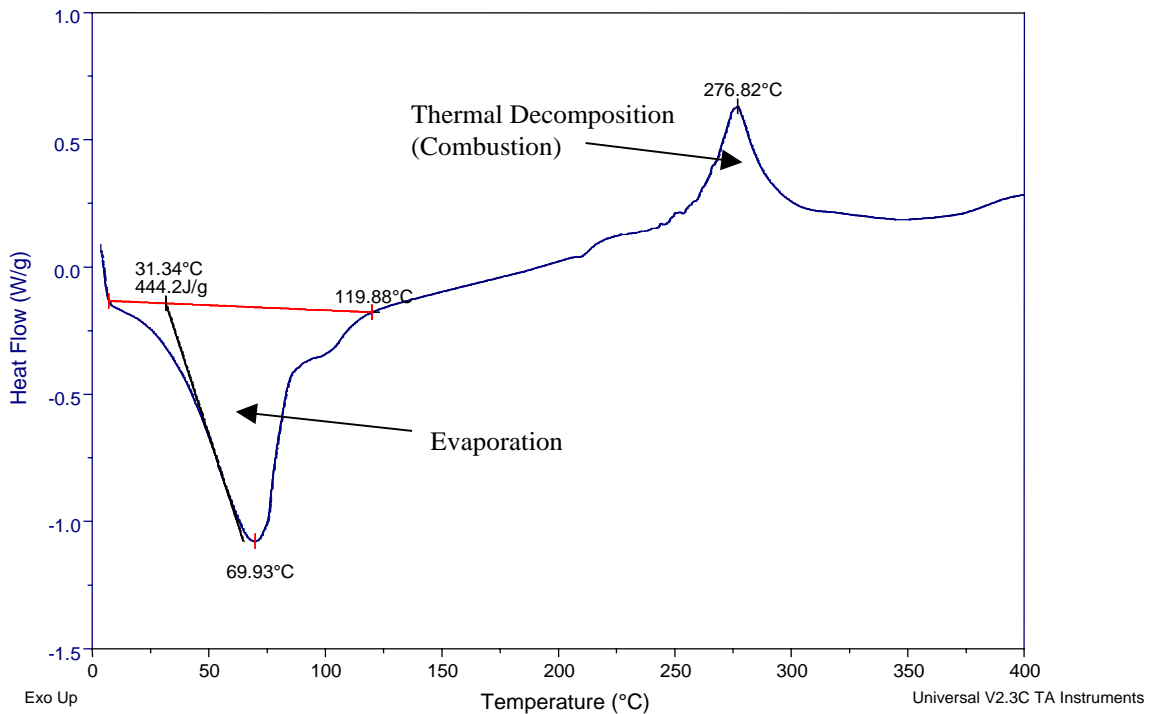


Figure 11: Mill C 71.5% 3.5% EA_r Black Liquor DSC

is burned for its heat content and the recovery of the pulping chemicals, it is important that the heat duty required to evaporate the remaining water from the liquor not increase. A decrease is not required, but an increase is certainly undesired. In light of this, Figure 11 presents a sample DSC curve showing the areas being considered in the comparison. The two important points being noted as mentioned previously are the area representing the evaporation region, and the peak representing the combustion (or in the N₂ purge system used the point where the carbon bonds break). Figure 12 shows a comparison of all of the different liquors, and how their evaporation characteristics changed as well as their “combustion” points.

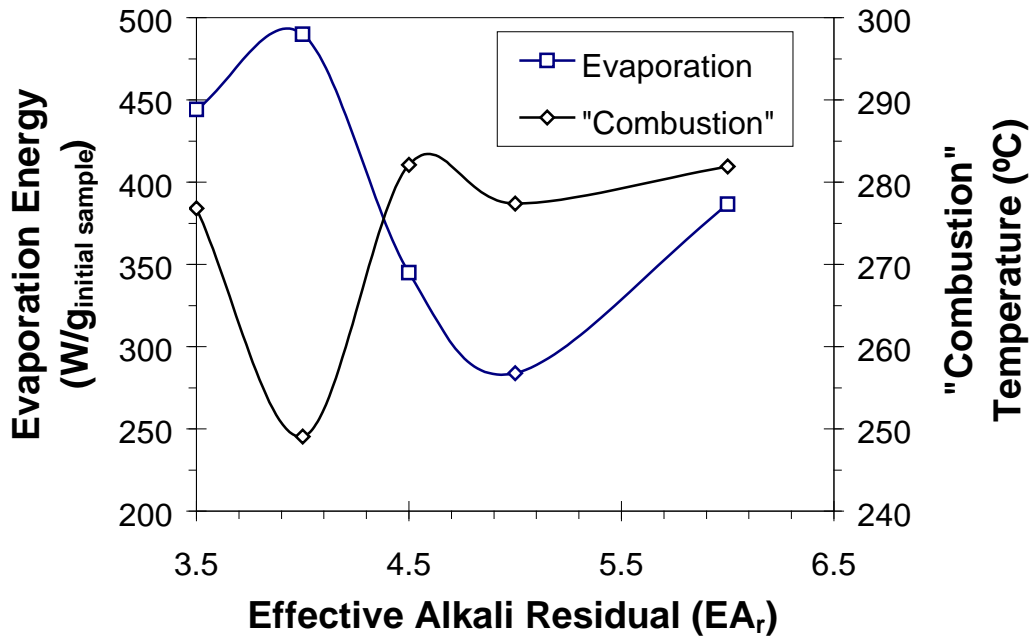


Figure 12: Mill C 71.5% DSC Comparisons

It is easy to see that while the curves move, there is not a distinct pattern over the whole range, and any one point could be simple noise in the data. The important point is to realize that the alkali addition does not have any apparent negative consequences on

either the evaporation or the combustion. If one or both of these were not the case, then alkali addition would not be as promising as it might possibly be.

Thermogravimetric Analysis Results

In a similar manner, alkali addition can only be considered further if it does not affect the drying patterns significantly. In order to determine this, the percent solids when particular transitions occurred should be considered to see if the changed alkali content affected the drying process. Four points, as introduced previously, were examined. First, however, it is important to look at a TGA curve and the derivative curve used to analyze what is happening.

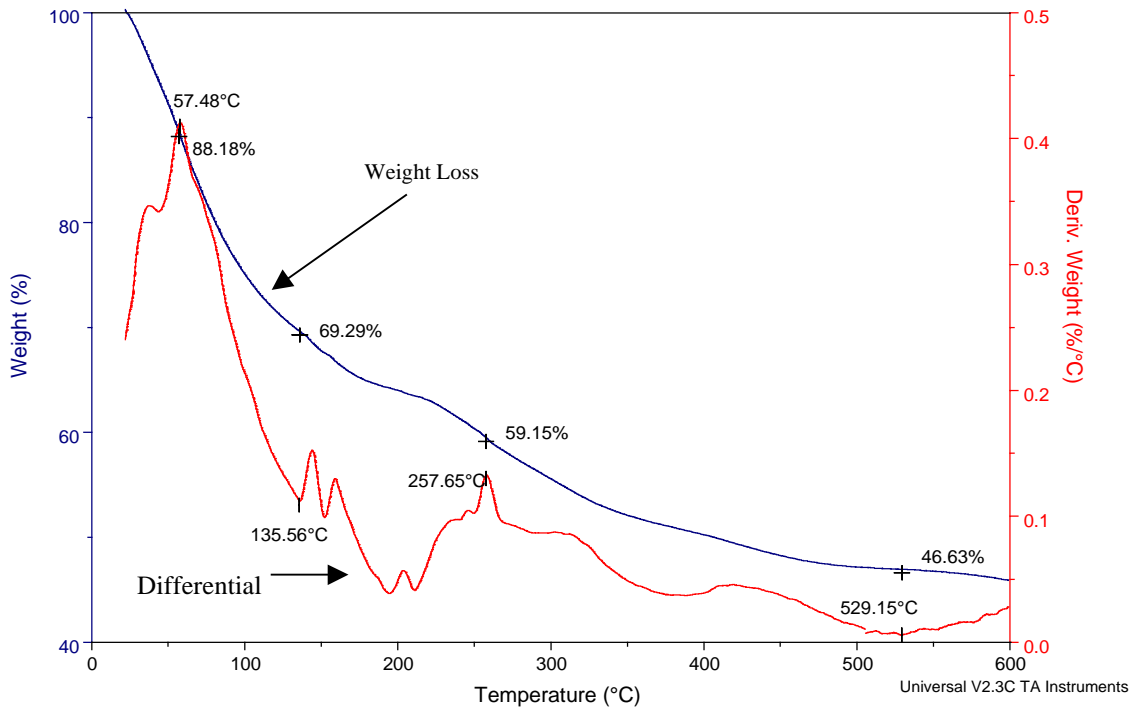


Figure 13: Mill C 71.5% TGA Curve

The initial peak (sometimes only an inflection point) is the point at which the liquor is evaporating water away at the greatest rate. The second point is where the liquor is approximately dry, but not yet losing mass due to hydrocarbon break-down and lost into the purge gas. The third peak is the point where maximum hydrocarbon loss is occurring. The last point is where the loss has minimized. After this point, some loss continues to occur, but primarily only alkali salts remain in some form. Since the melting point and eventual evaporation point was well beyond that achievable on the equipment used for testing, it is assumed that at this point, the sample has reached its theoretical weight loss limit. This occurs slightly before the final run temperature of 600°C.

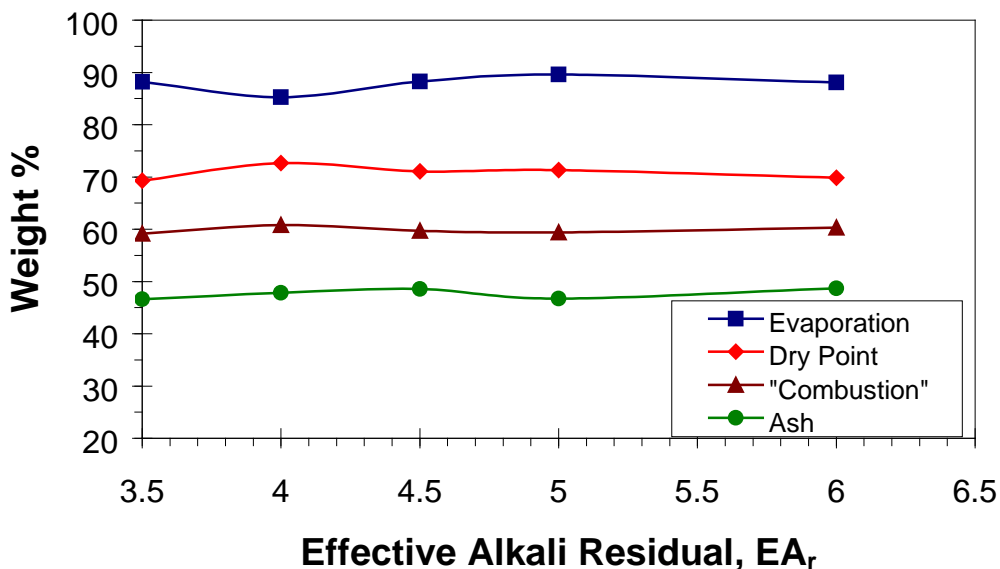


Figure 14: Mill C 71.5% TGA Comparisons

Figure 14 shows that the percentages where these transitions occurred was not appreciably impacted by the addition of alkali. The implication of this discovery is that the combustion process of the alkali enhanced liquor should occur in a manner essentially similar to that observed for non-alkali enhanced liquor. It is interesting to note that the

temperatures associated with each of these transition regions do not change appreciably either. These transition temperatures can be observed in the appendix where all experimental graphs are located.

IV. Conclusions and Discussion

Rheological Conclusions

The study shows that black liquor is a non-Newtonian fluid even at higher temperatures. This means that as the shear rate changes, so does the viscosity. At extremely high shear rates, the black liquor exhibits Newtonian characteristics. The consistent decrease in the low solids viscosity with shearing, but not in the higher solids could be due to experimental error from slight evaporation (any evaporation at 71.5% solids has a large effect). The internal structure or form of the black liquor is not yet well defined. It is important to recognize that any internal organization (gel formation) would cause a marked increase in viscosity. There is some indication of this due to the non-repeatability of the first run viscosity. This is also indicated by the decrease between first run and second run tests. However, this may be due to some detail of the specific piece of equipment used in this study. Further study would be required before a final conclusion is reached. None the less, if this viscosity decrease effect from shearing the liquor is genuine, it is an important piece of data that should be used appropriately by a mill. By maintaining sheared black liquor, the viscosity will remain lower. All three mill liquors also indicate that there is an alkali effect. Adding caustic to the liquor reduces the

viscosity. However, before simply adding caustic, a study should be made to determine the best operating point. In some processes, adding too much caustic may increase the liquor viscosity. Each process and chip supply is different, and these differences affect the black liquor. However, as a rule of thumb, from observation of Douglas Fir based liquors a value of $\sim 4.0\%$ EA_r should be maintained. Further work needs to be done on defining changes that occur when caustic is added to the black liquor. The data presented in this study is purely experimental. A better understanding and model of alkali effects on the liquor needs to be obtained. This will require the development of a better model liquor also.

Differential Scanning Calorimetry Conclusions

The DSC is a wonderful piece of equipment and extremely versatile. A more in-depth study of black liquor using the DSC is certainly in order. The previous works cited use the DSC to look at specific properties. It does not appear that a major work has been done to characterize black liquor using the DSC. Nor is there any ready information on interpreting the DSC results. A comprehensive study using both a nitrogen purge and an oxygen purge would be worth pursuing.

For this study, the DSC proved to be adequate for observing heating characteristics. General trends, such as evaporation and “combustion,” can be seen in all of the tests. There is no consistent trend in DSC heating properties due to alkali addition. The only

minor variations that appear are decreases, which are acceptable variations since they do not require more energy from the present system in order to achieve the current result.

Thermogravimetric Analysis Conclusions

The TGA was easy to use and provided consistent data which can easily be observed by an operator. For this reason, TGA should be explored further by industry in general and observations done to characterize the results better. As previously with the DSC, the current published work on the subject is not very broad. Again, the papers present individual uses for the TGA, not overall characterizations of the results which could be beneficially used by the industry. Additional work should also be done to determine what products are produced at what temperatures in the TGA. To do this a Gas Chromatograph/Mass Spectrometer or similar tool could be used. A comprehensive study could be easily used to better interpret TGA results. These results could then be applied to potentially better control recovery boilers on a daily basis.

Final Conclusion

By adopting a control strategy that involves alkali addition in some form, the viscosity can be reduced avoiding potential operation issues. EA_r changes will not benefit all mills, but the small price to have samples tested is far less expensive than the clean-up costs of a major liquor problem such as setting up. Also, day to day operating costs in the form of pump energies will be reduced since a higher viscosity requires more energy.

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