FROM KRAFT MILL TO FOREST BIOREFINERY: AN ENERGY AND WATER PERSPECTIVE. II. CASE STUDY

MARIYA MARINOVA, ENRIQUE MATEOS-ESPEJEL and JEAN PARIS

École Polytechnique, Chemical Engineering Department,
Montréal, QC, Canada

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In Canada, the pulp and paper industry, a major contributor to the economy, is facing one of the most severe crises of its history. The biorefinery concept offers an opportunity to revitalize the industry by producing high-value chemicals and biofuels, by developing new technologies and by penetrating new markets. To become successful, the biorefinery should address a number of challenges, associated to feedstock, products, markets, technology and sustainability. This paper is the second part of a work undertaken to evaluate the energy impacts of a Kraft pulp mill conversion into a biorefinery. In Part I, a methodology identifying the interactions between steam and water systems in the Kraft process and their effects on the implementation of energy efficiency measures has been developed. Part II deals with the application of this methodology in the specific Canadian biorefinery context. Hemicellulose extraction from wood chips prior to pulping and its transformation into high-value products is the biorefining technology identified for integration into the existing pulp mills. A Canadian hardwood Kraft pulp mill that has the opportunity to be converted into a dissolving pulp mill was selected as a biorefinery acceptor. Hemicellulose, used as a feedstock for promising products, such as furfural, xylitol and ethanol, has been analyzed. Issues related to the corresponding energy requirements of the biorefinery and to its sustainability have also been investigated.

Keywords: hemicellulose biorefinery, Kraft pulp mill, energy optimization, dissolving pulp, value-added products

INTRODUCTION

The Canadian pulp and paper industry is facing one of the most severe crises of its history, and probably the worst. In response to the declining demand for pulp and paper products, to their decreasing price and high energy costs, several mills have announced temporary or definite shutdowns. These actions highlight the unpredictable nature of global commodity markets and represent a clear warning to the industry. The efforts must now be focused on making the Canadian pulp and paper mills competitive and able to generate revenue.

Biorefinery is the conversion of forestry and agricultural biomass into a large spectrum of products by various extraction and transformation pathways, offering the opportunity to revitalize the Canadian pulp and paper industry.[1] The main biorefinery feedstocks are hemicelllose, cellulose, lignin and bark, used to generate building block molecules, chemicals, fuels, polymers or dissolving pulp. The large-scale implementation of the biorefinery will result in profitable and sustainable processes with positive environmental impacts.

Kraft pulp mills are the primary candidates to be transformed into biorefineries, as they have the infrastructure to process biomass feedstock. The retrofit integration of a biorefining technology into a Kraft process will add new operations and will increase the steam demand; also, if hemicellulose or lignin is removed, it will reduce the fuel available to the recovery boiler.[2] It is important that the base process, as well as the biorefinery unit, be optimized and highly integrated from the standpoint of energy, to satisfy the modified energy balance.

The paper is the second part of a work undertaken to evaluate the impact of a Kraft pulp mill conversion into a biorefinery on the energy supply and demand. In Part I, a methodology identifying the interactions between steam and water systems in the Kraft process and their impacts on the implementation of energy efficiency measures has been developed and illustrated by its application to a Canadian hardwood pulp mill currently producing 700 adt/day of Kraft pulp. In Part II, an example of biorefinery integration in the same mill is discussed. The potential application of the hemicellulose extracted from wood chips as a source of value-added products is evaluated. This work was also undertaken to assess the impact of hemicellulose extraction and of its conversion into furfural, xylitol and ethanol on the energy balance and to highlight the importance of energy optimization for the sustainability of the biorefinery.

Approach for developing a biorefinery

Hemicellulose is composed of carbohydrates based on pentose sugars, mainly xylose, as well as hexose sugars, such as glucose and mannose. The most important sources of hemicellulose are wood and agricultural wastes. Hemicellulose can be derived in two ways and its final product applications should be selected accordingly. The first strategy for hemicellulose utilization, *i.e.* its use in polymer forms, requires an appropriate pre-treatment of wood chips, so that the hemicellulose extracted by this method is cleaner and less depolymerised. Therefore, it is suitable for etherification and esterification reactions and production of polymers. Hemicellulose-based molecules and their chemically modified forms are released during pulping processes. In most cases, hemicellulose is decomposed into sugar molecules and is also chemically modified. Often, it does not have any value as a polymer. However, these streams can be converted into ethanol, furfural, xylitol, other polyols and bi-functional organic molecules. Acetic acid and hydroxy acid residues may be also generated.[3]

Conversion of a conventional Kraft pulp mill into a dissolving pulp mill represents a promising option to create a biorefinery. Dissolving pulp is a low-yield chemical pulp with high cellulose content suitable for making rayon, cellulose acetate and cellophane.[4] Dissolving pulp was produced until World War II exclusively from purified cotton linters, while today it is generated *via* acid sulphite and pre-hydrolysis Kraft processes (Fig. 1). Hemicellulose is solubilised when exposing wood chips to hydrolysis prior to pulping, the produced pre-hydrolysate contains sugars, such as monosaccharides (arabinose, xylose, mannose, galactose, glucose) and oligosaccharides (galactoglucomannan, glucuronoxylan), and other chemical compounds (acetic acid, furfural, phenolic compounds).

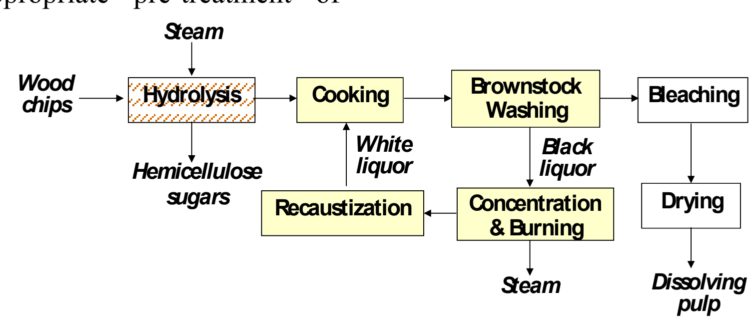

Figure 1: Schematic representation of dissolving pulp production based on a Kraft process

The hemicellulose extracted can be converted into a large number of sugar-derived chemicals. Taking into account the market trends (demand and price), in this article special attention is given to the use of the pre-hydrolysate as a feedstock in: a further acid treatment to produce furfural; a chromatographic/

crystallization system for the purification of xylose and xylitol, a fermentation plant for the production of ethanol.

Value-added products from hemicellulose

Furfural

Furfural, produced by acid hydrolysis of pentosans (C-5 carbohydrates), is the only organic compound derived from biomass that can replace the crude oil based organics used in industry. Furfural is used as a chemical feedstock for furfuryl alcohol (production of furan resins), in the manufacture of furan (as an intermediate in the synthesis of pharmaceuticals, agricultural chemicals, stabilizers and fine chemicals), as well as a solvent for refining lubricating oils, as a decolorizing and wetting agent. The world furfural production[5] is 250 000 t/a, its price being of 1 000 $/t. One of the commercially available methods to generate furfural is the "Westpro modified Huaxia technology"[6], the simplified diagram of which is given in Figure 2. The raw material, that could be either forest or agricultural, is charged to steel reactors or digesters. The furfural thus formed is entrained with steam and the furfural-saturated steam is condensed. The condensed solution is then fed to a furfural azeotropic distillation column, where the condensate is separated into two fractions. The light water phase is refluxed and the heavy furfural phase undergoes refining by continuous azeotropic distillation. The maximum furfural yield that could be obtained from wood using the "Westpro modified Huaxia technology" is of 8%. This process also generates by-products, such as acetic acid, acetone and methyl alcohol, which are not considered in this study.

Xylitol

Xylitol occurs naturally in fruits, in low amounts, which makes its extraction difficult and uneconomical. It has many applications in foods and confectionery, in the production of oral hygiene products (mouthwash and tooth paste), pharmaceuticals, dietetic products and cosmetics. The most popular method utilized in the synthesis of xylitol involves the chemical hydrogenation of xylose,[7] which in turn is obtained by the hydrolysis of the xylan present in hemicellulose. Figure 3 gives an overview of the method. The chemical method of xylitol production is based on the catalytic hydrogenation of the xylose-rich hemicellulose hydrolysate in the presence of the Raney nickel catalyst. The xylose and other carbohydrates are hydrogenated to their respective polyols. The xylitol is crystallized from the hydrogenated solution and the uncrystallized xylitol fraction is separated by liquid chromatography. Chromatographic separation is performed in a column containing cation exchange resin, in calcium or strontium form.

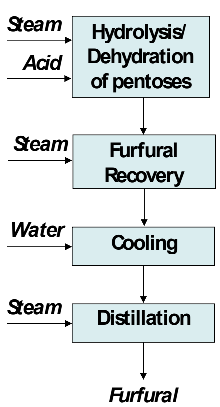

Figure 2: Simplified representation of "Westpro modified Huaxia technology" for furfural production

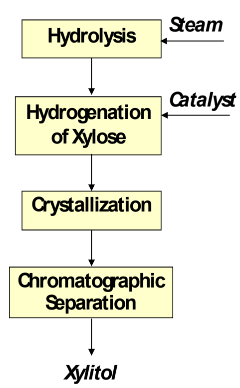

Figure 3: Schematic diagram of the chemical method for xylitol production

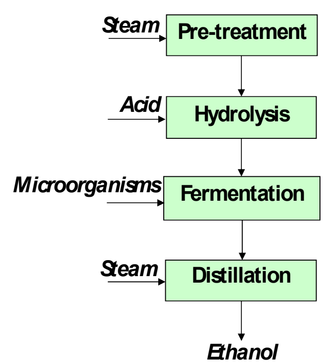

Figure 4: Simplified representation of biochemical ethanol production

The effluents collected from the chromatographic column had various proportions of polyols, such as mannitol, arabitol, galactitol and sorbitol. The fractions with very high xylitol concentrations are crystallized and the xylitol is recovered.
Biological methods for xylitol production using yeasts are investigated as an alternative to the chemical method. The world xylitol market[8] is under 100 000 t/a and its current price ranges from 4 000 to 5 000 $/t.

Ethanol

The ethanol produced from lignocellulosic biomass is a fuel with the potential to match the conventional features of petroleum at a low price. Processes capable to convert efficiently the soluble carbohydrates into hemicellulose hydrolysates to ethanol are necessary to achieve a high overall biomass-to-ethanol process yield. The pentose sugar xylose is the major carbohydrate component of hemicellulose in a wide variety of lignocellulosic biomass species. Consequently, the ability to ferment xylose is an important characteristic of microorganisms, being considered for the use in large-scale fermentation-based hemicellulose conversion processes. When steaming wood chips, the primary component of the feedstock substrate solubilised is hemicellulose. Depending on whether the solubilised fraction is separated from the pre-treated solids, different fermentation strategies need to be considered. When the liquid and solid phases are separated, the liquid stream (prehydrolysate) is rich in hemicellulose sugars, and the stream of the solids is rich in cellulose and lignin. Depending on the feedstock substrate, the prehydrolysate will contain primarily a five-carbon sugar (xylose), or a mixture of five- and six-carbon sugars (xylose and mannose). Downstream ethanol conversion of the prehydrolysate should therefore consider five-carbon sugar fermentation only, or five-and six-carbon sugar fermentation.[9]

To produce ethanol from lignocellulosic materials, an appropriate pre-treatment is required to open the bundles of lignocelluloses and to access the polymer chains of cellulose and hemicellulose. Subsequently, the polymers are hydrolysed to obtain monomer sugar solutions, which in turn are fermented to ethanol by microorganisms. The final step is the separation and purification of ethanol by distillation.[10] A simplified representation of the ethanol production is given in Figure 3.

The ethanol price depends on the prices of the feedstock and of a barrel of oil. World ethanol production[11] is of 50 Mt/a. Because of the relatively low selling price of ethanol, by-products credits will be needed for making any ethanol production process economically feasible. Thus, pre-treatment techniques that can produce valuable by-products are receiving research interest.

Three alternatives for the conversion of a base case mill into a biorefinery have been evaluated:
1. production of dissolving pulp and furfural,
2. production of dissolving pulp and xylitol,
3. production of dissolving pulp and ethanol.

RESULTS AND DISCUSSION

Revenues

Currently, by selling[12] Kraft pulp at 500 $/t, the base case mill generates 122.5 M$/a. The potential production of dissolving pulp, furfural, xylitol and ethanol, and the corresponding revenue that the mill could generate as a biorefinery is summarized in Table 1. The following product prices ($/t) have been used in the calculations: dissolving pulp: 800[13]; furfural: 1 000[5]; xylitol: 4 000[8]; ethanol: 620[14].

Table 1
Revenue assessment of a hemicellulose biorefinery

Product option	Production (t/day)	Revenue (M$/a)
Dissolving pulp	518	145
Furfural	35	12
Xylitol	28	39
Etanol	35	7.6

A mill with an integrated hemicellulose extraction and transformation technology could generate significant additional revenue, which will depend on the selected value-added product option.

Energy requirements

The base case mill considered in this study generates steam from 3 types of fuel. The concentrated black liquor is burnt in two recovery boilers, producing high pressure steam. High pressure steam is also generated in a hog fuel boiler and a fossil fuel boiler. The total steam production is of 179 MW. After hemicellulose extraction, the heating value of the spent liquor will be reduced and less steam will be produced. To contribute to the sustainability of the biorefinery and to reduce the operating costs, the fossil fuel boiler will be removed; consequently, the steam production capacity of the biorefinery would be of 119 MW. Data on steam production for the Kraft process and biorefinery are given in Table 2.

Table 3 shows the steam demand of a biorefinery. To produce dissolving pulp and furfural, the biorefinery will require additionally 28.9 MW. In the case of dissolving pulp and xylitol as product options, an additional 9.9 MW of steam will be necessary and, if the mill management chooses to produce dissolving pulp and ethanol, it will need 29.9 MW of steam over the production capacity of the boilers. To satisfy the additional steam demand of the process, the possibility to reduce the steam consumption of the base case mill before its conversion should first be considered. The detailed methodology providing guidelines for the conversion of a Kraft mill into a biorefinery – in an energy and water perspective – has been presented in Part I. The interactions among water system closure, internal heat recovery, condensate return and energy upgrading were analysed, and an in-depth energy optimization study was performed. The implementation of the identified energy efficiency measures reduces the steam consumption in a Kraft process by 46 MW, thus making possible to satisfy the steam demand of the biorefinery. Moreover, extra steam will become available for cogeneration or as a heat source for district heating.

Table 2
Steam production capacity for Kraft process and biorefinery

Fuel	Kraft process (MW)	Biorefinery (MW)
Spent liquor	106	71
Hog fuel	48	48
Fossil fuel	25	0
Total	179	119

Table 3
Steam demand of biorefinery with respect to product options

Product	Steam required (MW)
Dissolving pulp	122
Furfural	25.7
Xylitol	6.7
Ethanol	26.7

CONCLUSIONS

The conversion of a conventional Kraft pulp mill into a dissolving pulp mill represents a feasible approach to create a biorefinery. Hemicellulose, extracted during hydrolysis of wood chips, could be used as a feedstock for value-added products, such as furfural, xylitol and ethanol, allowing the mill to generate additional revenue. The integration of new operations will alter the energy balance of the mill. Steam could be liberated after the implementation of energy optimization measures, to satisfy the new demand and to contribute to the sustainability of the biorefinery. This study has shown that a biorefinery could generate additional revenue for a sustainable pulp and paper mill. Energy optimization is a very important issue to be considered, while transforming a conventional Kraft pulp mill into a biorefinery.

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REFERENCES

[1] M. Towers, T. Browne, R. Kerekes, J. Paris and H. Tran, *P&P Canada*, **108**, 26 (2007).
[2] M. Marinova, E. Mateos-Espejel, N. Jemaa and J. Paris, *Chem*. *Eng*. *Res*. *Des*., **87**, 1269 (2009).
[3] T. Werpy and G. Peterson (Eds.), "Top value added chemicals from biomass", Vol. I, US Department of Energy, 2004, pp. 1-76.
[4] H. Sixta, H. Harms, S. Dapia, J. C. Parajo, J. Puls, B. Saake, H.-P. Fink and T. Röder, *Cellulose*, **11**, 73 (2004).
[5] Furfural market overview, Dalinyebo Trading & Development, 2006, http://www.dalinyebo.co.za/old/dyT/FurfuralMarket.htm.
[6] D. T. Win, *Aust*. *J*. *Technol*., **8**, 4 (2005).
[7] A. J. Melaja and L. Hämäläinen, US Patent 4 008 285 (1977).
[8] K. L. Kadam, C. Y. Chin and L. W. Brown, *J*. *Ind*. *Microbiol*. *Biotechnol*., **35**, 5 (2008).
[9] T.-A. Hsu, in "Handbook on Bioethanol: Production and Utilization", edited by C. E. Wyman, Taylor & Francis, 1996, pp. 179-195.
[10] M. J. Taherzadeh and K. Karimi, *BioRes*. *Online J*., **2**, 707 (2007).
[11] A. V. Desai, *Businessworld*, 20 June, 2008, http://www.businessworld.in/index.php/Columns/Food-Supply-And-Ethanol.html.
[12] The pix pulp benchmarking indexes, *Paper Age*, 2009, http://www.paperage.com/foex/pulp.html.
[13] AV Group ramps up in dissolving market, Business publication Pulp & Paper, September (2007).
[14] G. Grassi, Low cost production of Bioethanol from Sweet Sorghum, European Biomass Industry Association, 2009, http://www.sseassociation.org/SS%20Publications/eubia/giulianograssi%20greenpower%20conference.pdf.