BIOREFINERY – AN OVERVIEW

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ABSTRACT

With the escalating crude oil price there has been a lot of discussion about producing ethanol from wood biomass. Additionally, due to the increasing competition for pulp and paper producers from overseas to increase profitability, there may be a need for North American industry to increase revenue by producing bio-energy and bio-materials in addition to wood pulp and paper products. In this paper, an overview of various options to produce ethanol from wood, e.g., wood biomass gasification, extracting hemicellulose prior to pulping, and repurposing a Kraft mill, will be presented.

To date significant efforts have been put into exploring the possibility of extracting hemicelluloses from the chip before pulping and converting these low heating value hemicelluloses to ethanol by fermentation. Various extraction conditions to maximize the yield of hemicellulose from maple and eucalyptus chips were investigated. Extracted chips were pulped by typical Kraft pulping conditions.

It was discovered that the yield of hemicelluloses was dependent on the severity of the extraction conditions (temperature and time). It was also discovered that the extracted maple chips require less H-factor and/or active alkali to pulp to the same Kappa number compared to unextracted chips. A similar study was done with eucalyptus chips. The strength properties of the pulp made from the extracted chips will also be presented.

INTRODUCTION

A forest biorefinery is a facility that integrates biomass conversion process and equipment into an existing chemical pulp mill to produce fuel, chemicals, and renewable energy in addition to manufacturing traditional pulp products (which may not be necessary in other concepts of biorefinery). The concept of biorefinery has gotten a great deal of attention of late due to i) the escalating cost of crude oil and hence the demand for more ethanol production as fuel[1,2,3], and ii) a potential solution for the North American pulp and paper industry to increase revenues by producing biomaterial and biofuel in addition to pulp and paper products. Integrating the concept of biorefinery into the paper industry is important not only for national energy security reasons, but for the success and survival of this industry against competition from overseas[4]. The fact that we have much of the infrastructure and expertise needed to rapidly implement biorefineries on a commercial scale, e.g. feed stock harvesting, transportation and storage, manufacturing and conversion infrastructure, waste handling and recovery[5] would help in commercialization of this concept at a rapid pace. However, the infrastructure to separate acetic acid, hemis, and lignin, and the fermentation unit need to be put in place.

When it comes to generating ethanol from wood chips through the use of existing Kraft mills there are two main schools of thought. Tom Amidon and Adriaan van Heiningen[6, 7] strongly believe that extracting hemis before pulping and subsequently making good pulp from the extracted chips is the right approach.

The other approach that is being investigated by Richard Phillips[8] is one where a shut-down Kraft mill or a mill which is not profitable making pulp and paper products can be repurposed to produce ethanol only.

In this paper a brief synopsis of these various options, e.g., value prior to pulping, repurposing of a Kraft mill, gasification of woody biomass, etc., will be presented. Some results on extraction, pulping, bleaching, and fiber characterization of the pulp made from maple and eucalyptus will also be presented.

EXPERIMENTAL

Never-dried industrial maple chips were used for the study. All the extraction and the pulping experiments were done in a 10-litre M&K digester. After the extraction the chips were washed to simulate counter current extraction. Kraft pulping was done by varying active alkali (AA) at constant sulfidity (25%) and/or H factor. Lower H factor pulping for extracted chips was done by lowering the pulping temperature. Kappa number of all pulps was done by TAPPI standard test method T236.

Eucalyptus chips were prepared in the lab from the logs obtained from the Mogi Guaçu area. All the extraction and pulping experiments were done in autoclaves. After the extraction the hydrolysate was drained off and the pulping was performed without intermediate washing of the chips. Kraft pulping was done at 1525 H factor at a 4 to 1 liquor-wood ratio. AA was varied at constant sulfidity (35%). The kappa number of the pulps was measured using TAPPI standard test method T236.

DISCUSSION

Value Prior To Pulping (VPP)

Of all the options, VPP is the most extensively investigated concept of the biorefinery platform. During the Kraft cooking certain hemis dissolve out of the wood and become part of the black liquor. These hemis are then burnt for their heat value which is half of that of lignin. If the hemis are extracted before the pulping and converted to acetic acid, ethanol, and other value-added products then it has a potential of improving the profitability of an existing Kraft mill. However, the pulp quality from the extracted chips should be better or equal to the pulp made from the chips without extraction.

In an ideal VPP scenario, if one could extract 15-20% hemis before pulping and get the same pulp yield as you did before, that would allow you to keep the same pulp mill production level without increasing the wood demand. This would also reduce black liquor solids going to the recovery boiler. Removing the recovery boiler bottleneck may allow the manufacturing of more tonnage, which will further improve the profitability of the Kraft mill.

The VPP concept has been funded by a VPP consortium of large pulp and paper manufacturers and is being operated under the auspices of Agenda 2020. The consortium recently received a $1.7 million grant from DOE. Tom Amidon and other universities have also been very active in this field for a number of years. International Paper has a pending patent that was recently published which covers aspects of VPP[9]. Some of the extraction, pulping, and bleaching results from the work done by IP will be presented in a later part of this paper.

Repurposing a Kraft Mill

More and more North American Kraft mills are being closed down or are on the verge of being closed down because these mills are not profitable in making pulp and paper products due to the high wood, energy, and labor costs. The recent announcement of the closure of many Canadian pulp mills in particular has had a very devastating effect on the local economy. The concept of repurposing a Kraft mill for biorefinery entails the use of existing infrastructure to convert the cellulosic material to ethanol without making pulp and paper products. The big advantage of this concept is that it makes use much of the existing infrastructure, e.g., chips handling, digesters, etc. Chips will be cooked in the digester and the pulp can then be converted into ethanol without worrying about the pulp quality. An additional benefit would be the closure of certain units of operation, such as the bleach plant, so the operating cost will be lower.

Mascoma Corporation[10] has announced to build and operate a 15,000 square foot cellulosic biomass to ethanol facility in New York State. In concept, agricultural and/or forest products as cellulosic biomass, including paper sludge, wood chips, switch grass and corn stover is acid pretreated with 1% H_2SO_4 at 180-200°C. The pretreated cellulosic substrate is then fed into a unit called SSF (simultaneous sacchrification and fermentation unit) where the treated chips are exposed to a cocktail of enzymes. After 4 – 7 days of incubation enzymatic activity results in a solution of ethanol and lignin. Ethanol is recovered by distillation and the lignin is filtered off. Conversion of cellulose into ethanol in the presence of large amounts of lignin by enzymatic hydrolysis could be very challenging and the commercial success of SSF is yet to be seen. Yet another approach to restarting a closed down sulfite mill has been proposed by American Processes[11]. American Value Added Pulping (AVAP) involved the cooking of chips with a mixture of ethanol/water in the presence of sulfite. Pulp produced by this process is easily bleached by TCF sequence and furnished to paper machines.

Lignin is precipitated to be gasified to produce syn-gases which can be converted to heat, power, and transportation fuel. The hemicelluloses are converted to ethanol by enzymatic hydrolysis. Conversion of sugars from sulfite pulping process has been successfully practiced for many years.

Wood Biomass Gasification

Wood biomass gasification is a known technology and there are a number of pilot plants in operation in Arkansas where they are converting wood biomass to ethanol through the gasification route. Biomass can typically be purchased at US$1-2 per million BTU and can be burned to replace steam which is valued at $4 per million BTU. It can also be gasified to produce syn-gases to replace natural gas which is valued at US $6-10 million BTUs[12].

Potlatch Corporation has been working with Winrock International and the State of Arkansas under the direction of Agenda 2020 to develop/commercialize the concept of biomass gasification at their McGhee, AR, Kraft mill. They are working towards a potential biorefinery demonstration mill site and their interest is to support whatever will "get this done." Their driver is to find a low-cost way to reduce or eliminate the mill's dependency on natural gas while developing new products from the forest residual. The project economics are based on the fact that 2/3 of the trees are left after harvesting in the forest and 2/3 plants are left from farming. Potlatch is taking a phased approach, i.e., starting out with wood biomass and then integrating other raw materials into their gasifier.

Potlatch Corp. recently issued a press release updating the progress of the project. According to the press release they claim to have all the funding in place, but before they move ahead they would like to have one of the petroleum companies as a partner, which has not happened yet. So they have put the project on hold.

RESULTS – VALUE PRIOR TO PULPING

Figure 1 represents a simple diagram for a proposed VPP scheme. The chips are extracted in a counter current mode with water. The extracted chips are then fed to a conventional Kraft digester to produce pulp. The hydrolysate is separated into acetic acid, lignin, and hemicellulosic streams. The hemicelluloses are fermented to produce ethanol.

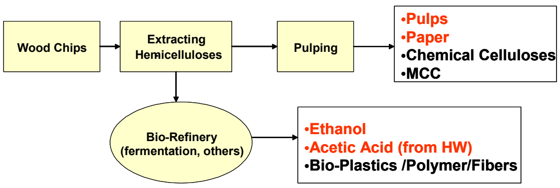

Figure 1 – A simple flow diagram for the value prior to pulping

Figure 2 shows the effect of time and temperature for the extraction phase for maple and Eucalyptus. It is evident that as you increase the time and/or the temperature the amount of wood mass removed increases. This is due to the fact that increasing time and/or temperature results in increased rate of hydrolysis of acetyl group, hence generating more acetic acid. Acetic acid generated *in situ* then facilitates the removal of hemis. It is interesting to note that the rates of hemi removal for maple and Eucalyptus are very different probably due to higher xylan content of Eucalyptus.

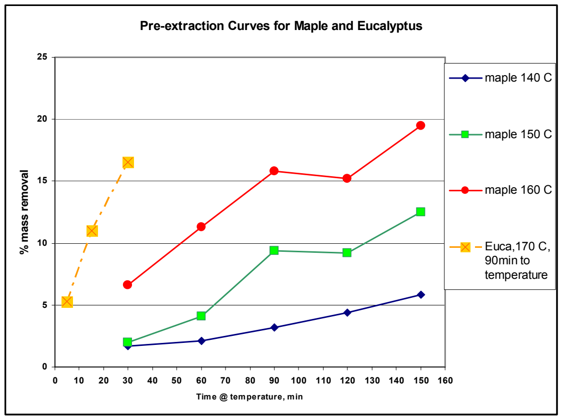

Figure 2 – Effect of time and temperature on mass removal for maple and Eucalyptus chips

Yield versus kappa relationship is plotted in Figure 3. As expected, as the kappa goes down so does the yield, regardless of the extraction level. For maple, although there is some scatter in the data there appears to be a clear trend that, at kappa 15, both 8% and 12% mass removal results in lower pulp yield compared to control (unextracted chips). However, if extracted chips are cooked to kappa 25 then the yield disadvantage for extracted chips disappears. There are limited data for Eucalyptus but the pulp yield for Eucalyptus extracted chips is approximately 6% lower. The different results for maple and Eucalyptus could be explained by the fact that the maple chips were subjected to modified washing after the extraction to simulate the counter current extraction. The Eucalyptus chips, on the other hand, were not washed.

Maple extracted chips always took less AA and almost half the H factor (986 and 531 for H-factor for control and extracted chips, respectively). It was also discovered that pulps made from maple extracted chips consumed 6 lb/ton less ClO_2 at 2.5 point (87.4 to 89.8) higher brightness. No such advantage in pulping and bleaching of pulp made from extracted Eucalyptus chips was observed.

From the preceding discussion on pulp yield for maple the following scenarios could be developed:

i) Pulping extracted chips to the same kappa results in a 2% lower pulp yield. For a 1,000 TPD mill the wood demand would go up by 367 tons/day (assuming 12% extraction and 48% yield from the extracted chips).
ii) Pulping to higher kappa, compared to control, the bleaching cost would be neutral due to easier bleachability of the pulp. The wood consumption would go up 272 TPD (assuming 12% extraction and 50% pulp yield from extracted chips).

If the revenues generated by ethanol produced from the 12% extracted hemis is higher than the increased wood demand, then only the VPP option would be viable.

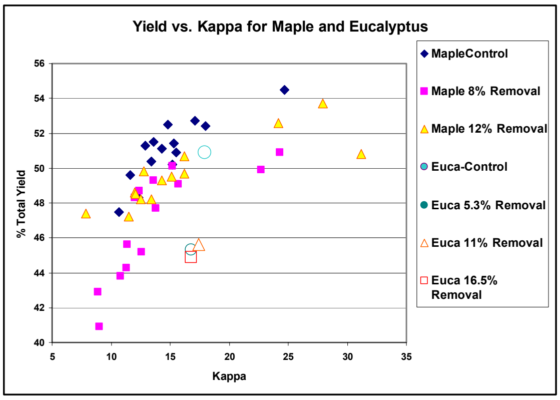

Figure 3 – Yield versus kappa relationship for control and extracted maple and Eucalyptus chips

Strength properties of fully bleached maple and Eucalyptus pulps were characterized by generating a PFI refining curve. Figure 4 shows the relationship between freeness and PFI revs. It is evident that the starting freeness of the pulps made from extracted chips is always higher and the pulp took significantly more refining energy to get to a certain freeness level. Similar increase in freeness and refining energy requirements were observed for Eucalyptus pulps as well.

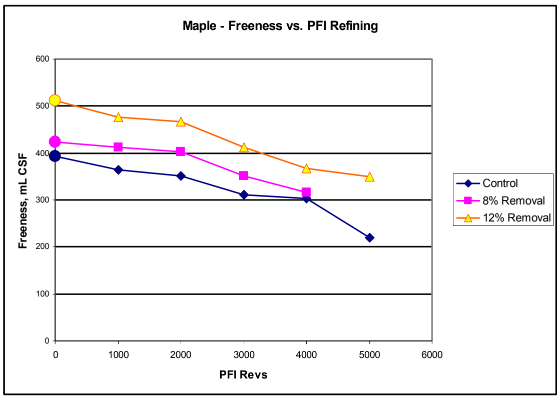

Figure 4 – Refining energy response for control and the pulp made from maple extracted chips

Tensile versus freeness (Figures 5 and 6 for maple and Eucalyptus respectively) relationship shows that for both maple and Eucalyptus pulp the starting tensile is lower, however, for maple the tensile at 400 CSF, which most mills refine to, is very comparable to control, whereas for Eucalyptus the tensile index even at 400 CSF is significantly lower.

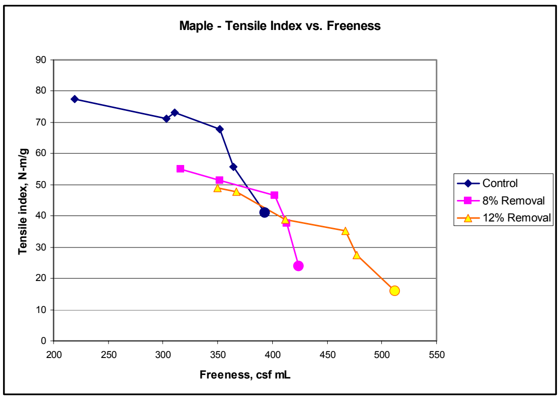

Figure 5 – Tensile index versus freeness for control and the pulp made from extracted chips for maple

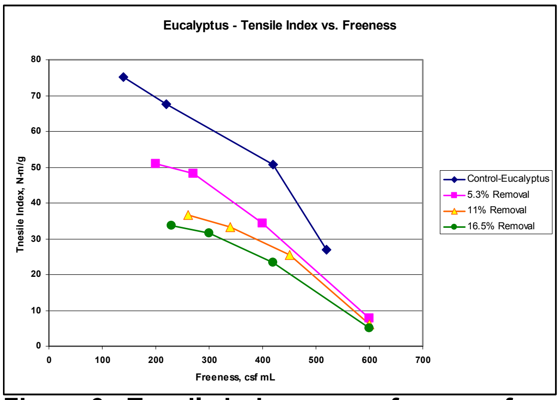

Figure 6 - Tensile index versus freeness for control and the pulp made from extracted chips for Eucalyptus

Tear index (Figures 7 and 8 for maple and Eucalyptus respectively) exhibit the similar trend as tensile index did. Once again the starting tear for both pulps is lower and upon refining to 400 CSF the tear index for maple pulp is slightly higher than control, whereas for Eucalyptus pulp the tear index even at 400 CSF is significantly lower than control.

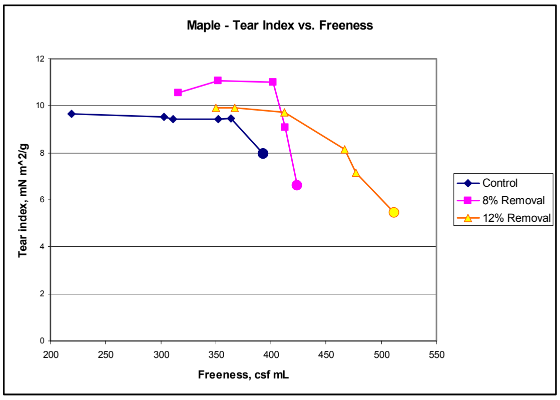

Figure 7 – Tear index versus freeness for control and the pulp made from extracted chips for maple

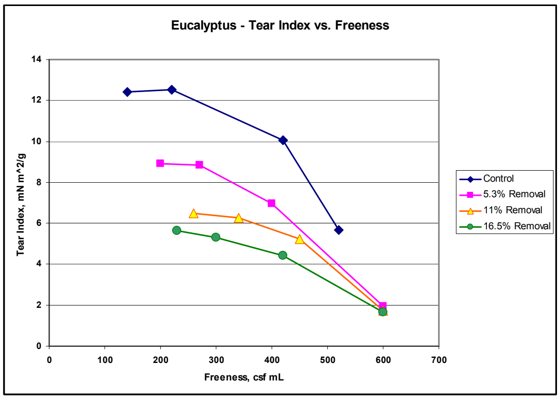

Figure 8 - Tear index versus freeness for control and the pulp made from extracted chips for Eucalyptus

CONCLUSIONS

- A great deal of effort is being put into exploring various options of converting an existing Kraft mill into a viable alternative to produce ethanol, so that an existing Kraft mill could become a more profitable operation.
- The VPP option is by far the most extensively investigated so far. If the yield disadvantages can be overcome so that the same amount of wood is required to keep the same pulp production level, then this could be a very attractive option.
- Repurposing a Kraft mill and gasification of biomass have their own merits, but commercial success of both these approaches is yet to be seen.
- Pulps made from extracted maple and Eucalyptus chips exhibited very different characteristics in terms of pulping, bleaching, and strength properties. Pulp with satisfactory strength properties from extracted maple chips could be made, whereas Eucalyptus pulps were significantly lower in tear and tensile properties.
- A thorough business case analysis needs to be done for any of the options because return on investment is very site specific depending on wood and energy cost.

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REFERENCES

1. Wising, U. and Stuart, P, *Pulp & Paper Canada*, 107:6 (2006) .25
2. Pervaiz, M. and Sain, M., *Pulp & Paper Canada*, 107:6 (2006) .31
3. Mabee, W. E. and Saddler, J. N., *Pulp & Paper Canada*, 107:6 (2006) .34
4. Agenda 2020. A Technology Vision and Research Agenda for America's Forest, Wood, and Paper Industry. AFPA, 1994
5. Van Heiningen, A., *Pulp & Paper Canada*, 107:6 (2006) .38
6. Amidon, T. E., *Pulp & Paper Canada*, 107:6 (2006) .47
7. Perine, L., *Paper 360*, (12):31 (2006)
8. Phillips, R., Jameel, H., and Chang H-m. 3rd ISETPP, Guangzhou, China, 2006, pp 11
9. Tan, Z., Goyal, G., and Koukoulas, A., U.S. Patent Pending U.S. 2007000627 A-1, January 4, 2007
10. Mascoma News Release, December 20, 2006
11. Pylkkannen, V. and Retsina, T., 2006 AIChe Annual Meeting, San Francisco, CA, Paper 701d, 2006
12. Thorp, B., *Paper 360*, (12):25 (2006)