



Titre: Development of Hemicelluloses Biorefineries for Integration Into
Title: Kraft Pulp Mills

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Date: 2014

Type: Mémoire ou thèse / Dissertation or Thesis

Référence: Ajao, O. A. (2014). Development of Hemicelluloses Biorefineries for Integration
Citation: Into Kraft Pulp Mills [Thèse de doctorat, École Polytechnique de Montréal].
PolyPublie. <https://publications.polymtl.ca/1556/>

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Program:

UNIVERSITÉ DE MONTRÉAL

DEVELOPMENT OF HEMICELLULOSES BIOREFINERIES FOR
INTEGRATION INTO KRAFT PULP MILLS

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ÉCOLE POLYTECHNIQUE DE MONTRÉAL

THÈSE PRÉSENTÉE EN VUE DE L'OBTENTION

DU DIPLÔME DE PHILOSOPHIAE DOCTOR

(GÉNIE CHIMIQUE)

SEPTEMBRE 2014

UNIVERSITÉ DE MONTRÉAL

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

Cette thèse intitulée:

DEVELOPMENT OF HEMICELLULOSES BIOREFINERIES FOR
INTEGRATION INTO KRAFT PULP MILLS

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en vue de l'obtention du diplôme de : Philosophiae Doctor

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DEDICATION

To my family,

ACKNOWLEDGMENT

Looking back at the past 4 years, I am leaving with a strong conviction that joining E²D²BF, a creative, supportive and culturally diverse team, was one of the best decisions I ever made.

Special thanks to Prof. Jean Paris, who made this possible in the first place. Thank you for being an inspiration, I am immensely grateful for the opportunity and the conducive environment for independent self-development that you fostered. My gratitude goes to Dr. Mariya Marinova for her advice, encouragement and helping me see my work from a different point of view. Prof. Savadogo, your kind suggestions, support and appreciation of my work means a lot to me. I count myself privileged to have had you all as my team of directors. *Merci à vous tous !*

Part of my work was carried out in the framework of a collaborative project at the *Centre National en Électrochimie et en Technologies Environnementales* in Shawinigan. I am grateful to Dr. Mohamed Rahni and Dr. Hassan Chadjaa and the entire CNETE team for their support.

I would not have made it without the timeless encouragement and words of advice from my dear friends, Miyuru, Indi, Mohammad, Samin, Enrique, Hilda, Walid, Tatiana, Radia and Salomeh.

Morgane, thank you for your interesting work on hemicelluloses and for translating the abstract. Maryam, Sourour, Francois, Olivier, Hana and all my other colleagues that I might not have mentioned here, thanks for the lunch break discussions, potlucks and unpaid French lessons.

Mr and Mrs Olowude, Prof. Akande and Prof. Erdtmann, your constant calls, support and encouraging discussions about your experience as international students in Europe and North America decades ago gave meaning to the African saying “*it takes a village to raise a child*”.

To my family who always found the time to call, visit and also welcomed me in Gastonia or Melbourne whenever I was homesick. Uncle Fola, Aunty Bunmi, the Awobusuyis and Dapo, *Ese gidi gan !*

My deepest gratitude goes to my parents as well as my siblings, Tope, Yemisi and Segun, for their enduring love and support, I'll make up for being absent during your important moments.

Anna and Jerry, it's been 6 years, 6 months and 13 days since you've always been there for me. Thank you for enduring me, I can't imagine myself without your unwavering love through these years. *Anna, du bist das Beste was mir je passiert ist!*

RÉSUMÉ

Le développement des installations de production de biocarburants, de produits biochimiques et de biomatériaux est une condition importante pour réduire la dépendance aux ressources fossiles limitées et permet une transition vers une bioéconomie mondiale. L'industrie des pâtes et papiers en Amérique du Nord est confrontée à une consommation importante d'énergie coûteuse entraînant des coûts de production élevés. D'autre part, elle doit faire face à une concurrence intense de la part des économies émergentes. Les Bioraffineries Forestières Intégrées (IFBR) ont été proposés comme un moyen de diversifier la production, d'accroître les revenus des industries des pâtes et papiers et d'atteindre un aspect durable. Cette intégration est réalisable car elle utilise la biomasse forestière comme source d'alimentation après la transformation du bois. De plus, l'intégration d'un processus de bioraffinerie partageant des infrastructures existantes et des services publics sur le site de l'usine de pâtes permettrait de diminuer les coûts d'investissement et les risques associés.

Les usines de fabrication de pâte par le procédé Kraft présente une possibilité d'intégration de bioraffinerie prometteuse car elles possèdent une étape de pré-hydrolyse pour extraire les sucres d'hémicelluloses avant la mise en pâte du bois ou encore lors du procédé de la mise en pâte. Les hémicelluloses extraites peuvent ensuite être transformées en une vaste gamme de produits à valeur ajoutée, ce qui élargirait la gamme de produits de l'usine réceptrice. Pour un bon fonctionnement d'une bioraffinerie utilisant les hémicelluloses, de nouveaux procédés qui sont techniquement et économiquement implantables sont nécessaires. Il est indispensable d'identifier les produits qui seraient rentables et d'imaginer des processus économes en énergie, qui permettraient aux industries de pâte réceptrice de produire de l'énergie et des produits chimiques et de répondre aux exigences matérielles de l'unité de bioraffinerie. L'objectif de cette thèse est de développer les bioraffineries ciblant les hémicelluloses pour leur intégration dans un procédé de mise en pâte Kraft. Une usine de pâte à papier était l'étude de cas de référence. La transformation des sucres hémicellulosiques par conversion chimique et biochimique en furfural et en l'éthanol comme produits représentatifs pour chaque voie a été étudiée.

En tant que première partie du travail, la faisabilité de la concentration d'un préhydrolysats grâce à une membrane d'osmose inverse a été étudiée. L'étape de concentration est nécessaire afin de

réduire le besoin en énergie pour les opérations de conversion ultérieures et permet de réduire la taille des équipements de traitement. Des solutions reconstituées de préhydrolysats contenant différentes concentrations de glucose, xylose de l'acide acétique, le furfural et syringaldéhyde ont été utilisées pour déterminer la faisabilité de leurs concentrations avec une membrane d'osmose inverse. Les effets de la composition de la solution et des conditions de fonctionnement (vitesse d'écoulement transversale, température et pression) sur la sélectivité de la membrane et le flux de perméat ont été étudiés. Les résultats ont révélé que, indépendamment de la composition de préhydrolysats, la pression d'alimentation et la température présentent l'effet le plus important sur le flux de perméat. Une baisse de flux de perméat a été observée dans toutes les expériences et les mécanismes responsables de cette baisse de flux ont été expliqués. Il a également été confirmé que l'encrassement de la membrane est réversible et que sa régénération peut être réalisée avec succès grâce à un nettoyage avec une solution d'hydroxyde de sodium.

La deuxième partie du travail a été consacrée à la conversion chimique lors de la production de furfural. Une solution de préhydrolysats a été générée en utilisant des copeaux de bois similaires à ceux utilisés par l'usine de référence. Ce préhydrolysats a été utilisé pour évaluer la concentration par membrane nécessaire pour une bonne production de furfural. Le taux de rétention et les caractéristiques de flux de six membranes organiques commerciales fabriquées à partir de différents polymères (polyamide, acétate de cellulose et polypiperazine amide) et avec des seuils de coupure différents (poids moléculaires coupés (MWCO) compris entre 100 et 500 Da ont été comparés. Une membrane présentant une rétention totale des sucres de 99% et un MWCO d'environ 200 Da a été mise en avant pour être la plus appropriée pour un processus de production de furfural à partir des critères suivants: une faible consommation d'énergie pour la concentration et un faible degré de colmatage et des rétentions importantes des composés désirés (sucres, l'acide acétique et du furfural). Le facteur de concentration volumique maximale a été déterminé égale à 4, le dépassement de cette limite entraîne une augmentation de l'encrassement de la membrane. Le nettoyage de la membrane est réalisé avec de l'hydroxyde de sodium par flux inverse, le flux de perméat à 75%, par rapport à une membrane vierge. Un modèle de réponse de surface de surface est développé pour minimiser la baisse de flux lors de la concentration.

La troisième partie de ce travail traite la conversion biochimique lors de la production d'éthanol. Les composés organiques du préhydrolysats qui sont capables d'inhiber la fermentation des sucres en éthanol en provoquant la mort des micro-organismes de fermentation doivent être éliminés.

Les membranes appropriées qui pourraient être appliquées pour la détoxification ont été identifiées lors d'un test de différentes membranes. L'efficacité d'élimination des composés inhibiteurs suivants ont été obtenus: composés phénoliques (20%), furfural (80%), acide acétique (94%) et hydroxyméthylfurfural (89%). La filtration sur membrane peut être utilisée pour la concentration et l'élimination de la plupart des inhibiteurs, elle ne présente cependant pas d'efficacité sur l'abattement des composés phénoliques. L'identification d'une étape de détoxification secondaire avec une haute spécificité pour l'élimination des composés phénoliques a été nécessaire. Des expériences visant à évaluer l'utilisation de l'adsorption sur charbon actif et la floculation avec du sulfate ferrique, de l'aluminium ou de la chitine ont montré que le sulfate ferrique réduit de façon significative la concentration en composés phénoliques en évitant une perte trop importante de sucres. L'élimination des composés phénoliques optimale tout en conservant une quantité importante des sucres a été déterminée en présence d'un rapport des ions fer/phénols: $[Fe] / [Phénols] = 1 \text{ g/g}$ et pour une opération réalisée à un pH compris entre 6,5 et 7,7. Une stratégie de détoxification pouvant être utilisée pour le préhydrolysats a donc été déterminée en combinant la nanofiltration membranaire et la floculation au sulfate ferrique.

Les modèles de simulation pour la production de furfural et d'éthanol à partir des hémicelluloses présentes dans le préhydrolysats ont été développés avec la contribution des résultats expérimentaux. La bioraffinerie pour la production de furfural est composée de 3 étapes : la concentration de préhydrolysats, la transformation des sucres et la valorisation des produits. Un réseau d'échangeurs de chaleur optimisé et une pompe absorbant la chaleur ont été avancés pour réduire la consommation d'énergie. La faisabilité de l'intégration d'énergie et du matériel pour l'intégration de la bioraffinerie a été justifiée et les demandes en électricité peuvent être égalées par la production de l'usine de référence. Une évaluation technico-économique du procédé développé a montré qu'il est économiquement viable et un retour sur les dépenses en capital (ROCE) atteignant 36% peut être obtenu. Le processus de bioraffinerie d'éthanol a présenté un besoin en énergie thermique plus faible que le processus furfural et peut également être intégrée avec succès à l'industrie réceptrice.

Dans la dernière phase de cette recherche, les stratégies pour la mise en œuvre des bioraffineries hémicellulosiques sont proposées pour les usines de pâtes et papiers canadiennes. Une analyse des modifications requises pour les différents types de procédés de fabrication de pâte Kraft, l'optimisation énergétique des approches pour répondre à la demande accrue d'énergie après

intégration, les facteurs à considérer lors de la sélection des bioproduits et les types de collaboration pouvant être utilisés pour réduire les risques et les coûts d'investissement plus faibles ont été approchés.

ABSTRACT

The development and wide spread acceptance of production facilities for biofuels, biochemicals and biomaterials is an important condition for reducing reliance on limited fossil resources and transitioning towards a global biobased economy. Pulp and paper mills in North America are confronted with high energy prices, high production costs and intense competition from emerging economies and low demand for traditional products. Integrated forest biorefineries (IFBR) have been proposed as a mean to diversify their product streams, increase their revenue and become more sustainable. This is feasible because they have access to forest biomass, an established feedstock supply chain and wood processing experience. In addition, the integration of a biorefinery process that can share existing infrastructure and utilities on the site of pulp mill would significantly lower investment cost and associated risks.

Kraft pulping mills are promising receptor processes for a biorefinery because they either possess a prehydrolysis step for extracting hemicelluloses sugars prior to wood pulping or it can be added by retrofit. The extracted hemicelluloses could be subsequently transformed into a wide range of value added products for the receptor mill. To successfully implement hemicelluloses biorefinery, novel processes that are technically and economically feasible are required. It is necessary to identify products that would be profitable, develop processes that are energy efficient and the receptor mill should be able to supply the energy, chemicals and material demands of the biorefinery unit. The objective of this thesis is to develop energy efficient and economically viable hemicelluloses biorefineries for integration into a Kraft pulping process. A dissolving pulp mill was the reference case study. The transformation of hemicellulosic sugars via a chemical and biochemical conversion pathway, with furfural and ethanol as representative products for each pathway was studied.

In the first part of this work, the feasibility of concentrating prehydrolysate solution with a reverse osmosis membrane was studied. The concentration step is required to reduce the energy demand of the subsequent conversion processes and the size of process equipments. Reconstituted prehydrolysate solutions containing different concentrations of glucose, xylose acetic acid, syringaldehyde and furfural was used to determine the feasibility of concentrating with a reverse osmosis membrane. The effect of the solution composition and operating conditions (cross flow velocity, temperature and pressure) on the selectivity of the membrane and

the permeate flux were investigated. The results revealed that irrespective of the prehydrolysate composition, the feed pressure and temperature had the most dominant effect on the permeate flux. A permeate flux decline was observed in all experiments and the mechanisms responsible for the flux decline were elucidated. It was also confirmed that the membrane fouling is reversible and regeneration can be successfully carried out by cleaning with a sodium hydroxide solution.

The second part of this work focussed on a chemical conversion pathway for furfural production. A prehydrolysate solution was generated by using a wood chips furnish that is similar to that of the reference mill and used to evaluate the membrane concentration requirements for furfural production. The retention and flux characteristics of six commercial organic membranes made from different polymers (polyamide, cellulose acetate and polypiperazine amide) and with molecular weight cut offs (MWCO) between 100 and 500 Da were evaluated. A membrane with total sugar retention of 99% and a MWCO of about 200 Da was shown to be the most suitable for a furfural process based on the criteria: low energy requirement for concentration, low degree of fouling potential and high retentions of the desired components (sugars, acetic acid and furfural). The maximum volumetric concentration factor was determined to be 4, exceeding this limit leads to increased fouling of the membrane. Cleaning of the membrane with sodium hydroxide returned the permeate flux back to 75%, relative to a virgin membrane. A response surface model was developed for minimizing the flux decline during concentration.

The third part of this work covered a biochemical conversion pathway for the production of ethanol. The organic compounds in the prehydrolysate, that inhibit fermentation of the sugars into ethanol and cause the death of the fermentation microorganisms, must be removed. Suitable membranes that could be applied for the detoxification were identified during the membrane screening. The following inhibitor removal efficiencies were achieved: phenols (20%), furfural (80%), acetic acid (94%) and hydroxymethylfurfural (89%). Membrane filtration could be used for concentration and elimination of most of the inhibitors, it was however not efficient for the removal of phenolic compounds. The identification of a complementary detoxification step with a high specificity for phenols removal was necessary. Experiments to assess the use of activated charcoal adsorption and flocculation with ferric sulfate, alum or chitin showed that ferric sulfate significantly removes the phenolic compounds relative to sugar loss. To maximize the removal of phenolic compounds, the optimum ratio of iron to phenols ions $[Fe]/[Phenols]$ was found to be

1g/g and the pH between 6.5 and 7.7. A detoxification strategy that can be used for prehydrolysate detoxification was developed by combining nanofiltration and flocculation with ferric sulfate as the coagulant.

Simulation models for the production of furfural and ethanol from hemicelluloses prehydrolysate were developed with inputs from the experimental results. The furfural biorefinery was made up of 3 steps, prehydrolysate concentration, sugars transformation and product recovery. An optimized heat exchanger network and an absorption heat pump for implementation were designed to lower the energy consumption. The feasibility of the energy and material integration of the biorefinery was demonstrated and the utility demands can be met by the reference mill. A techno-economic evaluation of the developed process showed that it is economically feasible and a return on capital employed (ROCE) as high as 36 % can be obtained. The ethanol biorefinery process was shown to have a lower thermal energy requirement than the furfural process and can also be successfully integrated with the receptor mill.

In the last phase of this research, the guideline for the implementation of hemicellulosic biorefineries in Canadian pulp and paper mills are proposed. It included analyses of the modifications required for different types of Kraft pulping processes prior to their conversion into a biorefinery, energy optimization approaches to address the increased energy demand after integration, factors that must be considered during bioproducts selection and types of collaboration that can be used to reduce risk and lower investment.

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LIST OF SYMBOLS AND ABBREVIATIONS

AC	Activated Carbon
adt	Air dry tonne
AFEX	Ammonium Fibre Explosion
AHP	Absorption heat pump
ANOVA	Analysis of variance
Aw	Solvent Transport Coefficient
BBD	Box-Behnken Design
BLGCC	Black Liquor Gasification Combined Cycle System
Bs	Solute Transport Coefficient
CCD	Central Composite Design
CF	Concentration Factor
C _F	Concentration in Feed
COP	Coefficient of Performance
C _P	Concentration in Permeate
d	Depth
D	Diffusion Coefficient at 25 °C
Da	Dalton
DAD	Diode Array Detector
DF	Degree Of Freedom
DME	Dimethyl Ether
DNA	Deoxyribonucleic acid
DNS	Dinitrosalicylic Acid
DOE	Design Of Experiments

DP	Degree Of Polymerization
EBIDTA	Earnings before Interests, Taxes, Depreciations and Amortizations
EBIT	Earnings before interest and taxes
EPA	United States Environmental Protection Agency
F	F-Value
FCI	Fixed Capital Investment
FTL	Fischer-Tropsch Liquid
GAE	Gallic Acid Equivalents
GAP TM	Generator Acid Purification
GDP	Gross Domestic Product
GJ/ODt	Gigajoule per oven dry tonne
h	Height
HEN	Heat Exchanger Network
ICP	Inductively Coupled Plasma
IFBR	Integrated Forest Biorefineries
J _s	Solute Flux
J _v	Solvent Flux
MA	Mixed Alcohols
MCC	Microcrystalline Cellulose
MS	Mean Sum Of Square
Mt/a	Global Market Volume
MVC	Mechanical Vapour Compression
MW	Molecular Weight
MWCO	Molecular Weight Cut Off

NF	Nanofiltration
odt	Oven Dried Tons
p	P-Value
PJ/year	Petajoules/year
pKa	Dissociation Constant
P&P	Pulp and Paper
Q_{P-f}	Final Permeate Flow
Q_{P-I}	Initial Permeate Flow
R_A	Acid Acetic Retention
RI	Refractive Index
RNA	Ribonucleic Acid
RO	Reverse Osmosis
ROCE	Return On Capital Employed
RSM	Response Surface Model
S/N	Signal-to-Noise Ratio
$(S/N)_S$	Smaller is better, Signal-to-Noise Ratio
$(S/N)_N$	Nominal is the best, Signal-to-Noise Ratio
$(S/N)_L$	Larger is better, Signal-to-Noise Ratio
SEW	SO ₂ -Ethanol- Water
SS	Sum of Squares
t	Tonne
T-H	Temperature Enthalpy
TFC	Thin-Film Composites
THF	Tetrahydrofuran

UF	Ultrafiltration
UV	Ultraviolet
VCF	Volumetric Concentration Factor
wt	Weight
w/v	Weight per Volume
ΔP	Transmembrane Pressure
ΔT_{\min}	Temperature Difference
$\Delta \pi$	Osmotic Pressure

INTRODUCTION

Pulp and paper mills in North America have been confronted with a decline in the demand for pulp and paper commodity products, high energy prices and intense global competition from emerging economies with lower production costs in the past decade. The conversion of a pulp and paper mill into integrated forest biorefineries (IFBRs) where lignocellulosic biomass will be converted into a broad spectrum has been proposed as a means for mills to diversify their sources of revenue and become more sustainable. In the past decades, this interest has led to widespread research on the best way to develop IFBRs.

Several alternatives for valorizing cellulose, hemicelluloses and lignin, the three main classes of wood components are being evaluated and in most cases, significant scientific and technological breakthroughs are still required. Several pulp mills in North America are characterized by high energy consumption and ageing equipments that must be upgraded or replaced before a biorefinery process can be integrated. Furthermore, the cost of producing biochemicals, bioproducts or biofuels from woody biomass is higher than for alternative feedstock such as sugar cane or corn due to its higher recalcitrance. Biorefinery processes that are technically and economically feasible must be developed in order for pulp and paper mills to play a role in the emerging bio-economy.

Wood pulping is a mature process that has been carried out since decades using mechanical, chemical or hybrid methods. The Kraft process, a full chemical pulping method, is the most utilized method for pulping globally[1] and it is a cost effective method because most of the chemicals used in the process can be recovered. The pulp produced also has a higher quality than the pulp produced with other methods due to the stronger fibre. Types of pulp that can be produced from hardwoods using the Kraft process include paper grade and dissolving pulp. Dissolving pulp has higher cellulose purity (≥ 96 compared to paper pulp (72-79%)) [2-4]. The hemicelluloses and lignin are typically combusted to produce energy in the Kraft process.

Hemicelluloses are polymers that comprise of hexoses (mannose, glucose and galactose) and pentoses (xylose and arabinose). They are typically burnt in the Kraft process to produce energy but they can be extracted prior to Kraft pulping and diverted for transformation into higher value products in a biorefinery. Hemicelluloses extraction would not lead to a significant reduction of the energy production capacity of the mill because the heating value of hemicelluloses is lower

than that of lignin[5]. On the contrary, the pulp production capacity can be increased if it is constrained by the recovery boiler. A suitable method for extraction must be compatible with the subsequent Kraft pulping step and not lead to a pulp yield reduction or a lower pulp quality. Furthermore, depending on the desired application of the hemicelluloses, attaining an acceptable level of sugar purity and a low amount of toxic compounds that can inhibit fermentation might be necessary.

Bridging the gap between research and implementation of IFBRs requires the development of novel process concepts and the adaption of process operations that would be economically feasible and ready for scale up within a short time frame. This thesis deals with biorefinery technology development and the main focus is to develop hemicelluloses biorefinery processes that can be integrated into Kraft dissolving pulp mills. To achieve this goal, retrofit biorefinery processes were developed for the production of ethanol and furfural from hemicelluloses prehydrolysate. Ethanol and furfural were selected as representative bioproducts via biochemical (fermentation) and chemical conversion pathways respectively. Furfural is a low market volume product while ethanol is a high market volume product. The composition of a prehydrolysate solution is pre-determined by the extraction step of the receptor Kraft process, therefore a dissolving pulp mill was used as a case study.

Concentration of the prehydrolysate stream is necessary to reduce the process equipment size and energy cost in both processes. In addition, the ethanol process requires a detoxification step for the removal of the organic compounds in the prehydrolysate, which are toxic to the fermentation microorganisms. Experiments revealed that nanofiltration membranes can be successfully used for concentration in the furfural process and the conditions that would lead to a low flux decline during membrane were identified with a response surface model. The ethanol process however needed a complementary process step for detoxification. A novel detoxification strategy that combines membrane filtration and flocculation with ferric sulfate was developed to this effect.

The experimental results were used for process design evaluation. Computer based simulation models were developed to compute the mass and energy balances of the alternatives. Energy optimizations of the biorefineries were carried out by performing a heat exchanger design and implementing an absorption heat pump. The level of integration that can be achieved between the receptor mill and the biorefinery plant was determined. The results revealed that energy, material

and chemical demands can be supplied by the receptor mill. The process development methodology has been used to develop practical guidelines for the integration of hemicelluloses biorefineries into Kraft pulp mills.

CHAPTER 1. LITERATURE REVIEW

1.1 Context and Motivation

The forest industry comprising of wood products, pulp and paper and wood derived value added products groups is an important sector of the Canadian economy. It contributes to the GDP, provides export earnings and creates employment. A comparison of the industry indicators for the pulp and paper segment between 2004 and 2011 showed that manufacturing revenues reduced by 28%, and the number of employees by 42 %. Several pulp and paper mills have closed down in Canada in the past decade. The closures can be attributed to a falling demand for paper and paper commodity products as illustrated in Figure 1–1, high production costs, intense global competition and high energy prices. [5] The mills are usually located in rural areas where they serve as drivers for economic activity and the impact of closures are disruptive to the communities.

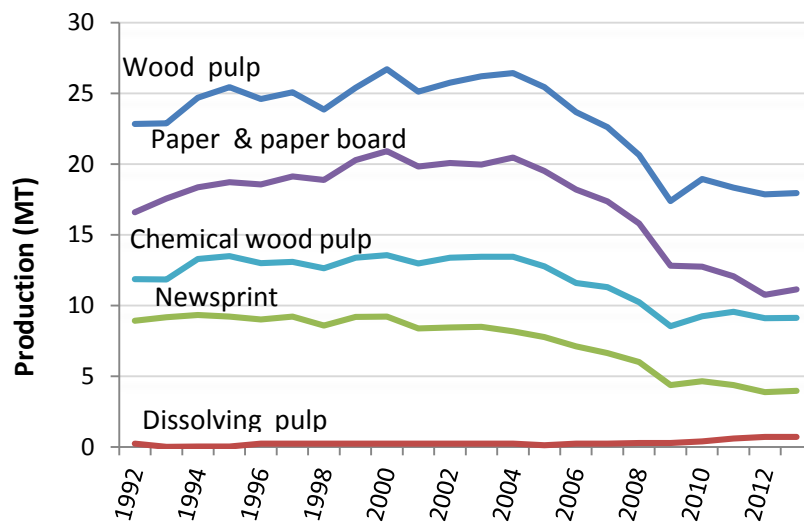


Figure 1–1: Forest industry production trend in Canada [6]

It is therefore imperative to develop a sustainable approach for using forest resources (biomass) in order to prevent the closure of currently operating mills and to also bolster the economy of several regions that are largely dependent on pulp and paper mills.

1.2 Biomass Potential

Biomass can be used to produce a broad spectrum of products that include energy, biomaterials and biochemicals. Biomass resources include sources of wood, wood waste, agricultural crops, algae and aquatic plants. The potential of biomass for different regions is shown in Table 1.1. The consumption in North America constitutes about 16% of the potential.

Table 1.1: Distribution and consumption of biomass by regions, 10^3 PJ/year [7]

Biomass potential	Middle East	Europe	Former USSR	North America	Africa	Latin America	Asia	World
<i>Woody biomass</i>	0.4	4	5.4	12.8	5.4	5.9	7.7	41.6
<i>Energy Crops</i>	0	2.6	3.6	4.1	13.9	12.1	1.1	37.4
<i>Straw</i>	0.2	1.6	0.7	2.2	0.9	1.7	9.9	17.2
<i>Other</i>	0.1	0.7	0.3	0.8	1.2	1.8	2.9	7.6
Total potential	0.7	8.9	10	19.9	21.4	21.5	21.6	103.8
<i>Use</i>	0	2	0.5	3.1	8.3	2.6	23.2	39.7
Use / Potential (%)	0	22	5	16	39	12	107	38

In the past decade, the use of renewable feedstock has gained acceptance as an important means for transitioning towards a global bioeconomy. Dale et al. [8] identified the key features of a mature bioeconomy. The success of industries could depend on factors such as:

- Production capacity and yield: High production yields and efficient processes are necessary, cost advantages improve as the capacity increases but after a certain point diminishing returns could set in
- Integration feasibility: The ease with which a biorefinery can be integrated with other well established processes and locations
- Market saturation: Products from biorefineries have different world demands, an oversupply of a product with a limited market size will lead to market saturation and affect the price
- Feedstock supply: having a guaranteed supply of feedstock is essential for a biorefinery or commodity process such as a pulping mill
- Technology diffusion: The rapid development and deployment of biomass conversion technologies and processes will influence the cost of production
- Substitute products: the availability of substitute products in the target market might pose a competition for bioproducts and hinder commercialization

A bioeconomy can lead to infrastructure development and the creation of jobs that are necessary for running the biorefinery and other associated industries.

1.3 Pulping Processes

Pulping refers to the separation of fibres (celluloses) that are fixed in a wood or plant matrix. Several bonds that exist within the wood structure must be ruptured in the process and it could be necessary to separate the other classes of wood components (hemicelluloses and lignin) from the fibres. Some of the existing methods for pulping can be grouped into four classes: chemi-mechanical and chemical pulping, semi-chemical, chemi-mechanical and mechanical [9]. The classifications are listed in the order of increasing dependence on mechanical energy and increasing dependence on the use of chemicals to facilitate fibre separation. Although mechanical pulping requires a higher amount of energy than the other methods, its main advantage is that a yield of up to 95% of the dry weight of wood can be obtained [4]. Chemical pulping on the other hand has a lower yield but the strength of the produced pulp is higher and the chemicals employed in the process can be recovered, a detailed description of the various pulping processes is available in published literature [4, 9]. Kraft pulping, a full chemical process is the most predominant pulping method in use worldwide and about 89 % of global pulp production is based on this process [1]. The process can be used to produce conventional Kraft pulp and Kraft dissolving pulp.

1.3.1 Kraft Pulp

Wood chips are composed primarily of cellulose (40-45%), hemicelluloses (softwood - 25-30%, hardwood – 30-35%) and lignin (softwood - 25-30%, hardwood – 20-25%) [10]. Delignification can be carried out in either a batch or continuous digester. It is known that the dissolution of lignin is a selective reaction which has three distinct kinetic phases, the initial, bulk and terminal phase [11]. In the first phase, the solubilisation of lignin and some hemicelluloses occurs; the second phase is characterized by selective lignin dissolution until about 90% of all lignin has been dissolved. In the final phase lignin cannot be removed easily without a consequential dissolution of cellulose. The delignification should be stopped prior to the terminal phase to prevent pulp yield losses and quality reduction. A schematic of the Kraft process is shown in Figure 1–2. The active chemical required is white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na_2S).

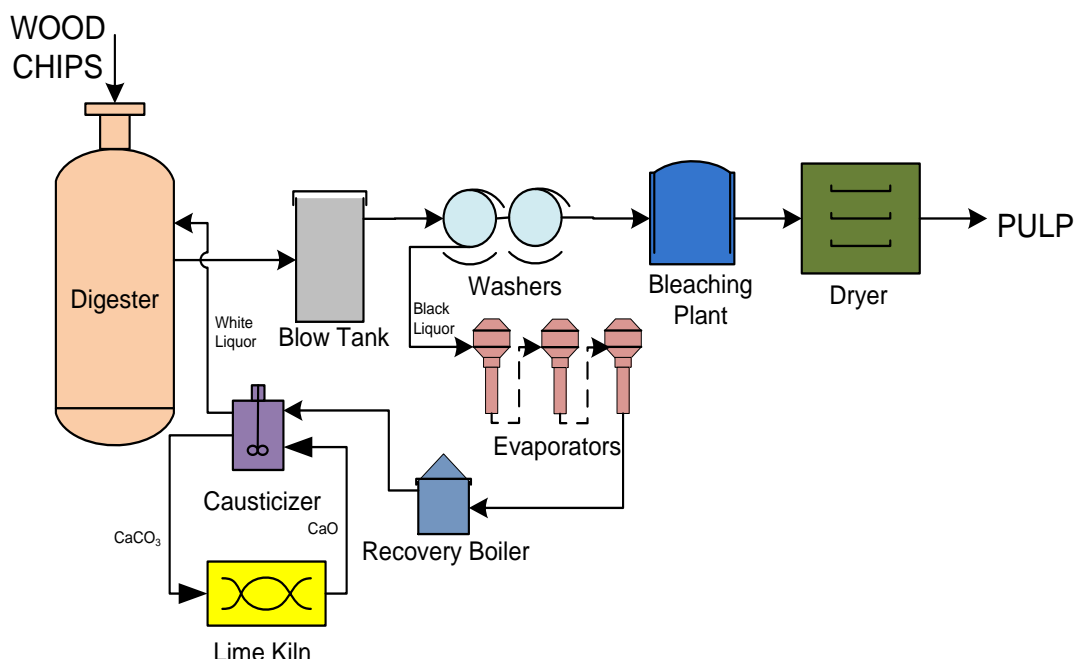


Figure 1–2: A simplified diagram of the Kraft process

Some of the important variables [4, 9] for Kraft cooking include:

1. Wood species and geometry or chip size, especially chip thickness.
2. Liquor sulfidity which is the ratio of sulphides to active alkali, $\text{Na}_2\text{S}/(\text{NaOH}+\text{Na}_2\text{S})$.
3. Ratio of active alkali to the weight of dry wood and liquor to wood.
4. The cooking time and temperature that are conveniently combined to a single parameter the H-factor.

After delignification, the cellulose fibres are separated from the spent liquor (black liquor) using countercurrent washers and subsequently bleached. Bleaching of pulp is carried out to further remove lignin which is present in pulp because not all the lignin present in the wood is liberated during cooking. Results from a study by Gellerstedt [12] indicate that this could be due to a condensation mechanism which involves sulphur elements. It is therefore necessary to control the degree of delignification in order to prevent a deterioration of pulp bleachability. The recovered black liquor is concentrated using a multi-effect evaporator train and sent to the recovery boiler where it is combusted to produce energy. A causticizer is used to regenerate white liquor from the smelt produced in the recovery boiler in a soda lime reaction.

1.3.2 Dissolving Pulp

Dissolving pulp has a higher cellulose content ($\geq 96\%$) than Kraft pulp (72-79%) [3]. The higher purity level is achieved by carrying out prehydrolysis to remove hemicelluloses prior to delignification. Prehydrolysis can be carried out sequentially in the same digester for delignification in a batch process but a separate digester dedicated to prehydrolysis will be necessary if the Kraft process utilizes a continuous digester. Traditional pre-hydrolysis processes use steam or hot at temperatures between 150–180°C but a lower temperature of about 110–120°C would be sufficient if dilute acid is used as catalyst. Some recent mediums for prehydrolysis that have been proposed include a near neutral liquor [13], SO_2 –Ethanol–Water [14], Formic Acid [15]. A comparison of the prehydrolysis methods is difficult because each method requires different levels of investment, level of chemical recovery, operating costs and secondary effects on the wood chips that cannot be quantified at an experimental scale. Furthermore, if the recovery and transformation of the extracted hemicelluloses into sugar based chemicals or fuels is desired, the prehydrolysis method will also influence the investment and operating cost of the biorefinery. Products such as rayon, cellophane and cellulose nitrates can be produced from dissolving pulp [16]. A list of derivatives and end use applications of cellulose is given in Figure 1–3.

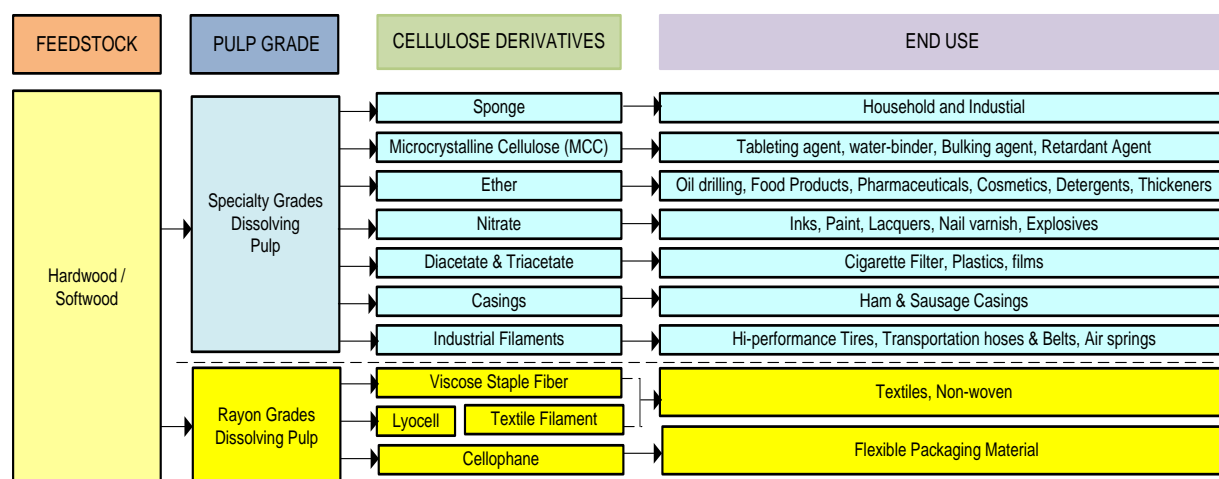


Figure 1–3: Dissolving pulp derivatives and end use [17]

A dissolving pulp process has a lower yield than a Kraft pulp but this could be compensated for by its higher price of the product. Dissolving pulp production is also economically attractive

when the price of wood is low or the prices of substitute natural fibres (cotton) or synthetic fibres (petroleum based) are high. A correlation between the economic feasibility of dissolving pulp production (pulp price) and the price of wood in relation to oil, process yield, pulp and the heating value of black liquor and oil has been proposed by Lonnberg [18].

1.4 Enhancing the competitiveness of Kraft pulp mills

Reported approaches for making Kraft pulp mills more competitive and sustainable can be categorized into three groups:

- Water and thermal energy consumption improvement
- Mill conversion and repurposing
- Development of integrated forest biorefineries

They can all be implemented while a mill is still operational except for the repurposing of a mill, which can be implemented after closure of a mill.

1.4.1 Improvement of water and thermal energy consumption

Improving the thermal energy and water consumption of Kraft pulp mills present an opportunity for cost savings. This is because most of the Canadian mills are older than those in competing countries and their respective consumptions are not at par with other modern mills. Reported typical steam and water consumption for the Canadian pulp and paper industry and the Scandinavian industry that is renowned for its best practice are compared in Table 1.2. Values presented are for both real and ideal mills.

Table 1.2: Steam and fresh water consumption for Canadian and Scandinavian industry [19-22]

	Real Mills		Model Mills	
	Canadian	Scandinavian	Canadian	Scandinavian
Water consumption (m³/adt)	70	15	40	15.9
Steam consumption (GJ/ODt)	22.10	13.20	9.18*	10.4
*Theoretical possible energy consumption				

Improving the water and steam consumption can be achieved by modifying the operating conditions, upgrading or changing inefficient equipments. The required adjustments can be identified by carrying out an equipment performance analysis [23].

Other means of reducing the energy and water consumption are internal heat recovery, water reutilization and energy upgrading. The recovery of internal heat that is hitherto unutilized in a process can be achieved by using the pinch analysis technique [24-26] or mathematical programming [27, 28].

Kraft pulping is a water based process in which the quality of the final product can be influenced by the presence of contaminants. Water contamination occurs during operations such as screening, scraping, equipment/product washing and extraction processes. Water pinch which is analogous to the thermal pinch technique can be used to determine the extent to which water can be reutilized based on the maximum allowable contaminant concentration in each process step [29].

Energy and water consumption are interrelated in the pulping process and a reduction of energy consumption in the form of steam consequently leads to a reduction of fresh water consumption. Methods which involve the simultaneous optimization of energy and water consumption have been proposed by Savulescu et al. [30] and a similar method has been applied for a case study in the pulp and paper industry by Mateos-Espeje et al. [31].

Heat pumps are devices for upgrading low temperature energy that is available in a process to a higher temperature. Heat pumps can be widely used in the petroleum refineries and petrochemical industry, food and beverages, utilities and the forest industry [32]. Areas of application in the forest industry include: black liquor concentration (pulp production), flash steam recovery (paper manufacturing), process water heating (paper manufacturing) and product drying (lumbering). Types of heat pumps include the closed-cycle mechanical heat pumps, open-cycle mechanical vapour compression (MVC) heat pumps, open-cycle thermo-compression heat pumps and closed-cycle absorption heat pumps (AHP). The implementation of an AHP has been shown to be a promising alternative for energy upgrade, especially at high energy costs [33] and guidelines for their implementation have been proposed by Bakhtiari [34].

1.4.2 Mill conversion

Another strategy for improving the economic viability of Kraft pulp mills is the conversion of the mills. Possible mill conversions can be grouped into three different scenarios.

1 Conversion from Kraft pulp to dissolving pulp production

- 2 Conversion from dissolving pulp (back) to Kraft pulp
- 3 Kraft process repurposing

The incentive for converting a Kraft pulp mill into a dissolving pulp mill is primarily an increase in the price of dissolving pulp coupled with increased demand for dissolving pulp. This spurred the conversion of about 5 mills in Canada within the last decade while 3 other mills were under conversion between 2010 and 2012 [2]. The dissolving pulp produced from the converted mill is a higher value product and it can be used to manufacture specialty products. The evolution of the global demand for dissolving pulp is illustrated in Figure 1–4. The yield of the dissolving pulp process (30 - 35% , of the wood input) is lower than that of the Kraft pulp process (~50%) [35]. Therefore, the price of dissolving pulp must be high enough to compensate for the lower process yield and to ensure profitability. Furthermore, hemicelluloses could also be extracted in the dissolving pulp process to provide additional source of revenue.

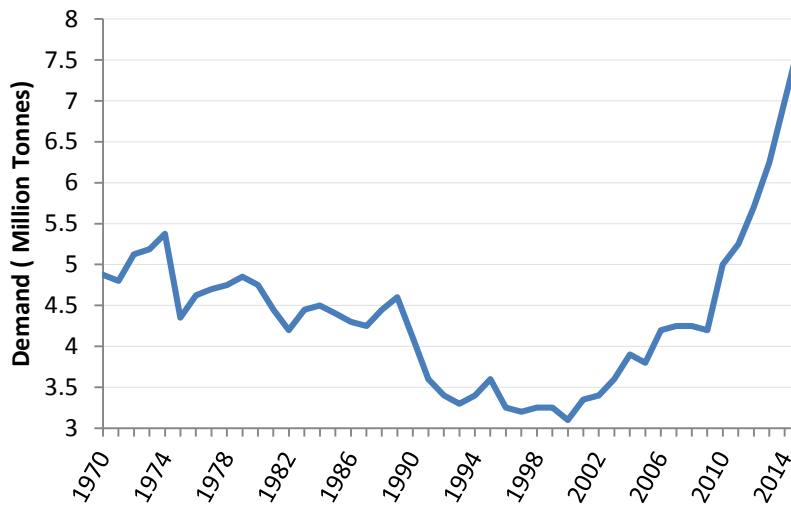


Figure 1–4: Global dissolving pulp demands [36]

The price of dissolving pulp (delivered to China) has fallen from the peak price of about 2,200 US\$ /tonne in 2011 down to about 950 US\$ /tonne in 2014 [36]. This could have been caused by additional dissolving pulp capacity that came online due to the conversion of several mills. Some consequences of the price drop include the reconversion of some dissolving pulp mill back to Kraft pulp, postponing of planned conversion from Kraft to dissolving pulp and implementing phased conversion into dissolving pulp mill to lower capital investment. The ease of conversion

between dissolving pulp and Kraft pulp indicates that both processes are mature with low technological risks. The associated risks are mainly related to the product prices.

Repurposing involves the conversion of a mill to produce a different product other than pulp. The equipments can be used to produce cellulose that can further be hydrolyzed into sugars for sale or for fermentation. Some studies on the repurposing of a mill to produce ethanol have been carried out [37-39]. Ethanol as an end product would not be cost effective in the IFBR context unless the cost of producing the fermentable sugars is low. This is because the value of ethanol is lower than that of pulp or dissolving pulp. A repurposed mill might also be economically viable if biochemicals or bioproducts with a higher price than pulp can be produced at a sustainable cost.

1.4.3 Development of integrated forest biorefineries

An Integrated Forest Biorefineries (IFBR) is the coupling of different biorefinery technologies that utilize lignocelluloses feedstock, with existing pulp and paper mills. In an IFBR with a Kraft pulp mill as the receptor process, the cellulose fraction of the wood feedstock is dedicated to pulp production while part of the lignin and hemicelluloses fractions can be extracted and transformed into value added products for the biorefinery. It is necessary that the extraction of these fractions do not negatively impact the pulp production capacity, chemical balance, power generation and production cost of the base pulping process. The IFBR should be capable of producing a broad spectrum of biochemical, biomaterial and /or biofuels.

Several studies on the integration of biorefineries with existing pulp and paper mills are ongoing. Pulp and paper mills especially Kraft pulp mills are ideal receptors for the integration of biorefinery processes because paper mills have vast experience with securing, handling and processing of biomass, they are situated in proximity to numerous sources of biomass, their thermal efficiencies can be improved to liberate enough for a biorefinery and some mills already have experience with the production of energy from biomass [40].

Different authors have highlighted the motivations, benefits and challenges that need to be surmounted in order to achieve successful integration of a biorefinery as shown in Table 1.3. Although some of the reviewed literature stated slightly varying justifications for why an integrated forest biorefinery should be set up, the reasons are all in mutual agreement and do not stand in contradiction with each other

Table 1.3: Motivations for developing integrated forest biorefineries

Incentive	Challenges (C)and/or limitations (L)	Source
<ul style="list-style-type: none"> • Diversification of business model 	<ul style="list-style-type: none"> • Transformation of the enterprise (C) • Selection of best product and product portfolio (C) • Phasing of biorefinery implementation (C) 	Chambostet al. [41]
<ul style="list-style-type: none"> • Energy affordability • Reduced environmental impact of energy supply 	<ul style="list-style-type: none"> • Shortage of capital for integration (C) • Based on syngas / Gasification only (L) 	Connor [40]
<ul style="list-style-type: none"> • Reliable energy supply • Reduction of emissions • Energy security over the importation of energy 	<ul style="list-style-type: none"> • Protection of core business of the industry (C) • Leveraging on the rare alignment of societal and industrial interests (C) 	Closset et al. [42]
<ul style="list-style-type: none"> • Changes to how forest resources will be processed and utilized 	<ul style="list-style-type: none"> • Research still needed for available technologies to reach level of commercialization (C) • Distinguishing between classes of products (main products, co- products & by products) and their long term interrelationship (C) 	Söderholm et al. [43]
<ul style="list-style-type: none"> • Energy supply assurance 	<ul style="list-style-type: none"> • Potential life cycle of plant (C) • Identifying the best pathways for production (C) • Identification of best projects by comparison of alternatives (C) 	Thorpet al. [44]
<ul style="list-style-type: none"> • Reduced pulp and paper production cost • Diversification of revenue sources for pulp mills 	<ul style="list-style-type: none"> • Smooth integration (C) • Ascertaining the impact of modernizing a mill (C) • Determining the order of magnitude of different biorefinery cases 	Hytönen et al. [45]

An incentive, which stands out from other sources is that biorefinery integration leads to reduced pulp and paper production cost by Hytönen et al. [45]. The focus of biorefineries has shifted in the past 5 years from focusing mainly on biofuels production to the inclusion of biochemicals and biomaterials, despite a smaller market size than for biofuels.

Some types of biorefineries that have been proposed for integration with a Kraft pulping process are gasification, lignin extraction and hemicelluloses extraction [46].

1.4.3.1 Gasification Based Biorefineries

Gasification is the conversion of low quality solids such as wood residue and low quality liquids such as black liquor into a fuel gas. The fuel gas is referred to as either synthesis-gas or syngas and comprises mainly of hydrogen and carbon monoxide. Fuel gas can be combusted in gas turbines for the production of electricity. Products that can be obtained from syngas include Fischer-Tropsch liquid (FTL), Dimethyl Ether (DME), and Mixed alcohols (MA). Consonni et al. carried out a study on gasification based biorefineries for the pulp and paper industry and

concluded that for products such as FTL and DME, the technology for gasification exists commercially and is being used in other non-pulp industries [47]. The challenge for a gasification based biorefinery lies in the integration. Only MA still requires much research on the production technology side. Black liquor gasification has also been proposed by Naqvi as an alternative to the Tomlinson recovery boiler for improving on safety, energy efficiency and the flexibility of a pulp mill [48]. Recently explored technologies for black liquor gasification include the Booster System and the Black Liquor Gasification Combined Cycle System (BLGCC) by Chemrec [49] as well as the Carbo-V® process developed by Choren [50].

1.4.3.2 Lignin Based Biorefineries

The lignin fraction of the wood fed to Kraft pulp mills end up in the black liquor that is normally concentrated using multi-effect evaporators before combustion in recovery boiler to produce energy. In several cases, the recovery boiler operates at its maximum thermal load and cannot be upgraded or replaced due to the high costs. This limits the pulp production capacity of the mill. The recovery and acid precipitation of lignin can be used for increasing the production capacity [51]. In addition, lignin based chemicals such as poly-urethane and vanillin, which can lead to increased revenue, can be produced. Some processes for lignin precipitation include the Lignoboost™ process developed by Innventia and more recent LignoForce System™ developed by FPInnovations [52, 53].

1.4.3.3 Hemicelluloses Based Biorefineries

In Kraft pulp mills, most of the hemicelluloses content from the wood feedstock is dissolved along with lignin during pulping and combusted in the recovery boiler. A better use of the hemicelluloses can be achieved by their extraction prior to pulping and subsequent conversion into value added products. To extract the hemicelluloses, a prehydrolysis step, which is also used in a dissolving pulp mill, is required. The prehydrolysis condition must be optimized to maintain a high pulp yield and maintain the pulp quality (fibre strength, length, bleachability). The composition of the generated prehydrolysate stream must also meet the requirement for the subsequent transformation process. To successfully develop an IFBR, all the steps required for the implementation (the extraction of hemicelluloses, conversion into value added product and the integration of the biorefinery process with a receptor pulp mill) must be studied collectively. Currently, there is limited information on such studies.

1.5 Hemicelluloses: Extraction, Concentration and Conversion

Hemicelluloses are polysaccharides of pentoses (xylose, arabinose) and hexoses (glucose, galactose, and mannose) that bind cellulose and lignin within the cell wall of plants. They rank behind cellulose as the second most abundant natural occurring polymer [54]. They have a lower degree of polymerization compared to cellulose [55, 56] and branches with short lateral chains that result in lower chemical and thermal stabilities, so they are more soluble and easily hydrolyzed [57].

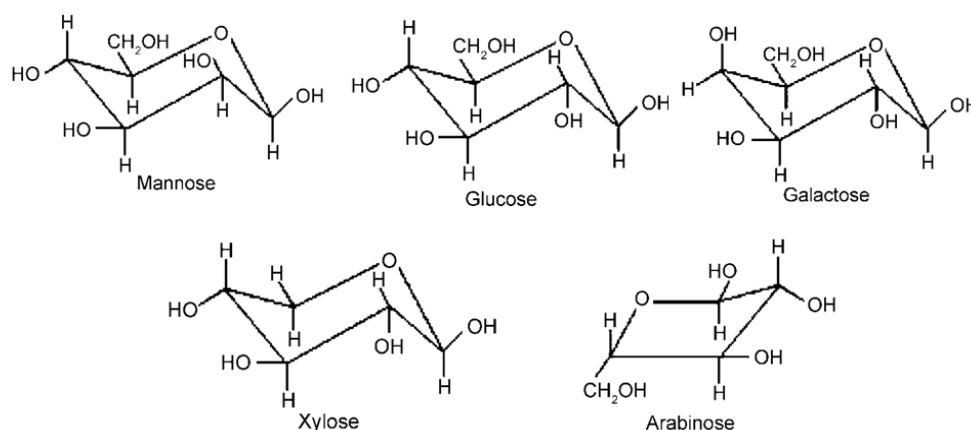


Figure 1–5: Structural representation of hemicellulosic sugar monomers [58]

Hemicelluloses are heterogeneous and their pentose and hexose distribution depends on the type of feedstock as illustrated in Table 1.4. The main difference between hardwoods and softwoods is that hardwood contains a higher fraction of pentoses. This also influences a decision on the target product of hemicelluloses biorefineries.

Table 1.4 Composition of different lignocellulosic materials [59]

	Hardwoods	Softwoods	Maize Straw	Cereal Straw	Recovered Paper
Celluloses (%)	30 -43	40 - 48	35-41	38-40	50-70
Hemicelluloses					
<i>Hexoses (%)</i>	2 – 5	12 -15	2	2-5	—
<i>Pentoses (%)</i>	17 – 25	7-10	15-28	17-21	6-15
Lignin (%)	20-25	26 – 31	10-17	6-21	15-25

1.5.1 Hemicelluloses Extraction

The selective extraction of hemicelluloses from woody biomass is possible because hydrolysis of hemicelluloses occurs more readily than cellulose [60-63]. In general, different methods such as dilute acid and concentrated acids, alkali, hot water, ionic liquids, steam explosion, ammonium fibre explosion (AFEX), ozonolysis and organosolv can be employed [64, 65]. However, selecting a method is constrained because it must not have a negative impact on the subsequent Kraft cooking of the chips, reduce the pulp yield and lower the pulp quality (tensile strength, tear strength, viscosity). The characteristics of the common extraction methods can be compared based on criteria that include: whether biomass size reduction is required, occurrence of lignin degradation, weight ratio of wood chips to aqueous medium, the amount of toxic compounds produced, occurrence of sugar degradation, quantity of sugars extracted, catalyst or regeneration requirement, quantity of waste produced, heat and power requirements. The most suitable method depends on the feedstock and the receptor mill requirement. Compromises have to be made in most cases between these characteristics. Some of the promising methods for the IFBR utilize hot water or steam with acids, alkali, or other solvents as catalysts.

1.5.1.1 Acid pre-treatment

This method is similar to that published in 1982 by Springer et al. [66]. It involves bringing biomass in contact with dilute or concentrated solutions of acids at temperatures between 160-180°C for a period that could range from a few seconds to minutes. The acid catalyzes the hydrolysis of hemicelluloses into sugar monomers. This method has the advantage that the acid charge and temperature which does not result in cellulose degradation is relatively known [67]. Dilute acid extraction can be carried out in a batch or flow through process. Acids that can be employed include nitric acid (HNO_3), phosphoric acid (H_3PO_4), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4). The most commonly used acid treatment catalyst is H_2SO_4 .

1.5.1.2 Alkaline pre-treatment

This requires the use of alkali such as ammonia (NH_3), sodium hydroxide (NaOH) or Lime ($\text{Ca}(\text{OH})_2$) [68, 69]. These processes generally require lower temperatures and pressure in comparison to acid hydrolysis pre-treatment, but consequently have a longer duration that can range from several hours to days, in comparison to a few minutes for dilute acid extraction [64,

68, 69]. An attribute which makes the alkaline extraction unattractive at a large scale is the fact that it is suited to small wood chips size, thus the size of the wood feedstock could need reduction prior to pulping [67]. It has been shown that using alkali pre-treatment is less effective for woody materials than agricultural residue [65]. Another undesired consequence of alkaline pre-treatment methods is the removal of lignin which is important for power generation in the chemical recovery cycle of the Kraft process [69]

1.5.1.3 Hot water or steam pre-treatment

These two methods can be used in Kraft pulp mills and are therefore adaptable for an integrated forest biorefinery. An important advantage of using either water or steam is that the hemicelluloses extraction is free of chemicals that might have to be neutralized, treated or recovered. The process effluents will therefore be easier to manage and the material for the reactor design would be less expensive due to a lesser degree of corrosion. A main difference between steam and hot water hydrolysis is that the extracted hemicelluloses remain within the wood chips when steam is used [3] while it is solubilised with hot water [70]. In a typical Kraft process, steam hydrolysis is followed by neutralization with a mixture of hot black liquor and white liquor, and this leads to a degradation of the sugars. Steam hydrolysis is more suitable when the main goal of the Kraft process is dissolving pulp and valorization of the sugars is not envisaged. Hot water hydrolysis on the other hand is advantageous when the hemicellulosic sugars are to be recovered for conversion in a biorefinery.

1.5.1.4 Other emerging extraction methods

Near neutral extraction method involves the use of chemicals already existing in the Kraft pulping process (a mixture of green and white liquor). A technical and economic analysis of this process has been carried out by Mao [13]. A complementary study has also been carried out by Umet et al. [71] and the mass balance was shown to be exact. Some of its reported advantages include the pulp quality and quantity being unchanged; it also brings about a reduction of the amount of organics in the black liquor. This reduction makes it possible to increase the pulp production if it is constrained by the calorific capacity of the recovery cycle. A disadvantage of the near neutral method is that the amount of extracted sugar is less than with the acid or hot water method. Inorganic salts are also introduced to the sugars stream. The use of organic solvents (organosolv) can also be employed for the extraction of hemicelluloses. Some of the

alternative solvents that have been reported include ethanol, formic acid, methanol, glycerol, acetone, propylene and 1,4 –butanediol. A mineral acid or alkali catalyst could be used as a catalyst for the solvents. One of the main advantages of this method is that it can be used for fractionating widely varying feedstock such as hardwoods, softwoods, municipal lignocellulosic wastes and agricultural residue [72]. The lignin fraction produced also has a low molecular weight and narrow distribution, and it can be separated easily from the pulping solvent [73, 74]. The use of formic acid or SO₂-Ethanol-Water (SEW) Pulping has been shown to prevent the formation of sticky lignin [14]. A major challenge associated with organosolv is that the solvent must be recovered and regenerated.

1.5.1.5 Selection of an extraction method for an IFBR

The cost effectiveness can be used as a selection criterion for the extraction methods but it is difficult to determine the costs associated with each method due to feedback effects which cannot be quantified directly in the pulping process. The pentose and hexose components of hemicelluloses have different degrees of resistance to the extraction methods, therefore a different method will be required for softwoods and hardwoods [75]. A list of some hemicelluloses extraction methods that have been proposed in the framework of an integrated forest biorefinery is given in Table 1.5. A direct comparison of the methods is not always possible as different feedstock, and conditions were used in all cases.

Table 1.5: Some proposed methods for hemicelluloses extraction in forest biorefineries

Method	Wood Species	Key Features	Ref
Near Neutral	Mixed hardwood	Green liquor is available in the Kraft process	[13]
NaOH	Aspen wood	Low temperature and clean prehydrolysate stream	[76]
White liquor	Birchwood	No decrease in pulp yield and paper strength properties	[77]
Hot water	Sugar maple wood	Significantly accelerates Kraft delignification	[78]
SO ₂ -Ethanol-Water	Spruce	Prevents the formation of sticky lignin	[14]
SO ₂	Maple, aspen & birch mix	High sugar monomers yield	[70]
Green Liquor	Eucalyptus	Increased pulping efficiency, lower black liquor solids	[79]
Formic acid	Southern hardwood	High sugar monomers concentration	[15]

The selection of a method for a specific biorefinery requires an evaluation of the Kraft pulp quality and impact on the Kraft process. These are acceptable criteria especially when the targeted hemicelluloses derivative has a lower value than the pulp.

1.5.2 Hemicelluloses Concentration and Detoxification

The prehydrolysate stream extracted prior to Kraft pulping usually contains less than 30 g/L of sugars. As shown in Table 1.6, it also contains lesser quantities of other organic compounds, furfural, phenolic compounds and organic acids. The typical sugar composition of the hemicelluloses extract is too low for subsequent conversion processes. It would lead to high energy requirement and cost due to the size of equipments. A concentration step is therefore necessary for process intensification (a reduction in the size of equipments or number of required unit operations).

Table 1.6: Composition of mixed maple aspen prehydrolysate solution [80]

Components	Concentration (g/L)
Pentose [†]	17.1
Hexose [†]	4.1
Phenolics	4.7
Acetic Acid	3.8
Furfural	0.7
Hydroxymethylfurfural	0.09
Lipids	0.2
Na	0.02
Ca	0.15
K	0.04
[†] Total monomers and oligomers	

Two potential methods can be employed for the concentration of prehydrolysate streams at an industrial scale, evaporation and membrane filtration. Types of evaporators include vacuum evaporation and multi-effect evaporators. The latter uses a series of evaporator vessels with each operating at a lower pressure than the previous. As a result of the boiling point decrease due to a lower pressure, the vapour that exits an evaporator vessel can be used to heat the subsequent vessel thus reducing the total energy consumption significantly. Nevertheless, evaporation is characterized by a high consumption of energy due to the phase change required. In comparison, membrane filtration requires a lower amount of energy because no phase change is involved. Energy savings of up to 84 % can be achieved through the use of membranes for sugars concentration in place of evaporators [81]. It is a well established method for concentrating dilute sugar streams and has also been proposed as a means for separation and purification of wood derived hemicelluloses [82]. Depending on the size and form of the hemicellulosic sugars, three

different membrane classes, Reverse Osmosis (RO), Nanofiltration (NF) or Ultrafiltration (UF), can be used for the recovery of the sugars as shown in Figure 1–6.

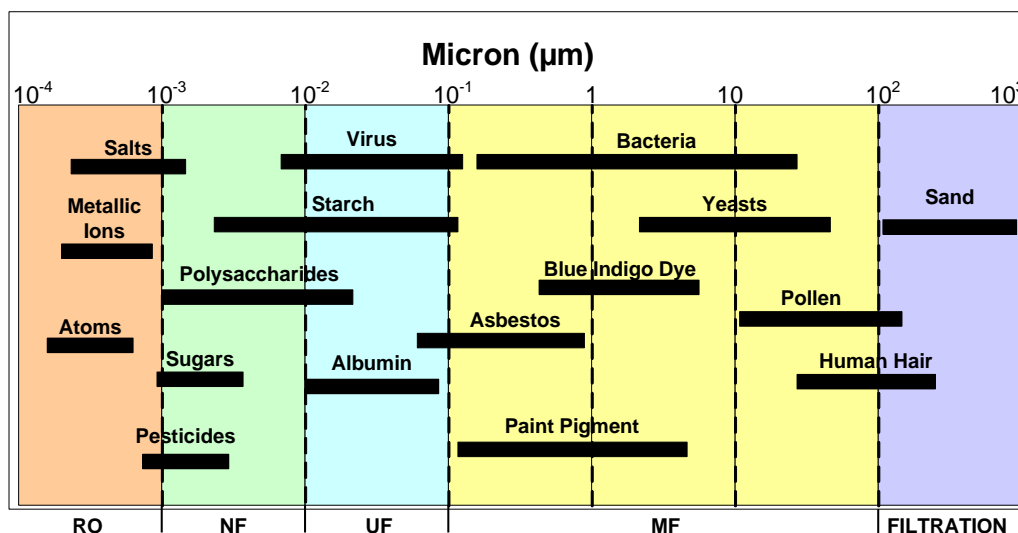


Figure 1–6: Classification of membrane filtration based on pore size

1.5.2.1 Membrane Concentration and Detoxification

RO, NF and UF utilize a pressure gradient to drive the diffusion of a solute and solvent through the membrane filter. The stream that is retained is referred to as concentrate or retentate while the stream that traverses the membrane is known as the permeate. The permeate flux is directly proportional to the pressure gradient. The retention (rejection) is measure of the selectivity of a membrane and can be calculated from $R = (1 - C_p/C_f) \times 100$, where C_p and C_f are solute concentration in the permeate and feed streams respectively. The retention exhibited by a membrane depends on three set of factors [83]:

1. Membrane intrinsic properties e.g. molecular weight cut off (MWCO), electrostatic charge and hydrophobicity
2. Feed solution characteristics e.g. solutes molecular size, electrostatic charge, geometry and hydrophobicity, the ionic strength and pH of the solution, presence of organic and inorganic compounds
3. Operating conditions and parameters e.g. cross flow velocity, trans-membrane pressure, flow channel configuration

Most state-of-the-art organic membranes are thin film composites (TFC) that have a dual layer, a thin layer that is selective and a porous support layer [84]. The three main kinds of active layers are made from cellulose acetate, polyamide or polypiperazine amide, and they all have different properties. The membrane requirement for prehydrolysate concentration depends on the desired hemicelluloses derivative as shown in Figure 1–7. The removal of only water might be sufficient in applications that involve a thermo-chemical conversion of the sugars while the removal of the toxic compounds (acetic acid, furfural and phenolics) might be necessary when fermentation of the sugars by microorganisms will be carried out.

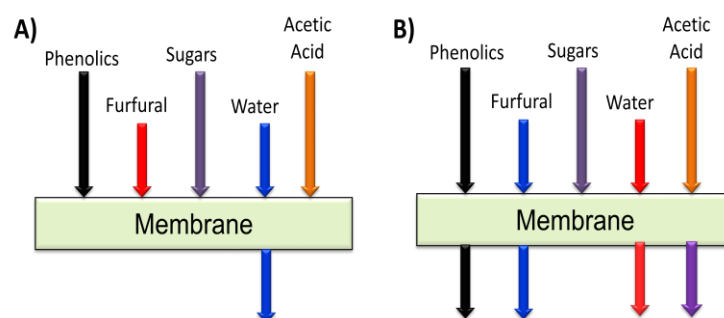


Figure 1–7: Membrane requirement for A) concentration B) concentration and detoxification

It is difficult to predict the separation of components that can be achieved for the prehydrolysate solution because the organic compounds have different molecular weights, degree of ionization, hydrophobicity and hydrophilicity. The classifications of some compounds that can be found in a hemicelluloses prehydrolysate solution are shown in Figure 1–8.

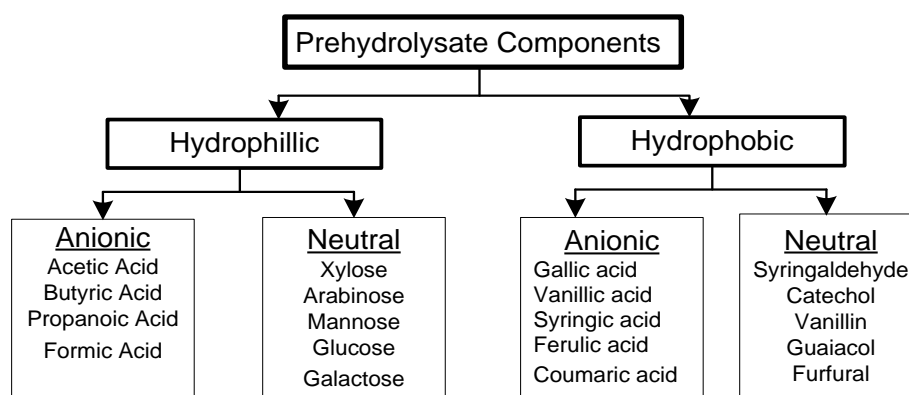


Figure 1–8: Classification of organic compounds in hemicelluloses prehydrolysate

Previously reported studies on prehydrolysate treatment were carried out under different experimental conditions; using prehydrolysate generated with different methods, and mainly with

the objective of producing fermentation based biofuels but not chemicals. The retention mechanisms of some of the organic compounds are considered to be complex and contrasting explanations have been reported [85]. In process applications, data on rejection of organic compounds by high pressure membranes have been derived mainly from pilot and industrial scale experimental observation and this has resulted in only empirical and limited knowledge [86].

Several challenges limit membrane applications in hemicelluloses based biorefineries: Firstly, identifying and selecting a membrane for specific hemicelluloses prehydrolysate solutions is required. In addition, the operating conditions (temperature, pressure and cross flow velocity) must be identified and the target flux level for different concentration factors must be defined. The viscosity of a prehydrolysate solution increases during concentration and as a result, the permeate flux might become too low and place a limit on the extent of concentration that can be achieved. Lastly, several flux decline mechanisms might occur over the life of the membrane at intervals which could range from a few days to months. This makes it mandatory to evaluate whether the flux decline would be tolerable or if it would necessitate regular membrane cleaning and replacement. The main causes of flux decline include compaction of the membrane, concentration polarization, increased osmotic pressure and fouling [87, 88].

Compaction (creep) is a reversible or irreversible deformation of the membrane active layer due to physical compression [89] and it decreases the permeability of the membrane. Creeping of the membrane is dynamic and a function of the state of the membrane, the pressure to which it is subjected and the duration of exposure [90]. In membrane applications, carrying out a pre-compaction of the membrane prior can be used to limit the consequent flux decline during filtration operation.

During concentration of a solution, the osmotic pressure which depends on the solute concentration increases. Consequently, this reduces the permeate flux and a higher operating pressure would be required to return the permeate flux to the desired level. The flux decline can be compensated by increasing the operating pressure for membranes that have a high permeate flux at its lower operating pressure limit.

Concentration polarization is a phenomena that occurs when solutes accumulate near the membrane active surface due to convective mass transport, and lead to a lower trans-membrane flux [91]. Consequently, the solute concentration near the surface exceeds that in the feed

solution [92] and this can also lead to scaling, precipitation and crystallization on the membrane surface [93]. Concentration polarization can be controlled by the cross flow velocity of the feeds solution and the use of a temperature high enough to reduce precipitation where applicable.

Fouling is an increase in resistance to mass transfer that takes place when materials (foulants) that interact with the membrane surface are deposited and accumulate on the active layer. It leads to a reduction of the permeate flux and can also change the retention characteristics of a membrane.

The main types of foulants can be grouped into four categories [94, 95]:

- Particulates inorganic or organic colloidal particles
- Microorganisms that cause the formation of a biofilm on the membrane surface
- Organic matter that are adsorbed on the active surface of the membrane
- Inorganic dissolved components that cause scaling due to their limited solubility

Fouling is inevitable but it can be managed, reduced and the membranes can be cleaned periodically. The development of cleaning strategies and fouling resistant membranes has evolved to be a research area [96-98]. Currently proposed approaches for cleaning include physical strategies (flushing, scrubbing, sonication and vibration) [99, 100], chemical reaction strategies (solubilisation, hydrolysis, saponification, dispersion and chelation), and biological strategies (enzymes, bacteriophages) [101, 102]. A decline ranging from insignificant to almost 100 % decline of the permeate flux has been observed during the concentration of hemicelluloses prehydrolysate [80]. The retention characteristics of a membrane can be altered by all the flux decline mechanisms.

1.5.2.2 Detoxification of hemicellulosic prehydrolysate

In addition to C₅ and C₆ sugars, hemicelluloses prehydrolysate solution also contains furans (furfural and hydroxymethylfurfural), organic acids (acetic and formic acids) and phenolic compounds (syringaldehyde, vanillin), which are toxic for fermentation microorganisms. These compounds (inhibitors) are the degradation products of hemicelluloses, celluloses and lignin, which are produced during the extraction step [103].

Organic acids are generally weak acid and they exhibit incomplete dissociation in water. Their effect on fermentation microorganisms is pH dependent [103]. In the case of yeast fermentation, the undissociated acid penetrates the cell membrane and dissociates in the cell cytoplasm where it

lowers the otherwise neutral pH [104]. The cell consequently tries to regulate the pH by diverting energy to pump out the protons (H^+) ions, this leads to inhibition of cell growth and death [105]. Both furfural and hydroxymethylfurfural (furans) inhibit the metabolism pathway of many organisms (growth). The synthesis of protein and RNA is deteriorated; there is breakdown of DNA and a decrease of ethanol yield in a similar manner due to both inhibitors [104, 106, 107]. The inhibition mechanisms for the phenolic compounds are not well understood but a proposed mechanism is that it breaks down biological membranes resulting in a loss of integrity and difficulty for the membrane to have a selective barrier [107, 108]. The low molecular weight phenolic compounds are considered to have the inhibitoriest effect on fermentation microorganisms [105, 109].

The extracted sugars are mainly in oligomeric form with a low fraction of monomers. A finishing hydrolysis step using inorganic acids or enzymes is required to convert the sugar oligomers into monomers because microorganisms only ferment the sugars in monomer form. The use of an acid hydrolysis method leads to the production of more inhibitors for the fermentation microorganisms that produce biofuels such as ethanol [110-112] and butanol [113-116]. Enzymatic hydrolysis on the other hand produces less inhibitory compounds but it is itself affected by the presence of inhibitors [117-119] and it has longer hydrolysis duration. Its milder hydrolysis conditions, high sugar monomers yield and absence of corrosive inorganic acids that introduce metal ions into the prehydrolysate makes the use of enzymes a widespread method for hydrolysis. The tolerance to different amounts of inhibitors is organism specific and the presence of several inhibitory compounds could also lead to a synergy effect. The removal of the compounds is therefore an important step in the development of hemicellulosic biorefineries.

Detoxification refers to the removal of the inhibitory compounds from the prehydrolysate solution. The selection and use of an appropriate membrane during the concentration step could help to achieve a simultaneous partial detoxification of the prehydrolysate. Efficient and near complete removal of organic acids and furans from a sugar maple prehydrolysate solution with a nanofiltration membrane has been demonstrated [115]. However, only about 50% of the phenolic compound could be eliminated during the process. A complementary detoxification method would therefore be required to achieve a high removal of all inhibitory compounds. Detoxification methods can be classified as chemical, physical and biological as shown in Table 1.7.

Table 1.7: Classification of different detoxification methods for inhibitors removal

METHODS	FEATURES	REFERENCES
Physical		
<i>Membrane</i>	Nanofiltration or ultrafiltration membranes (pressure driven)	[82, 115]
<i>Evaporation</i>	Vacuum evaporation (thermal energy driven)	[120]
Chemical		
<i>Neutralization</i>	Addition of alkali e.g. $\text{Ca}(\text{OH})_2$, NaOH or NH_4OH	[121, 122]
<i>Overliming</i>	Use of $\text{Ca}(\text{OH})_2$ to raise pH to ≈ 10 before neutralizing	[121, 123]
<i>Activated charcoal</i>	Variables are Temperature, pH, ratio of charcoal to liquid	[124-126]
<i>Ion exchange resins</i>	Functional groups important for selectivity	[125-128]
<i>Extractive solvents</i>	Use of solvents such as ethyl acetate, Trialkylamine	[107]
<i>Oxidative processes</i>	Use of hydrogen peroxide (H_2O_2) or ozone (O_3)	[129]
Biological		
<i>Microbial treatment</i>	Use of bacteria, fungi and yeasts	[106, 130]
<i>Enzymatic treatment</i>	laccase or peroxidase for phenolics removal	[106, 131]

The inhibitory compounds have widely varying characteristics (molecular weight, degree of ionization, solubility, volatility and conductivity) hence it is not feasible that a single method would be capable of eliminating all inhibitors. A detoxification strategy for the hemicellulose prehydrolysate in an IFBR can be developed by combining two or more methods.

A suitable detoxification method or strategy should have the following characteristics:

1. Concentration and detoxification of the prehydrolysate stream should be feasible
2. Lead to removal of volatile and non-volatile inhibitors
3. Be selective for inhibitors removal and not lead to loss of hemicellulosic sugars
4. Have a low energy requirement
5. Have a short duration
6. Regeneration of the chemicals or materials employed should be cost effective
7. Generate no waste
8. Contain no compounds or ions that could be potential inhibitors

The development of a detoxification strategy must be case specific and should only be developed after the hemicelluloses extraction method has been optimized for low inhibitors production

1.5.3 Hemicelluloses Conversion Pathways and Derivatives

Hemicelluloses can be utilized directly or after a chemical or biochemical transformation into a broad range of products in different industries as shown in Figure 1–9. The prehydrolysate solution is a crude mixture of pentoses and hexoses and other inhibitory compounds. To use the sugars directly, pure sugars could be required and this is a drawback for prehydrolysate use. Other promising uses of the hemicellulosic sugars include for the production of enzymes, ethanol, organic acids and furfural and xylitol [1, 132]. Some of the derivatives can only be produced from either pentoses or hexoses, therefore the sugars composition (ratio of pentoses to hexoses) should be an important factor for selecting a target product.

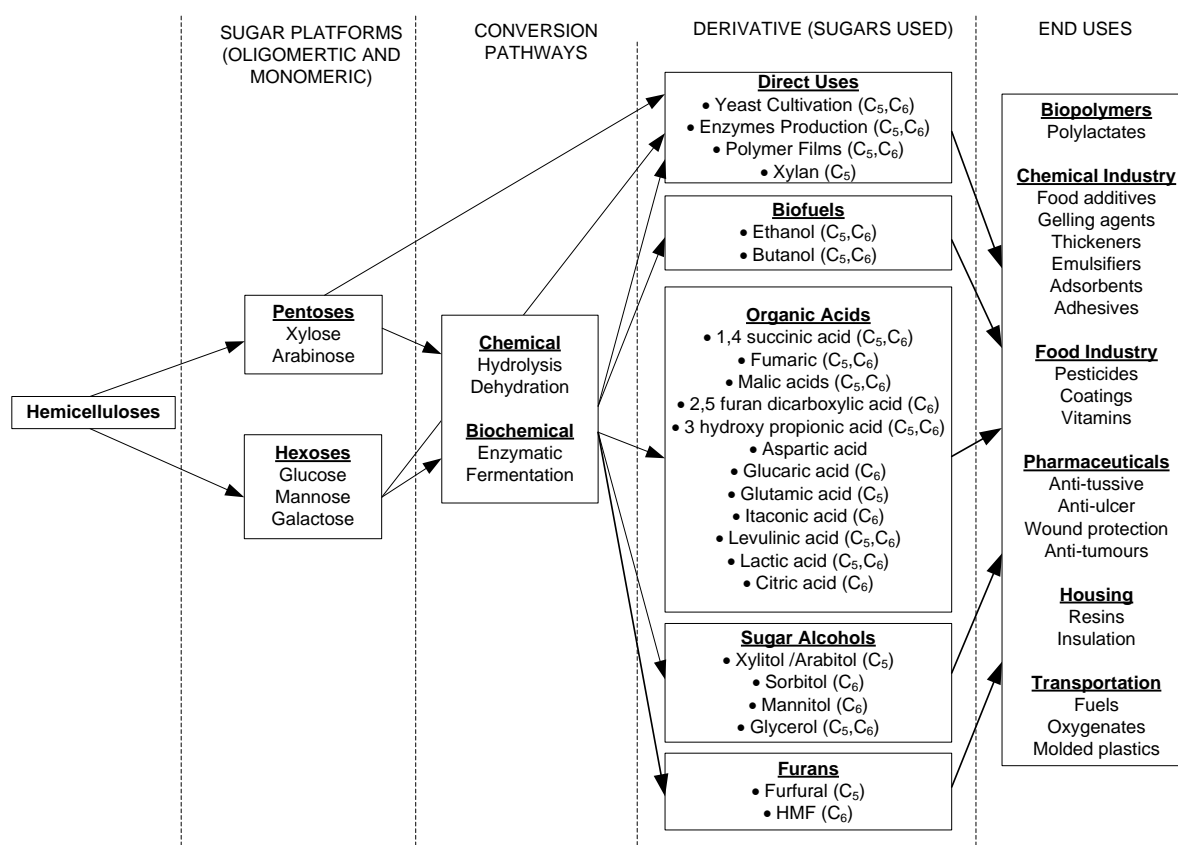


Figure 1–9: Schematic hemicelluloses derivatives production and end uses

The development of technologies that can be used industrially is required for most of the proposed products. An example of a mature biochemical conversion process for the transformation of sugars is ethanol production. The production of ethanol from the hemicellulosic sugars would be advantageous because both the pentose and hexose fractions can be utilized. Some of the most studied organisms for the production of ethanol are the yeasts (*saccharomyces*

cerevisiae and *pichia stipitis*) and bacteria (*escherichia coli* and *zymomonas mobilis*) [110, 133]. Essential characteristics for any selected organisms include: having a high ethanol yield, being tolerant to ethanol, resistant to inhibitors, capable of carrying out fermentation at a low pH and being able to utilize a broad range of substrates [134]. *Saccharomyces cerevisiae* is the most commonly used ethanologens but its disadvantage is the inability to ferment xylose (pentoses) [135]. To correct this, yeasts that can ferment xylose have been discovered through investigation and genetic modification [136, 137].

Another promising chemical that can be produced from hemicelluloses prehydrolysate is furfural. In contrast to ethanol, only the pentose fraction is utilized for furfural production and a chemical conversion process is required. Two sets of reactions in series are required for furfural formation. In the first reaction, the hydrolysis of the pentose oligomers into monomers takes place while in the second reaction, a dehydration reaction to remove three molecules of water from the pentose to form furfural occurs. Both reactions require identical conditions (high temperature, high pressure and a low pH). The kinetics of the hydrolysis reaction is faster than the formation of furfural [138], hence both reactions can be carried out in the same reactor. Several existing and proposed furfural production processes have been reported [138-142]. Furfural can be utilized directly or converted into derivatives for use in a wide range of industries.

1.6 Critical Review

There have been several suggestions on approaches to the development of an Integrated Forest Biorefinery (IFBR). Most of them however focus on specific aspects and not the entire process chain. Examples of this include: product selection [143, 144], pre-treatment and hemicelluloses extraction [67, 70, 79, 145-148], production technology and optimization [6, 149, 150] and products recovery [151, 152]. A comprehensive investigation that combines all steps of the process could lead to the identification and development of novel processes and implementation methodologies. In addition, it is necessary to determine and maximize the levels of material, energy and chemical integration that can be achieved between the biorefinery plant and receptor Kraft pulp mill. This could significantly enhance the technical and economic feasibility of forest biorefineries.

Based on the review of literature, the following areas were identified to require further investigation:

- There is limited knowledge on the implementation of membrane filtration as an energy efficient method for the concentration and detoxification of prehydrolysate solution
- Energy requirement minimization and upgrading are rarely considered in proposed biorefinery processes for integration into Kraft pulp mills
- Previous studies focused mainly on the production of biofuels and there is lack of knowledge on integrated biorefineries for the production of biochemicals
- The energy, material and chemical integration of an hemicelluloses biorefinery with a receptor Kraft process is not typically evaluated
- Only few studies involving the techno-economic evaluation of a hemicelluloses based IFBR has been carried, previous work focused on biorefineries using agricultural feedstock
- The modifications required to a receptor mill are not typically taken into consideration while selecting a biorefinery product
- Hemicelluloses biorefinery proposals are developed under different hypothesis, no practical guidelines for implementation exists

All the above mentioned points were treated in this thesis.

CHAPTER 2. METHODOLOGY, OBJECTIVES AND THESIS ORGANIZATION

2.1 Objectives

The literature review showed current work on a broad range of methods for extracting hemicellulosic sugars from wood chips prior to pulping, the potential conversion pathways and some hemicelluloses derivatives. Despite the well known hemicelluloses conversion mechanisms and the end uses of the sugars that have been proposed, based on laboratory scale studies, significant scientific and technological breakthroughs are necessary to enhance industrial applications and commercialization. Hence, the development of processes that can be implemented in Kraft pulp mills for the valorization of hemicelluloses deserves investigation.

This research deals with biorefinery process technology development and the main objective is to develop energy efficient and economically viable hemicelluloses biorefineries for integration into Kraft pulp mills.

The sub objectives are:

1. To propose novel wood prehydrolysate concentration techniques for hemicelluloses biorefineries and evaluate their feasibility
2. To develop detoxification strategies for wood prehydrolysate, and evaluate their feasibility
3. To develop and evaluate hemicellulosic biorefinery processes suitable for integration into Kraft pulp mills based on the previous objectives
4. To optimize the energy and material requirements of the biorefineries and determine the degree of integration with a receptor mill that can be achieved
5. To propose practical guidelines for the implementation of forest biorefineries in the Canadian forest industry sector

2.2 Methodology

Two products, furfural and ethanol, were selected as case studies in order to bracket the range of conversion pathways, product value and the size of the market for hemicelluloses derivatives. These products are representative for a chemical and biochemical conversion pathways. However, the identification of novel process technologies for each pathway would be applicable for other bioproducts with similar pathways. A qualitative comparison of the differences between the products is given in Table 2.1. The prices are given in US\$ (globally adopted currency) to enable a comparison.

Table 2.1: Comparison of biorefinery products selected as case studies

	FURFURAL	ETHANOL	Ref
Conversion Pathways	Chemical (Dehydration)	Biochemical (Fermentation)	-
Selling Price (\$/t)	1,400-1,500	695*	[153, 154]
Market Volume (Mt/a)			
<i>Global (Mt/a)</i>	0.35	69	[155, 156]
<i>North American (Canadian)</i>	0.02 (n/a)	41 (1.6)	[156, 157]
* 0.55 \$/L, Prices for August 2014 in the US			

An eastern Canadian Kraft dissolving pulp mill that produces 670 odt/d (odt = oven dried tons) of dissolving pulp from hardwood (a mixture of maple and aspen) was selected as a receptor mill.

The process development methodology consisted of different aspects:

1. Experimental investigation to generate data
 - a. The prehydrolysate generation experiments were carried out at FPInnovations, 570 St Jean, Pointe-Claire, QC H9R 3J9
 - b. The experiments on membrane concentration and the development of a detoxification strategy were conducted at the Centre National en Électrochimie et en Technologies Environnementales, 2263, avenue du Collège, Shawinigan (QC) G9N 6V8
2. Computer based process simulation and integration studies at Polytechnique Montreal

All the prehydrolysate solutions that were used in the concentration and detoxification experiments were generated from a wood furnish similar to that of the case study receptor mill. The proximate compositions of the wood species are given in Table 2.2.

Table 2.2: Composition of wood species used for generating prehydrolysate solutions

Percentage Composition %	Maple	Aspen
Arabinan	0.9	0.5
Xylan	15.7	16
Mannan	2.3	2.1
Galactan	0.6	0.4
Glucan	47.9	53.5
Cellulose	44	49.6
Hemicellulose	23.4	22.9
Lignin	30.7	24.3
Acetone extractives	1.9	3.2
Total	100	100

The process simulation was based on the capacity of the receptor mill. The methodology for the process development for the biorefineries is illustrated in Figure 2–1.

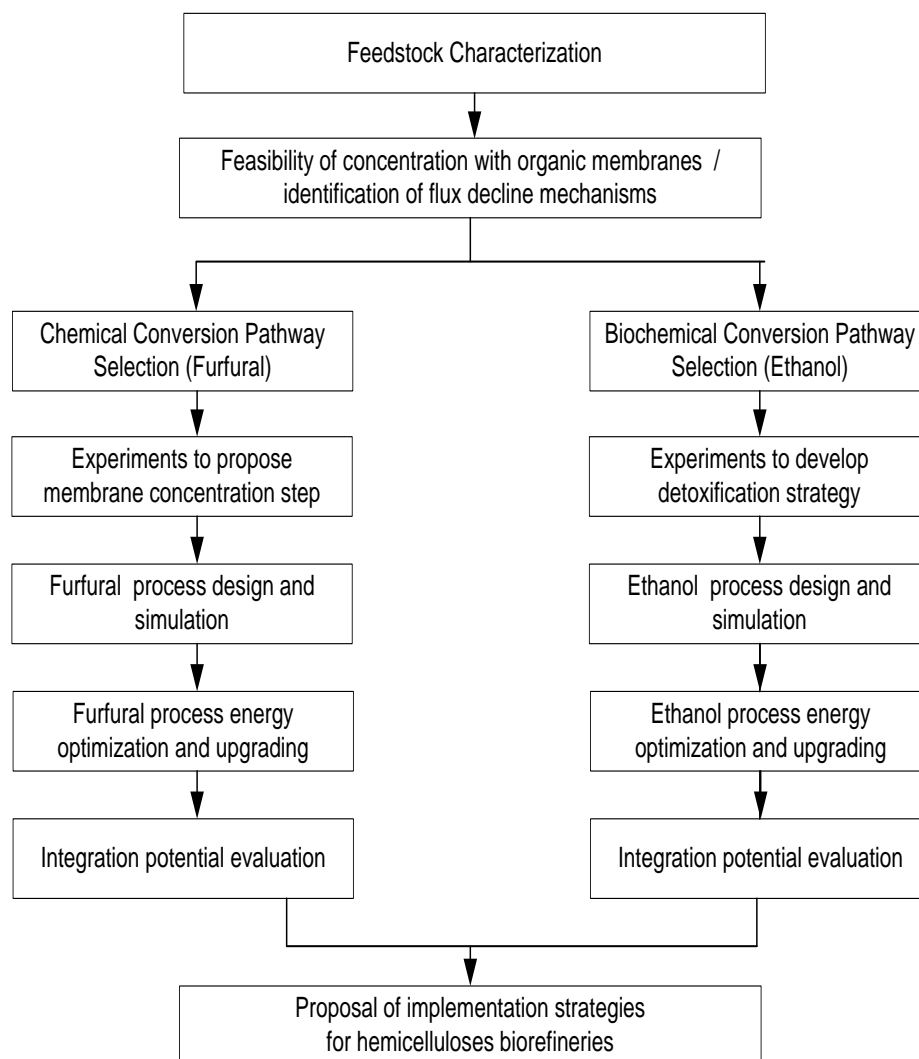


Figure 2–1: Stepwise approach for biorefinery processes development

2.3 Structure and Organization

2.3.1 Presentation of Publications

The six following chapters contain the results of this thesis. The first paper is presented in chapter 4. It is entitled “Concentration of hemicelluloses prehydrolysate by membrane filtration: Feasibility and effect of composition on flux decline mechanisms” and it has been submitted to Separation and Purification Technology in May 2014. The flux decline mechanisms resulting from the main prehydrolysate components were identified by using a synthetic prehydrolysate solution identified in this fundamental investigation.

The second article entitled “Retention and flux characteristics of nanofiltration membranes during hemicelluloses prehydrolysate concentration” is an applied research investigation of the feasibility of utilizing nanofiltration membranes for concentration of real hemicelluloses prehydrolysate solutions. It involved the screening of six commercial organic membranes with varying molecular weight cut off (MWCO) and different active layers made of polyamide, cellulose acetate and polypiperazine amide polymers. A membrane that produced high sugars retention was identified for concentration and a response surface model to minimize the flux decline during concentration was developed. This article has been accepted for publication in the chemical engineering journal.

Article 3 is presented in chapter 5 under the title “Furfural production in an integrated forest biorefinery: process development and techno-economic assessment”. This article documents the development of novel biorefinery process for furfural production that utilizes 69% lower energy than existing processes and is suitable for integration into a Kraft dissolving pulp mill. This article has been submitted to Chemical Engineering Research and Design in August 2014.

The fourth article will be submitted to Biomass and Bioenergy in October 2014. It is titled “Concentration and detoxification of Kraft prehydrolysate by combining nanofiltration with flocculation”. A novel detoxification strategy that can be successfully used to remove most of the inhibitory compounds from a prehydrolysate solution was developed and proposed.

The evaluation of the requirements for integrating an ethanol plant into a Kraft dissolving pulp mill was presented in chapter 5. The results may be extended into a paper that will be submitted to the Canadian Journal of Chemical Engineering.

“Hemicelluloses based integrated forest biorefineries: implementation strategies” is presented as in chapter 7. This chapter discusses proposed guidelines for the implementation of integrated forest biorefineries. The results may be extended into a paper that will be submitted for Biofuels, Bioproducts and Biorefining

2.3.2 Link between Publications

Chapter 3 (Article 1) is a fundamental study and it establishes the feasibility of membrane applications to the treatment of hemicelluloses prehydrolysate. The types of flux decline mechanisms caused by solution components were determined. Chapter 4 (Article 2) is specific to

a furfural biorefinery process and it shows the suitable operating conditions for membrane concentration and a modeling approach to minimize the flux decline. Chapter 5 (Article 3) summarizes the furfural biorefinery process development and evaluation of its technical and economic feasibility. Articles 4 and 5 focus on the ethanol biorefinery. Chapter 6 (Article 4) presents a novel detoxification strategy that can be used to remove inhibitory compounds from hemicelluloses prehydrolysate while Chapter 7 covers the integration of the developed ethanol process with a receptor mill. Chapter 8 discusses the perspectives for future integrated biorefinery development based on the results and knowledge acquired during this doctoral research. Implementation strategies for integrated biorefineries are also proposed.

CHAPTER 3. ARTICLE 1: CONCENTRATION OF HEMICELLULOSES PREHYDROLYSATE BY MEMBRANE FILTRATION: FEASIBILITY AND EFFECT OF COMPOSITION ON FLUX DECLINE MECHANISMS

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Abstract

Prehydrolysate, a dilute solution comprising mainly of C₅ and C₆ sugars as well as lesser quantities of organic acids, furfural and phenolics is generated in the Kraft dissolving pulp process prior to wood chips cooking. A more profitable alternative for pulp and paper mills in comparison to the typical practice of combusting the concentrated prehydrolysate solution, is to valorize the sugars by conversion into value added bioproducts such as furfural. Prior to conversion, it is important to concentrate the stream to reduce the energy cost and capital investment of the subsequent conversion and separation stages. Retaining the organic acid during concentration also lowers the pH that favours the conversion of pentose into furfural. The purpose of this work was to evaluate the impact of prehydrolysate composition and main operating parameters such as the feed temperature, pressure and tangential velocity on the component separation and permeate flux during concentration of model prehydrolysate solutions. Using model prehydrolysate solutions, two commercial reverse osmosis (RO) membranes were screened and one was selected for use based on its higher sugar and acetic acid retention. A

Taguchi L18 experimental design array was then applied to determine the dominant parameters. Results showed that the feed pressure and temperature have the highest impact on permeate flux but the least effect on sugar retention. Further experiments to quantify how fouling and osmotic pressure contribute to flux decline showed that furfural has the highest membrane fouling tendency and can limit the lifetime of a membrane. Regeneration of the membrane by cleaning with a solution containing sodium hydroxide is also effective for reversing fouling. It has been demonstrated that RO concentration can be accomplished.

Keywords

Membrane filtration, Prehydrolysate, Kraft Process, Furfural Production

3.1 Introduction

Since the closure of several Kraft pulp mills in the past decade, efforts to reposition the sector has resulted in a revision of the business model of presently operating mills by transforming them into Integrated Forest Biorefineries (IFBRs) [1]. An IFBR generally involves the diversification of the product portfolio of a mill by integrating new processes for sustainable products such as biochemicals, bioenergy, biofuels or biomaterials, which are new sources of revenue. Other advantages of a biorefinery integrated into a Kraft dissolving pulping mill include: i) the existing infrastructure on site can reduce the investment costs for the biorefinery ii) skilled manpower with experience in biomass handling and processing is available on site iii) the heating and cooling utility requirements can be provided by the mill. Five Kraft pulp mills in Canada have been converted from paper grade to dissolving grade pulp processes in the past. Three other mills are currently under conversion due to an increase in the price and global demand for dissolving grade pulp, which can be used for the manufacture of textile fibres [2]. Dissolving Kraft pulp mills are suitable for the integration of a sugar platform biorefinery because the prehydrolysis of the wood chips to remove the hemicelluloses fraction is carried out prior to cooking. Presently, the hemicelluloses are typically combusted to produce energy in the chemical recovery cycle of the pulping process. Several methods exist for the prehydrolysis of wood chips. The use of hot water is advantageous because it is a mature, cost efficient technique and does not require the use of additional chemicals. Furthermore, the hemicellulosic sugars can be easily extracted and recovered. The resulting stream is dilute and contains a mixture of pentose and hexose sugars

with less than 4% wt/vol total sugars [3] and lesser quantities of organic acids and phenolics. Valorization of this stream via a biochemical pathway to produce biofuels such as ethanol and butanol or a chemical pathway for bioproducts such as furfural or xylitol is possible. It is advantageous to utilize a chemical conversion pathway in mills that utilize hardwood as feedstock. This is because the pentoses, which make up the highest proportion of the prehydrolysate stream, are more difficult to ferment into biofuels than hexoses but are valuable feedstock in biochemical production. Also, it is not yet economically competitive to produce biofuels from such a stream because the cost of production from alternative feedstock like sugar cane or corn is comparatively lower [4]. Furfural is a platform chemical that can replace many industrial organic compounds that are presently produced from crude oil. Currently, it is mainly produced from agricultural residue such as corn cobs. The production cost and energy requirement in existing processes for furfural production are high (~42 GJ/t) but it can be reduced by integrating a furfural biorefinery with other processes that utilize biomass as feedstock [5, 6], such as the Kraft pulping process. It is projected that the growth in demand for furfural will rise from 300 kt/a to 1,000 kt/a in 2020 [6]. Some of its promising applications include the production of tetrahydrofuran (THF) which is an important industrial solvent [7]. Resins and biopolymers can also be derived from furfural [8, 9]. As a result of the “*Montreal Protocol on Substances that Deplete the Ozone Layer*”, the use methyl bromide for soil fumigation is being phased out by the United States Environmental Protection Agency (EPA). The use of furfural and its derivatives is being investigated and already has been identified as an alternative nematocide [10, 11].

To produce high purity furfural from prehydrolysate in an IFBR, three main steps are required: (i) concentration of the generated prehydrolysate, (ii) sugars (pentose) conversion by a dehydration reaction into furfural and (iii) product purification by distillation as shown in Figure 3–1. The concentration step is specific to an IFBR based on Kraft pulp mill for dissolving pulp production and it is essential for reducing the energy cost and process equipment dimension.

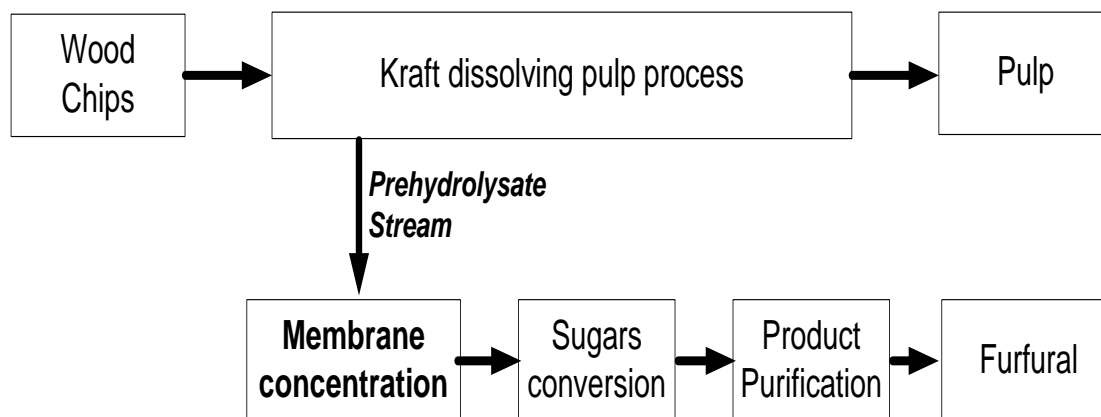


Figure 3–1: Schematic representation of an Integrated Forest Biorefinery for furfural production

A low pH is required to catalyze the conversion of sugars into furfural. Organic acids such as formic [12] and acetic acids are suitable catalysts that can also reduce the mineral acid requirement. It is therefore important that the method for concentration retains the organic acids present in the prehydrolysate along with the sugars during concentration. Multiple-effect evaporators are efficient and widely used in many industrial applications for concentration when large volumes of water must be recovered but two drawbacks are associated with its potential use in the furfural biorefinery. Firstly, a large amount of energy in the form of steam is required and acetic acid, the main organic acid will be lost because it is volatile. These drawbacks can be avoided by membrane filtration, an energy efficient technique of concentration and water recovery in a wide range of industrial applications. No previously reported studies on the application of reverse osmosis or nanofiltration membranes for concentration in a furfural process were found in existing literature. Furthermore, earlier studies conducted on membrane application focused mainly on the removal of inhibitors from real and synthetic [13] hydrolysate solutions for biofuels production. This is not required when producing furfural. To the best of our knowledge, no investigation of the flux decline mechanism caused by the main prehydrolysate components has been carried out, although it is important for evaluating the feasibility of membrane concentration. Also, the effect of varying prehydrolysate composition and filtration conditions on the separation characteristics and permeate flux has not been investigated. The objective of this work is to evaluate the potential of technologically and economically feasible membrane concentration in a furfural biorefinery. Synthetic solutions that bracket the wide range of compositions that can be found in a furfural process using prehydrolysate from dissolving pulp mills were employed. The experiments were carried out in three phases:

- To identify membranes with suitable component retention
- To determine the optimum conditions for high permeate flux
- To evaluate the impact of prehydrolysate composition and feed conditions on flux decline

3.2 Material and methods

3.2.1 Membranes

Two similar spiral wound commercial RO membranes, Dow Filmtec TW30-2540 and Dow Filmtec BW30-4040 were used in this study. They were made of polyamide thin film composites, had a continuous operation pH Range of 2-11, maximum operating temperature of 45°C, maximum operating pressure of 4100 kPa and Molecular Weight Cut Off (MWCO) of about 100 Da. The new membrane element were cut length wise and opened up. They were then immersed in a solution of 1% wt/vol of sodium metabisulfite to loosen the membrane pores and prevent the growth of microorganisms. Prior to filtration experiment runs, flat sheets were cut from the membrane roll and placed in distilled water for at least three days to remove the sodium metabisulfite and condition the membrane.

3.2.2 Experimental Setup

A lab-scale SEPA CF II (GE Osmonics, United States) cross-flow flat-sheet membrane test unit was used in this experimental study. It had a rectangular tangential flow canal that can accommodate any type of flat-sheet membrane with dimensions: 9.6 cm (breadth) and 14.5 cm (length). A hydraulic hand pump (SPX maximum pressure 70000 kPa) was used to pressurize the flat sheet between the two stainless steel half cells. The feed tank is made of stainless steel and it had a capacity of 4 Litres. It had a hollow wall with glycol circulated between the walls to control the temperature of the model solution in the tank. A Hydra Cell M03 type high pressure pump (11.25 L/min maximum volume flow delivery) is used to feed the solution to the membrane cell.

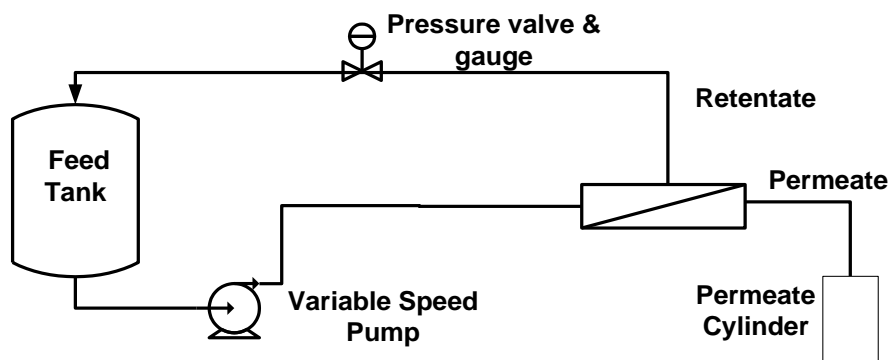


Figure 3–2: Schematic of the reverse osmosis concentration setup, batch mode

In a batch run for concentration, the permeate stream is collected in a cylinder while it is directed back into the feed tank in a closed loop. A closed loop makes it possible to evaluate the membrane separation without any interference from the concentration of the model solution.

3.2.3 Model Solutions Preparation

All chemicals were reagent grade and obtained from different suppliers. D-Xylose was obtained from Bioshop Canada. D-Glucose and Acetic Acid were obtained from Fisher Scientific while Furfural and Syringaldehyde were from Sigma Aldrich. They were used as received without any further purification. Some physico-chemical properties of the compounds are summarized in Table 3.1.

Table 3.1: Physico chemical properties of the model solution compounds

Chemical	D-Glucose	D-Xylose	Acetic Acid	Syringaldehyde	Furfural
Formula	$C_6H_{12}O_6$	$C_5H_{10}O_5$	$C_2H_4O_2$	$C_9H_{10}O_4$	$C_5H_4O_2$
Molecular Structure					
MW (g/mol)	180.16	150.13	60.05	182.17	96.08
D (x $10^{-5}cm^2/s$)	0.67 [14]	0.75 [14]	1.29 [15]	N.A	1.01 [16]
pKa	12.46 [15]	12.14 [15]	4.76 [15]	7.34 [17]	N.A-
MW: Molecular Weight; D= Diffusion coefficient at 25°C and pKa: Dissociation constant					

Model solutions for each experimental run were prepared by dissolving predetermined amounts of glucose, xylose, syringaldehyde, acetic acid and furfural in distilled water. The mixture was then heated to 40°C and thoroughly mixed with magnetic stirrers before allowing it to cool to the test temperature level. All final solutions contained 35 g/L of glucose and 10 g/L of xylose, which are typical sugar compositions of prehydrolysate generated by hot water hydrolysis. The compositions of the other chemical compounds were varied to investigate their effects on filtration performance. No pH adjustment of the solutions was carried out.

3.2.4 Filtration Procedure

Preliminary characterization tests were carried out on a virgin membrane to determine the pure water permeate flux and its evolution over extended periods of use. This served as a benchmark for all the membranes used in the concentration experiments. Prior to concentration experiment runs, the two membranes (TW30 and BW30) were screened under identical conditions to select one with the most suitable separation characteristics for the 18 concentration runs. A fresh membrane sheet was used in all experiment runs. In the screening run, 1.5 L of model solution is supplied into the feed tank and continuously filtered in a close loop run (the permeate stream was directed back into the feed tank). Approximately 10 mL was collected at 15 minutes interval for a total of 90 minutes from the permeate and retentate streams. The permeate flow rate was also measured at the same interval. During the batch concentration operation mode (Figure 3–2), 1.6 L of model solution was introduced into the feed tank and the permeate was collected in a cylinder. Approximately 10 mL of permeate sample is taken after each 200 mL of withdrawn permeate. To have a sugar concentration factor of 3, a total of 1.06 L of permeate was withdrawn. Samples of the model solution in the feed tank were taken before and after concentration. All the collected samples were analyzed for the concentrations of glucose, xylose, acetic acid, furfural and syringaldehyde. Before and after filtration of the model solutions, the permeate flow (L/min) at 690, 1378 and 2068 kPa was determined using distilled water at a constant cross flow velocity of 0.4 m/s in order to determine the fouling of the membrane.

3.2.5 Analytical Methods

The concentrations of xylose and glucose were quantified by HPLC (Agilent Technologies, Germany) equipped with a Refractive Index (RI) detector and Inertsil NH2 (250 X 4.6 mm) column. An Acetonitrile - Water mixture (CH_3CN 80% – H_2O 20%) was used as eluent. The flow rate of the mobile phase was 2 mL/min and the column temperature was 40 °C. Furfural concentration was analyzed by the same HPLC using a 280 nm diode array detector (DAD) and a Nucleosil C18 (150 X 4.6 mm) column. A mixture of Acetonitrile – Water – Acetic Acid (CH_3CN 15% – H_2O 84% – $\text{C}_2\text{H}_4\text{O}_2$) was utilized as eluent. The flow rate of the mobile phase was 1 mL/min and the column temperature was 25°C. Acetic Acid was analyzed using a 210 nm (DAD) coupled with an Inertsil ODS-3 (150 X 4.6 mm) column. The mobile phase was a mixture of 50 mM potassium phosphate that was adjusted to a pH of 2.8 with phosphoric acid (H_3PO_4) and acetonitrile (KH_2PO_4 99% - CH_3CN 1%) that was fed at 1.25 L/min into the column at 40°C.

Syringaldehyde quantification was done by colorimetric analysis using Folin–Ciocalteu reagent in a procedure similar to that described by Singleton and Rossi [18]. In each tube, 500 µL of diluted model solution sample was added followed by 3.8 mL of water and 200 µL of Folin–Ciocalteu reagent. After 3 minutes, 500 µL of sodium hydroxide (6%, w/v) was added into the tube and the tube allowed to stand at room temperature in the dark. After 1 hour, the absorbance (725 nm) was measured with a visible Novaspec II spectrophotometer (Pharma Biotech, Cambridge). A calibration curve was prepared, using a standard solution of gallic acid (50, 100 and 150 mg/L). Results were expressed as mg gallic acid equivalents (GAE)/L of syringaldehyde.

The pH and conductivity of the feed, permeate and concentrate streams were determined by an Accumet AB250 pH/ISE Meter (Fisher Scientific, USA) and a Orion 3-Star Benchtop Conductivity Meter (Thermo Scientific, Canada)

3.3 Theory and computation method

3.3.1 Design of experiments (DOE) by the Taguchi method

The Taguchi method was used for designing the experiments. It is a simple, systematic and efficient approach of determining the factor levels that will result in the best performance of a process. It requires the use of special arrays (standard orthogonal arrays) that are derived from the

degree of freedom of the process parameters [19]. The steps for carrying out a Taguchi experiment design are: experiment planning, conducting the experiments and results analysis and evaluation [20]. Experiment planning consists of defining the variables, selecting their levels and using standard orthogonal arrays to determine the number of experiments. After the experiments are conducted, an analysis of variance (ANOVA) is carried out. This is followed by determining the optimum combination of variables and confirmatory experiments to validate the predictions obtained by the analysis of variance. The Taguchi method involves a data transformation for analysis of the experimental data, the variation of the measured responses is expressed as the Signal-to-Noise ratio (S/N) [21]. Three different standard types of S/N ratios can be used depending on the desired objective, they are characterized as:

- Smaller is better (S/N)_s, to minimize the measured response
- Nominal is the best (S/N)_N, to attain a set value for the measured response
- Larger is better (S/N)_L, to maximize the measured response

For 6 parameters having 3 levels each, 18 experiment runs were required with the adopted L18 orthogonal array. The six controlling factors were A (Furfural concentration), B (Acetic Acid concentration), C (Phenolic concentration), D (Temperature), E (Pressure), F (Cross Flow Velocity). Their levels are given in Table 3.2. All the solutions contained a fixed amount of sugars, 35 g/L of xylose and 10 g/L of glucose.

Table 3.2: Experimental design of six controlling factors with three levels

Controlling Factors	Levels			Units
	1	2	3	
A (Furfural concentration)	0.6	1.8	3.5	g/L
B (Acetic Acid concentration)	0.5	3.5	10	g/L
C (Phenolics concentration)	0.3	2.8	6	g/L
D (Temperature)	20	30	40	°C
E (Pressure)	3100	3800	4500	kPa
F (Cross Flow Velocity)	0.3	0.4	0.5	m/s

3.3.2 Measures of membrane performance

The volumetric concentration factor (VCF) achieved with a membrane can be defined by equation 1, where V represents the volume. In a closed loop run with no concentration such as the membrane screening experiments, $V_{\text{feed}} = V_{\text{concentrate}}$.

$$\text{VCF} = V_{\text{feed}} / V_{\text{concentrate}} \quad (1)$$

For a two component system, it is assumed that the solution diffusion model is a valid means of relating the flux with the operating pressure of the membrane [22]. Based on the model, the permeate flux can be expressed as the solvent flux (J_v) and the solute flux (J_s) given by equations 2 and 3 respectively. The solvent transport coefficient (A_w) and solute transport coefficient (B_s) are membrane dependent. In equation (3), C_f is the concentration of the solute in the feed and C_p its concentration in the permeate.

$$J_v = A_w (\Delta P - \Delta \pi) \quad (2)$$

$$J_s = B_s (C_f - C_p) \quad (3)$$

They are both related by equation 4 at low solute concentration,

$$J_s = J_v \cdot C_p \quad (4)$$

where ΔP is the transmembrane pressure and $\Delta \pi$ the osmotic pressure difference between the feed and permeate side. The application of the solution diffusion model to the experiments was limited in some experimental runs as the solutions used were multicomponent mixtures. Also, the model is not considered to be applicable for the separation of organic systems [23]. In such cases, the permeate flux J , was therefore estimated from a simplified relationship between the volume of permeate V , that flows through a specific surface area of the membrane A over a period of time t .

$$J = Q / A \cdot t \quad (5)$$

To assess the separation performance of the membranes at different conditions, the percentage retention of all the components in the feed model solution were calculated from equation 6.

$$\% R_i = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}} \right)_i \times 100 \quad (6)$$

where the C_{permeate} is the concentration of the i^{th} component in the permeate and C_{feed} its concentration in the

feed. The recovery of the i^{th} component can be obtained from the mass balance equation given in equation 7

$$C_{\text{feed}}V_{\text{feed}} = C_{\text{permeate}}V_{\text{permeate}} + C_{\text{concentrate}}V_{\text{concentrate}} \quad (7)$$

During membrane operation, reduction of the permeate flux over time occurs and this can be due to any or a combination of increased osmotic pressure, compaction of the membrane, membrane fouling, or concentration polarization. As the solutes become more concentrated, the osmotic pressure, a function of solute concentration, also increases. A higher feed pressure is required to compensate for this increased osmotic pressure (equation 2). Compaction is a deformation of the membrane as a result of physical compression when it is placed under pressure and it could either be reversible or irreversible [24]. It leads to a decline of the permeate flux and can also alter the separation efficiency of a membrane. However, compensation for compaction can be made at the design stage of a membrane system. Concentration polarization is a phenomena that arises when the solute concentration near the surface of the membrane exceeds the concentration in the bulk liquid resulting in lower trans-membrane flow [25]. Fouling is a resistance to mass transfer leading to a reduction in the permeate flux of a membrane. It occurs as a consequence of the deposition and accumulation of materials on the surface during operation. The main types of fouling are classified in four groups [26]:

- organic fouling from organic compounds
- particulate fouling due to the presence of suspended and colloidal matter
- biofouling due to the growth of bacteria after their adhesion to the membrane surface
- scaling due to the precipitation of compounds that are sparingly soluble.

Fouling is inevitable and cannot be completely eliminated, but it can be reduced [27].

3.4 Results and Discussion

3.4.1 Membrane screening

Two different model solution compositions were used for comparing the separation characteristics of the two membranes (Dow Filmtec TW30 and BW30). The concentration levels were selected to cover the minimum and maximum combination of component concentrations that can be obtained from the levels of furfural concentration, acetic acid and phenolics for the

experimental design given in Table 3.2. The membrane system was run in closed loop to avoid the effect of interference from concentration on the components separation. All screening experiments were carried out at a feed temperature of 36 °C, pressure of 1380 kPa, cross flow velocity of 0.4 m/s and a duration of 90 minutes. Samples of the permeate and concentrate were taken at 15 minutes interval. Three criteria were used for selecting a membrane. They were the permeate flow, flux decline (fouling potential) and most importantly the retention of the sugars and acetic acid. The component retention results are shown in Figure 3–3.

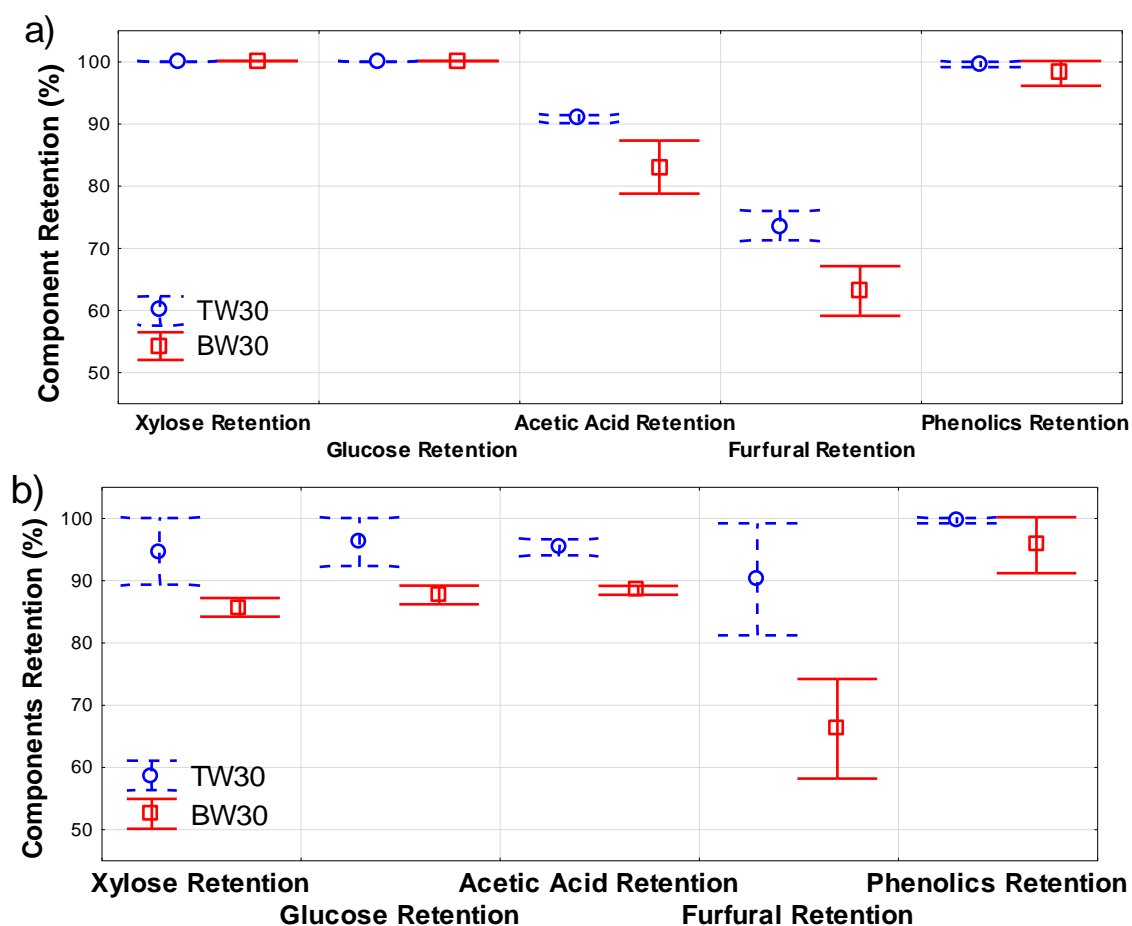


Figure 3–3. Retention of components by membrane at a) minimum and b) maximum component concentrations

All the screening tests model solutions contained the same amount of sugars (35 g/L of xylose and 10 g/L of glucose). At the minimum concentration of the other components, the pH and

conductivity of the model solution were 3.55 and 171.8 $\mu\text{S}/\text{cm}$ while they were 2.55 and 904 $\mu\text{S}/\text{cm}$ at maximum concentration of the other components.

For the screening at minimum concentration, the retention for xylose, glucose and phenolics by both membranes were comparable. However, the retentions of acetic acid and furfural were slightly higher with the TW30 than the BW30 membrane. At the maximum concentration, the TW30 exhibited higher retentions than the BW30 for all components. The permeate flux for the TW30 membrane was 11 % higher than for the BW30 for the minimum concentration solution but it was 33% less for the maximum concentration solution. The flux decline, indicated by the ratio of pure water flux achieved with the membrane after use to the pure water flux of the virgin membrane, was comparable for both membranes. A decline of 12% was observed for the TW30 membrane and 13% for the BW30 membrane. The difference in separation characteristics and permeate flux with the two different solutions can be explained as an effect of the interaction between the solution and the membrane. At maximum concentrations, the membranes were prone to flux reduction mechanisms such as fouling and concentration polarization which leads to a lower permeate flux. The pH and conductivity of the solution can also influence the isoelectric pore and therefore the observed difference in component separation. Due to the higher component retention with the TW30 membrane, it was selected for use in all the subsequent experiments.

3.4.2 Influence of variables on permeate flux

The ANOVA described in the experimental design section performs a statistical test for determining the most significant factors and their order of significance. Its main goal is to compute the ratio of variation within each factor level to the observed total variation of the results. The computed result consists of several statistical terms: the sum of squares, the mean square (variance), degree of freedom, F-ratio and p-value. The sum of squares reflect the deviation of each run result from the mean of all the results, the degree of freedom is $(n-1)$, where n is the number of experiments in a set. The mean square is the ratio of the sum of squares to the degree of freedom. The F-value reveals the magnitude of the influence for each parameter and it is the ratio of the variance by each parameter divided by the residual variance (error). The p value is the test for significance that shows the probability of obtaining the calculated F-values. A parameter is considered to be significant if its p value is less than 0.05. The residue represents the

level of uncertainty associated with the experiments. It may represent factors that are beyond control in the experiment design, parameters that were not included in the experiment or errors while conducting experiments. ANOVA was used to determine which of the six factors has the most significant effect on the permeate flux, the results for the L18 orthogonal arrays are shown in Table 3.4. The sugar content of the model solutions was the same for all the experiments (35 g/L of xylose and 10 g/L of glucose).

Table 3.4: ANOVA table: Impact of parameters on permeate flux

		SS	DF	MS	F	P	I (%)
1	A (Furfural concentration)	35.7	2	17.9	1.4	0.3	10.8
2	B (Acetic Acid concentration)	5.2	2	2.6	0.2	0.8	1.6
3	C (Phenolics concentration)	51.8	2	25.9	2.1	0.2	15.6
4	D (Temperature)	67.7	2	33.9	2.7	0.2	20.4
5	E (Pressure)	85.6	2	42.8	3.5	0.1	25.8
6	F (Cross Flow Velocity)	23.5	2	11.7	0.9	0.4	7.1
	Residue	61.9	5	12.4			18.7
SS: sum of squares; DF: Degree of freedom; MS: Mean sum of square; F: F-value; p: P-value and I (%) ; the factor influence							

The results from the experiments with the TW30 membranes indicate that out of the six parameters studied, the pressure had the highest influence on the permeate flux, followed by the temperature, phenolics concentration, furfural concentration, cross velocity and acetic acid. Although, no single factor exhibited a dominant effect, all the factors contributed to the permeate flux in different degrees given by the percent factor influence, I. To visualise how the response relates to each of the variables, a graphical representation by the main effects plot is used. It shows the $(S/N)_L$ ratios for the experiment parameters (Figure 3–4). The difference between the highest and lowest $(S/N)_L$ ratio for each parameter indicates the influence of the parameter on the permeate flux.

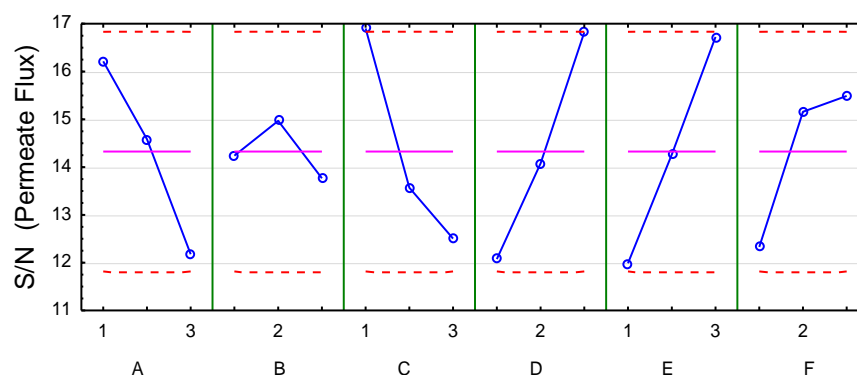


Figure 3–4: Main effect plots for permeate flux (dashed line indicates standard error)

The larger the better quality characteristic was used to determine the optimum combination of factors. The optimum combinations to achieve high permeate flux were the highest values for each parameter from the main effects plot and is A1/B2/C1/D3/E3/F3. Importantly, this optimum combination of variables was not among the L18 treatments in Table 3.3. Confirmation of the predicted optimum combination gave a permeate flow of 22 mL/min, the highest permeate flux obtained in all experiment runs.

3.4.3 Influence of variables on sugar retention

ANOVA was also used to evaluate the influence of the variables on the retention of sugars. Two mechanisms (size exclusion and electrostatic repulsion) determine the retention of a specific component during membrane filtration. The average retention of the sugars in all experiments shown in Table 3.3 was 97%. Results from the analysis of variables given in Table 3.5 showed that the temperature and pressure had the least influence on the retention of the sugars. It can be implied that since the temperature and pressure directly influence the size exclusion characteristics while the composition influences the electrostatic repulsion of the membrane, the composition of the model solution and the cross flow velocity plays the most important role in sugar retention.

Table 3.5: ANOVA table: Impact of parameters on retention of sugars

		SS	DF	MS	F	P	I (%)
1	A (Furfural concentration)	0.3	2	0.2	1.7	0.3	15
2	B (Acetic Acid concentration)	0.3	2	0.1	1.5	0.3	13
3	C (Phenolics concentration)	0.3	2	0.2	1.7	0.3	14.5
4	D (Temperature)	0.2	2	0.1	1.1	0.4	9.8
5	E (Pressure)	0.1	2	0	0.3	0.7	3
6	F (Cross Flow Velocity)	0.5	2	0.3	2.7	0.2	23.1
	Residue	0.5	5	0.1			21.7
SS: sum of squares; DF: Degree of freedom; MS: Mean sum of square;							
F: F-value; p: P-value and I (%) ; the factor influence							

The optimum points for high total sugar retention are A3/B3/C1/D1/E1/F3 as shown in Figure 3–5. Nevertheless, the increase in sugar retention that can be achieved using this point is limited since the average retention observed was 97 %.

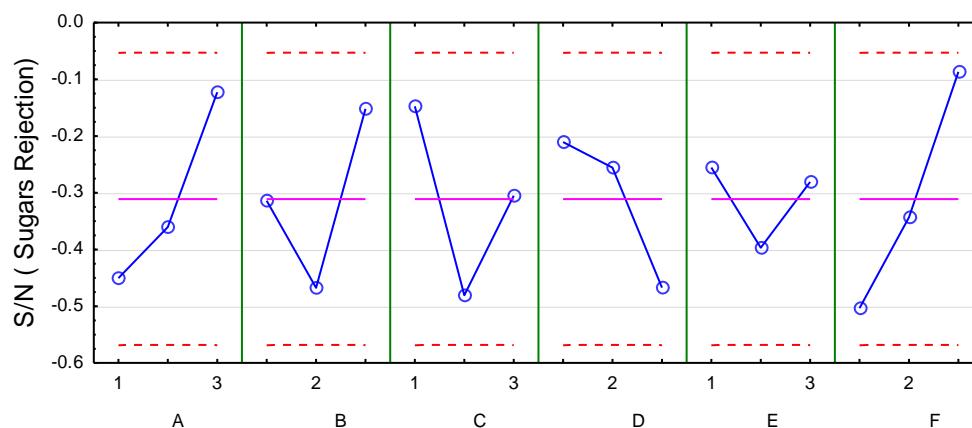


Figure 3–5: Main effect plots for sugar retention (dashed line indicates standard error)

Further confirmatory experiments were conducted with 2 model solutions. The sugar compositions, xylose (35 g/L) and glucose (10 g/L) were the same in both solutions. The first solution contained no furfural, acetic acid and phenols while the other contained furfural (3.5

g/L), acetic acid (3.5 g/L) and syringaldehyde (2.8 g/L) It was observed that the sugar retentions when only the sugars are present in the model solution was 100 %. However, with the presence of the other compounds in the model solution the retention fell to 97 % for xylose while the glucose retention remained at 100 %. Despite the lower molecular weight of xylose compared to glucose (150 vs 180 g/mol), the observed difference of 3% was not significant.

3.4.4 Influence of variables on acetic acid retention

It was observed from the analysis of the results that the retention of acetic acid did not depend on the composition of the model solution only. The highest influence came from the cross flow velocity followed by the pressure as shown in Table 3.6. It can be inferred that since the molecular weight of acetic acid of 68 g/mol is less than the molecular cut off weight (MWCO) of the membrane of 100 g/mol, electrostatic repulsion plays a dominant role in the observed retention. In summary, the retention of acetic acid is strongly affected by any or a combination of electrostatic repulsion of all the other components and acetic acid itself. The electrostatic charge interaction at the membrane surface depends on the pH of the solution, which is also determined by the degree of ionization of the acid, the membrane characteristics and operating conditions.

Table 3.6: ANOVA table: impact of parameters on acetic acid retention

		SS	DF	MS	F	P	I (%)
1	A (Furfural concentration)	0.03	2	0.02	0.04	0.96	0.1
2	B (Acetic Acid concentration)	1.40	2	0.70	1.61	0.29	4.7
3	C (Phenolics concentration)	2.4	2	1.22	2.82	0.15	8.3
4	D (Temperature)	4.6	2	2.27	5.28	0.06	15.5
5	E (Pressure)	7.6	2	3.81	8.84	0.02	25.9
6	F (Cross Flow Velocity)	12.9	2	06.45	14.94	0.01	43.8
	Residue	2	5	0.43			1.7
SS: sum of squares; DF: Degree of freedom; MS: Mean sum of square;							
F: F-value; p: P-value and I (%) ; the factor influence							

Acetic acid retentions were between 61 and 91 % as shown in Table 3.3. The optimum point for high acetic acid retention is A2/B2/C3/D2/E3/F3 and it is illustrated in Figure 3–6. Confirmatory

experiments at the optimum condition showed that 92 % retention of acetic acid can be achieved. This does not differ significantly from the highest value obtained in the experiment design which was 91 %.

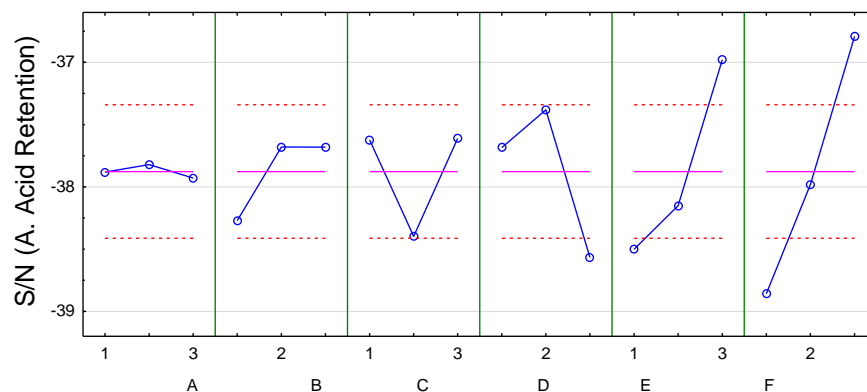


Figure 3-6: Main effect plots for acetic acid retention (dashed line indicates standard error)

Further experiments to expand the observed trend were carried out with two different model solutions. The first solution contained only acetic acid, while the second had all the other components, furfural (3.5 g/L), acetic acid (3.5 g/L) and syringaldehyde (2.8 g/L), in addition to sugars. The acetic acid retention in the mixture was 74%, and 51 % for the solution containing only acetic acid. It was evident that a complex mixture results in higher acetic acid retention, this could be due to the accumulation of the other compounds on the membrane or to an increased electrostatic effect between the acetic acid and the membrane surface.

3.4.5 Influence of variables on flux decline

The C₅ sugars concentration has to be increased from 35 g/L to at least 105 g/L (a concentration factor of 3) to obtain a furfural composition comparable to state of the art furfural processes in the subsequent conversion step. Comparison of the permeate flow at the beginning of concentration and end of concentration was carried out and is shown in Figure 3-7. The flux at the beginning and end of each experiment depends on the combination of the model solution composition and operating conditions shown in Table 3.3.

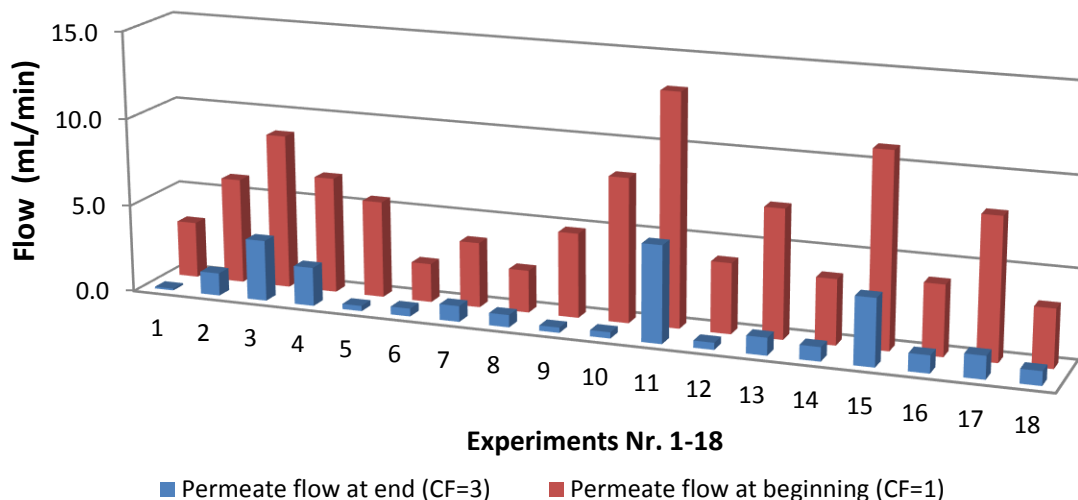


Figure 3–7: Initial and final permeate flux for the L18 Taguchi experiments

A permeate flux decline was observed during all the concentration experiment runs. Some of the experiments with the highest initial flux (experiments 3, 11 and 15) were carried at the highest feed pressure. Although the concentration factor for all the 18 model solutions was 3, the flux decline was greater than a factor of 3 in about 77 % of the experiments. This indicates the presence of other flux decline mechanisms, different from the osmotic pressure increase. Furthermore, the permeate flux observed in half of the experiments was lower than a typical heuristic design permeate flux (20 L/m²h) that corresponds to 5 mL/min in Figure 3–7: Initial and final permeate flux for the L18 Taguchi experiments

The influence of the six factors by the analysis of variables is given in Table 3.7. The order of ranking is Cross Flow Velocity > Pressure > Temperature > Phenolics > Acetic Acid > Furfural. The results imply that an interaction between the physical parameters and the model solution components was responsible for the flux decline. In addition, compaction can be excluded from the main flux decline mechanisms because the preliminary characterization tests described in section 2.4 did not reveal compaction of the membrane for the selected cross flow velocity, pressure and temperature.

The results made it possible to identify the different flux decline mechanisms present. As shown in Figure 3–8, the initial permeate flux measured in terms of the initial permeate flow was approximately 45 mL/min for all experiments. Concentration by withdrawal of the permeate stream commenced 3 minutes after the feed pump was started and this corresponds to a concentration factor of 1.0. The lowest permeate flux decline was observed for the model solution containing only acetic acid. A pure water flux of 43 mL/min was achieved after this concentration run and flushing of the system with distilled water. This indicated that the presence of acetic acid in the model solution did not contribute to the flux decline observed. The permeate flow for the sugar only solution fell from 24 mL/min at the onset to about 6 mL after concentration. The ratio of initial to the final permeate flow was 4 and it can be concluded that since the ratio is in the same range as the concentration factor which is 3, the reduction experienced with sugars only solution can be attributed to the osmotic pressure which is directly proportional to the concentration factor. The difference in flux between the beginning and end of concentration was less than 5 mL/min for the three other model solutions: furfural only, phenols only and mixture. It can also be seen that the decline with these 3 solutions were present from the onset of concentration.

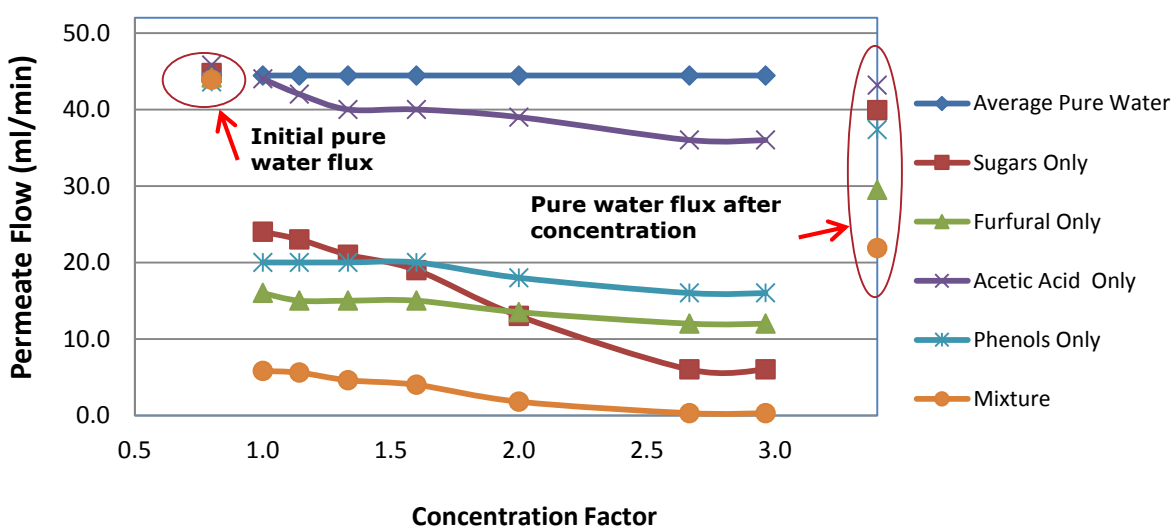


Figure 3–8: Comparison of flux decline caused by the model solution components

A comparison of the pure water flux obtained after each concentration experiment revealed that the model solutions that contained furfural resulted in the highest pure water flux decline. The flux reduction by the phenolic compound is less than that of furfural. Experiments to determine

the osmotic pressure contribution of each component with the same composition shown in Table 3.8 was also performed. Results showed that the osmotic pressure in acetic acid only, phenols only as well as the furfural only solution tends to zero. The effect of the model solution component on the osmotic pressure using the same graphical approach is shown in Figure 3–9.

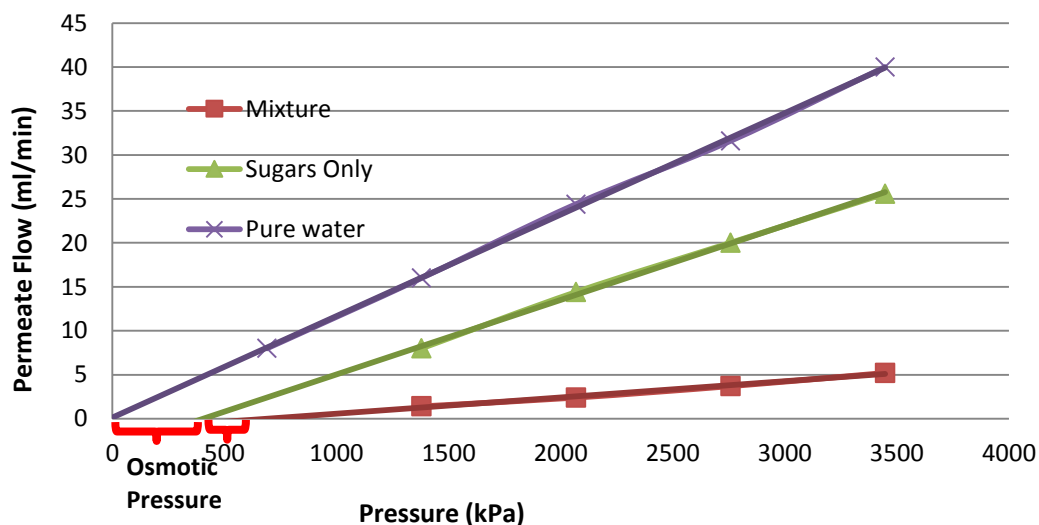


Figure 3–9: Effect of model solution components on the osmotic pressure

The difference between each intercept and the pure water intercept is a simplified estimate of the osmotic pressure.

The difference in osmotic pressure between the sugars only and mixture solutions can be explained by the occurrence of flux decline mechanisms. It can thus be inferred that the flux decline caused by the presence of sugars is due to the osmotic pressure while for furfural and the phenolic compound; it can be due to either fouling of the membrane, concentration polarization or both. The flux decline experienced due to each of the models solution components can be classified as either physically or chemically reversible. Physical reversibility refers to the fraction of the initial pure water flux that can be obtained after the membrane has been used and subsequently cleaned with distilled water. Chemically reversibility is the fraction that can be obtained after use and subsequent cleaning with a sodium hydroxide solution, a base cleaning agent. As a result, chemical cleaning (NaOH solution) also did not result in increased flux either. It became evident that, the presence of furfural contributes to the flux decline of the membrane by fouling. This can be seen in Figure 3–10 a) and 10 e), for which the highest flux decline was

observed. The effectiveness of using a cleaning agent can also be seen. This suggests that a sodium hydroxide based cleaning agent can partially reverse the fouling caused by furfural.

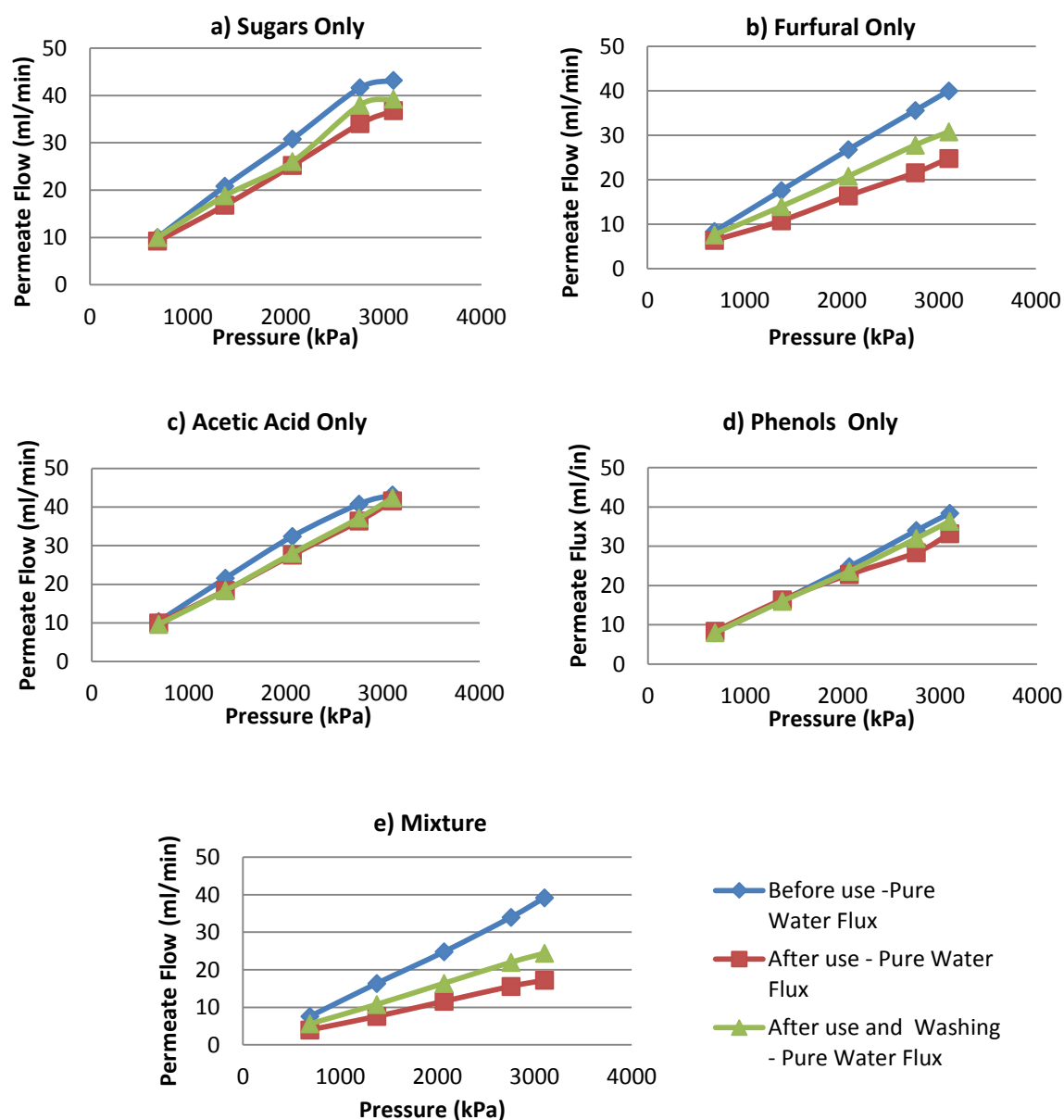


Figure 3–10: Permeate flow against feed pressure to differentiate fouling from concentration polarization

Since fouling of membrane cannot be completely eliminated, being able to regenerate a membrane by cleaning is an essential factor to be considered to make membrane concentration feasible.

3.5 Conclusions

The feasibility of concentrating hemicelluloses prehydrolysate using RO membrane filtration was studied using model solutions containing glucose, xylose, acetic acid, furfural and syringaldehyde. Two commercial membranes, the BW30 and TW30 were evaluated and the TW30 membrane was shown to be the most efficient for the simultaneous concentration of the sugars and acetic acid. The dependence of the component retention on the composition and operating conditions was determined. The permeate flux decline mechanisms caused by each of the main compounds that can be found in prehydrolysate solutions have been identified. It is expected that since membrane cleaning after use with a solution containing only sodium hydroxide was possible, the use of commercial cleaning agents will also be possible for regenerating the membrane. The experimental results suggest that RO membrane filtration can be successfully applied to the concentration of hemicelluloses prehydrolysate in a furfural production process.

3.6 Acknowledgment

This research is supported by the Natural Sciences and Engineering Research Council of Canada University & College I2I program and BioFuelNet Canada. The authors thank all the technicians at CNETE for providing assistance during the experiments. The authors are indebted to Prof. Jean Paris for his valuable contributions to this work.

3.7 References

- [1] M. Benali, Z. Périn-Levasseur, L. Savulescu, L. Kouisni, N. Jemaa, T. Kudra, *et al.* ., "Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment," *Biomass and Bioenergy*, 2013.
- [2] E. Mateos-Espejel, T. Radiotis, and N. Jemaa, "Implications of converting a kraft pulp mill to a dissolving pulp operation with a hemicellulose extraction stage," *Tappi Journal*, vol. 12, pp. 29-38, 2013.
- [3] L. Kang, Y. Y. Lee, S.-H. Yoon, A. J. Smith, and G. A. Krishnagopalan, "Ethanol production from the mixture of hemicellulose prehydrolysate and paper sludge," *BioResources*, vol. 7, pp. 3607-3626, 2012.
- [4] A. v. Heiningen, "Lignocellulosic Biorefinery Research; a Personal View," presented at the 63rd Canadian Chemical Engineering Conference, Fredericton, New Brunswick, 2013.

- [5] C. M. Cai, T. Zhang, R. Kumar, and C. E. Wyman, "Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass," *Journal of Chemical Technology and Biotechnology*, 2013.
- [6] G. Marcotullio, "The chemistry and technology of furfural production in modern Lignocellulose-Feedstock biorefineries," Ph.D Thesis, Process and Energy Department, TU Delft, Delft, 2011.
- [7] K. J. Zeitsch, *The Chemistry and Technology of Furfural and its Many By-Products*: Elsevier, 2000.
- [8] F. B. Oliveira, C. Gardrat, C. Enjalbal, E. Frollini, and A. Castellan, "Phenol–furfural resins to elaborate composites reinforced with sisal fibers—Molecular analysis of resin and properties of composites," *Journal of Applied Polymer Science*, vol. 109, pp. 2291-2303, 2008.
- [9] S. K. Sharmā, A. Mudhoo, and J. H. Clark, *A Handbook of Applied Biopolymer Technology: Synthesis, Degradation and Applications*: Royal Society of Chemistry, 2011.
- [10] F. H. Abdel-Rahman, S. Clark, and M. A. Saleh, "Natural organic compounds as alternative to methyl bromide for nematodes control," *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, vol. 43, pp. 680-685, 2008.
- [11] J. A. Johnson, S. S. Walse, and J. S. Gerik, "Status of Alternatives for Methyl Bromide in the United States," *Outlooks on Pest Management*, vol. 23, pp. 53-58, 2012.
- [12] K. Lamminpää, J. Ahola, and J. Tanskanen, "Kinetics of Xylose Dehydration into Furfural in Formic Acid," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 6297-6303, 2012/05/09 2012.
- [13] B. Qi, J. Luo, X. Chen, X. Hang, and Y. Wan, "Separation of furfural from monosaccharides by nanofiltration," *Bioresource Technology*, vol. 102, pp. 7111-7118, 7// 2011.
- [14] N. Mogi, E. Sugai, Y. Fuse, and T. Funazukuri, "Infinite Dilution Binary Diffusion Coefficients for Six Sugars at 0.1 MPa and Temperatures from (273.2 to 353.2) K," *Journal of Chemical & Engineering Data*, vol. 52, pp. 40-43, 2007/01/01 2006.
- [15] W. M. Haynes, *CRC handbook of chemistry and physics*: CRC press, 2012.
- [16] K. Yui, N. Yamazaki, and T. Funazukuri, "Infinite Dilution Binary Diffusion Coefficients for Compounds Derived from Biomass in Water at 0.1 MPa and Temperatures from (298.2 to 353.2) K," *Journal of Chemical & Engineering Data*, vol. 58, pp. 183-186, 2013/01/10 2012.
- [17] M. Ragnar, C. T. Lindgren, and N.-O. Nilvebrant, "pKa-values of guaiacyl and syringyl phenols related to lignin," *Journal of Wood Chemistry and Technology*, vol. 20, pp. 277-305, 2000.
- [18] V. L. Singleton and J. A. Rossi, "Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents," *American Journal of Enology and Viticulture*, vol. 16, pp. 144-158, January 1, 1965 1965.

- [19] K.-S. Wang, J.-H. Chen, Y.-H. Huang, and S.-L. Huang, "Integrated Taguchi method and response surface methodology to confirm hydrogen production by anaerobic fermentation of cow manure," *International Journal of Hydrogen Energy*, vol. 38, pp. 45-53, 2013.
- [20] A. Chowdhury, R. Chakraborty, D. Mitra, and D. Biswas, "Optimization of the production parameters of octyl ester biolubricant using Taguchi's design method and physico-chemical characterization of the product," *Industrial Crops and Products*, vol. 52, pp. 783-789, 1// 2014.
- [21] R. K. Roy, *Design of experiments using the Taguchi approach: 16 steps to product and process improvement*: Wiley. com, 2001.
- [22] S. Sundaramoorthy, G. Srinivasan, and D. V. R. Murthy, "An analytical model for spiral wound reverse osmosis membrane modules: Part II — Experimental validation," *Desalination*, vol. 277, pp. 257-264, 8/15/ 2011.
- [23] D. R. Paul, "Reformulation of the solution-diffusion theory of reverse osmosis," *Journal of Membrane Science*, vol. 241, pp. 371-386, 10/1/ 2004.
- [24] S. Stade, M. Kallioinen, A. Mikkola, T. Tuuva, and M. Mänttari, "Reversible and irreversible compaction of ultrafiltration membranes," *Separation and Purification Technology*, vol. 118, pp. 127-134, 10/30/ 2013.
- [25] B. Mareth, "A reverse osmosis treatment process for produced water: optimization, process control, and renewable energy application," Master's thesis, Texas A&M University, 2006.
- [26] A. Alhadidi, B. Blankert, A. J. B. Kemperman, J. C. Schippers, M. Wessling, and W. G. J. van der Meer, "Effect of testing conditions and filtration mechanisms on SDI," *Journal of Membrane Science*, vol. 381, pp. 142-151, 2011.
- [27] J. I. Marriott, "Detailed modelling and optimal design of membrane separation systems," University of London, 2001.

CHAPTER 4. ARTICLE 2: RETENTION AND FLUX CHARACTERISTICS OF NANOFILTRATION MEMBRANES DURING HEMICELLULOSE PREHYDROLYSATE CONCENTRATION

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Abstract

The prehydrolysate generated in the Kraft pulping process prior to cooking of wood chips can be converted into value added products such as furfural, ethanol or xylitol. To make a furfural biorefinery economically feasible, it is proposed to reduce the energy use and process equipment size by concentrating the prehydrolysate stream prior to conversion. This work demonstrates the feasibility of simultaneously concentrating the hemicellulosic sugars and acetic acid in the prehydrolysate solution from a Kraft dissolving pulp mill by nanofiltration membrane. The performances of 6 commercial organic membranes made of polyamide, cellulose acetate and polypiperazine amide polymers and of different Molecular Weights Cut Off (MWCO) were evaluated. Special attention was directed to high retention of sugars, acetic acid and furfural. A membrane with a MWCO of about 200 Da and total sugars retention of 99% was selected. Cleaning of the membrane using NaOH returned the permeate flux up to 75% of the pure water flux level prior to use. A response surface model correlating the permeate flux to the temperature and pressure of the system has been developed.

Keywords

Membrane filtration, Prehydrolysate, Kraft Process, Furfural Biorefinery, Hemicelluloses Concentration

Highlights

- Six organic membranes were screened for concentrating a Kraft dissolving pulp mill hemicellulose prehydrolysate
- The influence of the feed conditions on the retention properties and flux decline of a selected membrane (NF90) was evaluated
- A response surface model was developed for optimizing the membrane filtration system
- Nanofiltration membranes can be utilized in integrated biorefinery processes

4.1 Introduction

Forest biomass comprises of three main types of polymers; cellulose, hemicellulose and lignin. In a Kraft dissolving pulp process, the hemicelluloses are typically extracted in a prehydrolysis step prior to chemical delignification of the wood chips. The prehydrolysate stream obtained is made up mainly of the hemicellulosic sugars along with lesser quantities of organic acids, phenolic compounds and furfural. The cellulose fibres are processed into pulp after delignification. The extracted hemicelluloses fraction is merged with the lignin fraction that is removed during delignification and typically directed to the recovery cycle where it is combusted to produce energy. A better use of the hemicelluloses would be to divert the prehydrolysate stream and convert the sugars into biofuels or bioproducts such as ethanol, furfural or xylitol [1]. To minimize the cost of valorizing the sugars, concentration of the prehydrolysate is mandatory before the conversion of the sugars into any value added product. Concentration allows to reduce the energy consumption and the investment cost for the subsequent process steps of the biorefinery. The concentration objectives (component separation and final sugars concentration) depend on the targeted biorefinery final product. For a Kraft pulp mill that uses hardwood as a feedstock, it is proposed to produce furfural from the prehydrolysate through the dehydration of the C₅ sugars. The C₅ sugars in the prehydrolysate make up to 80% of the total sugars. Furfural is a platform chemical for bio-products that can substitute industrial organic compounds, which are currently produced from fossil sources. Furfural can also be converted into liquid biofuels [1, 2] or used as a solvent in petrochemical refineries [3] and as pesticides or nematocides [4]. A process for producing furfural from hemicelluloses prehydrolysate has been proposed by Ajao et al. [5] and it is illustrated in Figure 4–1. After concentration of the prehydrolysate, the furfural is

produced by two subsequent reactions; the oligomeric sugars in the prehydrolysate are hydrolyzed into sugar monomers which are then converted into furfural. A low pH is required to enhance the conversion process and this can be provided by introducing mineral acid into the reactor. Purification of furfural is done by distillation. Since furfural forms an azeotrope with water and has an azeotropic point of 35 % wt, a decantation step is required between the two distillation columns to get above the azeotropic point.

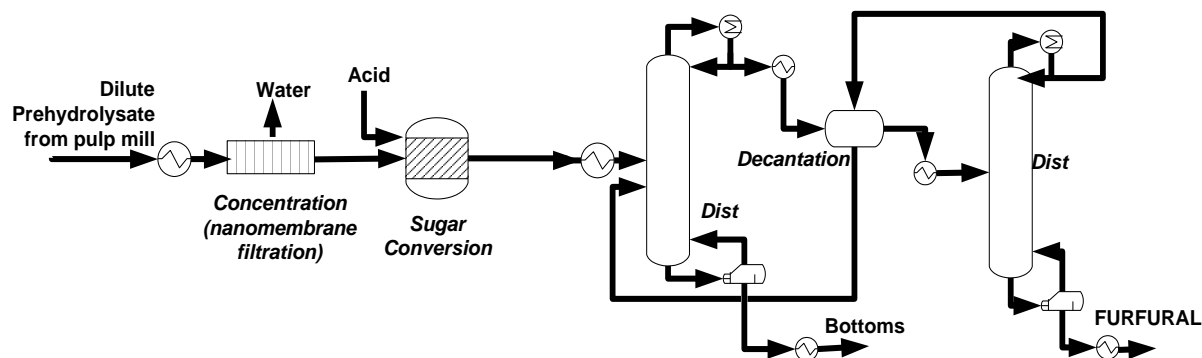


Figure 4–1: Proposed biorefinery for producing furfural from hemicellulose prehydrolysate [5]

In a biorefinery for furfural production, an important requirement for the concentration step is to retain the acetic acid along with the sugars; organic acids provide a low pH and act as catalysts, thereby reducing the mineral acid required for pentoses conversion to furfural [6]. Concentration with the typical use multi-effect evaporators is not feasible because the organic acids in the prehydrolysate are volatile and would be lost. Furthermore, evaporators have high energy consumption due to the latent heat for water that must be supplied. Membrane concentration on the other hand requires a lower amount of energy as it does not involve a phase change. The hemicellulose prehydrolysate treated in this work is a complex solution containing several organic compounds and the sugars present range from simple monomers to oligomers. The organic acids, phenolic compounds and furfural also influence the retention and flux that can be obtained during concentration [7]. The use of membrane filtration presents some challenges that must be addressed before economically feasible membrane concentration of prehydrolysate can be carried out. A suitable membrane that is capable of simultaneously retaining the sugars and organic acids with acceptable energy consumption must be used. Also, the occurrence of flux decline over the life of a membrane makes it important to determine if the operation would

necessitate frequent cleaning or changing of the membrane. Lastly, there is a limit beyond which the permeate flux of the membrane would be too low and further concentration of the prehydrolysate will not be possible. To the best of our knowledge, the application of membrane filtration to real prehydrolysate solution for a furfural biorefinery has not been investigated. Also, the effect of varied operating conditions on the flux decline has not been investigated. Thus, the objectives of this work have been to screen commercially available membrane suitable for hemicelluloses concentration, determine the flux reduction of a selected membrane over extended periods of use and develop a model relating the operating conditions to the membrane flux and useful life. Screening of six commercial organic membranes made of polyamide, cellulose acetate and polypiperazine amide polymers and having different Molecular Cut Off Weights (MWCO) between 100 and 500 Da was carried out. In the screening experiments, the separation of components in a prehydrolysate solution generated from a wood supply similar to that of a Canadian dissolving pulp mill was determined for all membranes. The selected membrane for the concentration studies had a MWCO of about 200 Da. The effect of feed condition on flux decline has already been documented [7], this is the first paper to clearly demonstrate how it relates to the concentration of hemicelluloses prehydrolysate from a Kraft dissolving pulp process. The generated data could be applied to the design of efficient membrane concentration systems and successfully used in forest biorefinery processes.

4.2 Materials and methods

4.2.1 Prehydrolysate Generation

The prehydrolysate used in this study was generated in a 56 litre digester using a 60 % Aspen- 40 % Maple wood furnish. The typical compositions of the wood chips are shown in Table 4.1.

Table 4.1: Composition of maple and aspen wood chips (% by weight, dry basis)

Component	Maple Wood wt. %	Aspen Wood wt. %
Cellulose	44%	50%
Hemicellulose	23%	23%
Lignin	31%	24%
Extractives	2%	3%

The wood chips had a moisture content of 37% and were purged with steam (138 kPa) to remove the air content and preheat the chips prior to cooking. After the digester had been sealed, prehydrolysis of the wood chips was carried out in two successive steps. In the first step, steam was introduced directly into the digester for 50 minutes until a pressure of 700 kPa and a temperature of 170°C were reached, the temperature was held at this value for another 60 minutes. In the second step, deionized water at 80 °C was introduced into the digester and subsequently circulated through an external liquor heater to maintain the digester at 170°C. The final prehydrolysate liquor to wood ratio was of 3:1. The key components of the prehydrolysate are given in Table 4.2. The pentoses (xylose and arabinose) and hexoses (glucose, galactose and mannose) are mainly in oligomeric form with only about 15 % as monomers. The prehydrolysate had a total solid content of 3.4%. The pH and conductivity of the prehydrolysate solution were 3.52 and 1620 $\mu\text{S}/\text{cm}$ respectively.

Table 4.2: Composition of hemicelluloses prehydrolysate generated for use in the experiments

Components	Concentration (g/L)
Total Sugars*	20.3
Total monomeric pentose	2.55
Total monomeric hexose	0.74
Acetic Acid	3.8
Furfural	0.7
HMF	0.09
Phenolics	4.7
Lipides	0.2
Na	0.02
Ca	0.15
K	0.04
*Ratio of pentose to hexose is 4:1	

4.2.2 Screened Membranes

Six commercially available spiral wound organic membrane types were used in this study. They represent a broad range of material and molecular weight cut off (MWCO). The names and main characteristics of each membrane are given in Table 4.3. All membranes had similar pH operating range (2-11) and maximum temperature (45°C).

Table 4.3: Characteristics of the reverse osmosis (RO) and nanofiltration (NF) membranes provided by suppliers

	TW30	NF90	NF270	XN45	TS40	SB90
Manufacturer	Dow	Dow	Dow	Trisep	Trisep	Trisep
Polymer	Polyamide	Polyamide	Polyamide	Polypiperazine amide	Polypiperazine amide	Cellulose acetate blend
Max. Pressure (kPa)	4100	4100	4100	4100 ^A	4100 ^B	4100 ^C
Max. temperature (°C)	45	45	45	45	45	45
pH operating range	2 – 11	2 – 11	2 – 11	2 – 11	2 – 11	2 – 11
MWCO	~100	~200 - 400	~200 - 400	500	200	150
NaCl Rejection (%)	99.5	>97	>97	10 - 30	40 - 60	85
Classification	RO	NF	NF	NF	NF	NF

^{A, B, C} Recommended applied pressures (kPa), A: 275-1380; B: 275-1380; C: 275-1380 kPa;

Each membrane element was cut lengthwise and opened up. It was then soaked in a solution of 1% wt/vol of sodium metabisulfite to enable the pores to loosen up and prevent the growth of microorganisms. Prior to use, flat sheets were cut from the membrane roll and placed in distilled water for at least three days to remove the sodium metabisulfite and condition them for use.

4.2.3 Membrane Setup

The filtration experiments were carried out using a lab-scale cross-flow flat-sheet membrane test unit (SEPA CF II, GE Osmonics). It had a rectangular filtration channel with dimensions 14.5 cm x 9.6 cm x 1.0 mm for accommodating various kinds of flat-sheet membrane. The feed pressure to the unit was varied using a hydraulic hand pump (SPX maximum pressure 70,000 kPa).

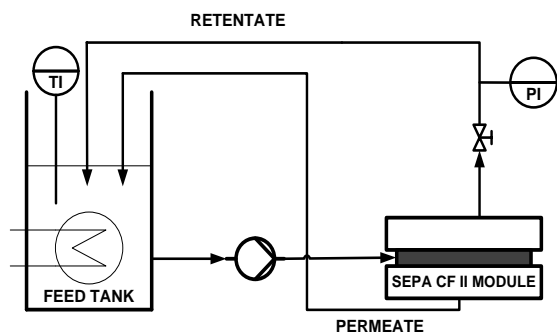


Figure 4–2: Schematic membrane screening setup in closed loop mode

The stainless steel feed tank had a capacity of 4 Litres and a hollow wall in which glycol is circulated to control the feed temperature. To screen the membranes in a continuous filtration mode, the permeate stream is directed back into the feed tank. Continuous filtration eliminates the effect of concentration on component separation during screening of the membranes. Concentration of the prehydrolysate was carried out in a batch mode during which the permeate stream is directed to a permeate cylinder.

4.2.4 Filtration Procedure

Prior to concentration experiments, the six membranes were screened under similar conditions. A fresh membrane sheet was used for each experimental run. Prehydrolysate (1L) was supplied into the feed tank and continuously filtered in a close loop run during the screening experimental runs, samples of about 10 mL were collected from the permeate and retentate streams over 90 minutes at 15 minutes intervals. The flow rate of the permeate stream was also measured at same intervals. During the concentration trials (batch mode), 2.5 L of prehydrolysate was introduced into the feed tank and a total of 2 L of permeate was withdrawn in a graduated cylinder to reach a volumetric concentration factor of 5. About 10 mL of permeate sample was taken after each 200 mL of withdrawn permeate. Samples of the retentate were taken from the feed tank before and after concentration. The amounts of sugars, organic acids, furfural and phenols in the collected samples were analyzed. In order to determine the degree of membrane fouling, the permeate volume flow (L/min) at specific pressures was measured before and after filtration of the prehydrolysate, using distilled water at a constant cross flow velocity of 0.4 m/s.

4.2.5 Analytical Methods

Initial monomeric sugars concentration was measured using a Dionex DX600 ion chromatograph equipped with a pulsed amperometric detector and CarboPac PA1 column [8]. The total solubilized sugars were determined by hydrolyzing the sugars with 2.5 % wt/vol of sulphuric acid for 20 minutes in an autoclave followed by sugar analysis. Organic acids were characterized by HPLC (Agilent Technologies, Germany) equipped with 210 nm diode array detector (DAD) and an Inertsil ODS-3 (150 X 4.6 mm) column. The mobile phase was a mixture of 50 mM potassium phosphate that was adjusted to a pH of 2.8 with phosphoric acid (H_3PO_4) and acetonitrile (KH_2PO_4 99% - CH_3CN 1%) that was fed at 1.25 L/min into the column at 40°C. Furfural and hydroxymethylfurfural were analyzed with the same HPLC but equipped with a 280 nm diode array detector (DAD) and a Nucleosil C18 column. The eluent used was a mixture of acetonitrile, water and acetic acid (CH_3CN 15%, H_2O 84% and $\text{C}_2\text{H}_4\text{O}_2$ 1%). The flow rate of the mobile phase was 1 mL/min and the column temperature was 25°C. Phenols quantification was determined using Folin–Ciocalteu reagent colorimetric analysis, a method adapted from Singleton and Rossi [9]. After the membrane experimental runs, the dinitrosalicylic acid (DNS) colorimetric method [10] was used to determine the total reducing sugars in the feed, permeate and concentrate. The metal ions were quantified with an Optima 4300 DV Inductively coupled plasma atomic emission spectroscopy (PerkinElmer Inc., USA).

4.2.6 Experimental design and data analysis

Two design of experiments (DOE) methods were used in this study. The first was a $(2)^2$ factorial parametric study to determine the effect of pressure and cross flow velocity on separation characteristics of a selected membrane at a constant temperature. Response surface methodology (RSM), a DOE approach for developing a mathematical correlation between the operating conditions and observed responses of a process, was used to design the subsequent set of experiments. RSM can be applied to the development, improvement or optimization of processes. The main advantages of RSM are that it can be used to study the effect of multiple variables without neglecting the interaction effects using a small number of experiments [11]. Central composite design (CCD) and Box-Behnken design (BBD) are the two main RSM experiment designs [12]. RSM-BBD requires a lower number of experiments than CCD and was therefore

selected for this study. Each measured response from the experiments (permeate flux and flux decline) was correlated with a second degree polynomial equation (1).

$$Y_i = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (8)$$

In the equation, Y_i is the predicted response, b_0 the intercept term, b_i the linear coefficients, b_{ii} the 2nd order polynomial coefficient, b_{ij} the interaction term and x_i , x_j the coded values for the variables. In general a model with fewer terms which allows for good fit with the experimental data is selected while the terms that are not considered to be significant are neglected. STATISTICA 10 (StatSoft software, Inc.), was used for design of the experiments, data analysis and model building.

4.2.7 Measures of membrane performance

The volumetric concentration factor (CF) achieved during concentration with a given membrane can be defined in terms of the volume (V) of the prehydrolysate fed into the tank as given in equation (2).

$$CF = V_{\text{initial}} / V_{\text{final}} \quad (9)$$

In a closed loop run with no concentration such as the membrane screening experiments, $V_{\text{initial}} = V_{\text{final}}$ and the concentration factor is 1. The equivalent permeate flux J for the experimental runs, was estimated from a simplified relationship between the measured volume flow (Q) per unit membrane surface area (A) as shown in equation (3).

$$J = Q/A. \quad (10)$$

To assess the separation performance of the membranes when subjected to different operating conditions (temperature, pressure and cross velocity), the percentage retention of the main organic compounds in the prehydrolysate were determined using equation (4).

$$\% R_i = \left(1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}} \right)_i \times 100 \quad (11)$$

Where C_{permeate} represents the concentration of the i^{th} component in the permeate stream and C_{feed} , the concentration in the feed solution. The recovery of the i^{th} component can be calculated using mass balance relationship shown in equation (5).

$$C_{\text{feed}} V_{\text{feed}} = C_{\text{permeate}} V_{\text{permeate}} + C_{\text{concentrate}} V_{\text{concentrate}} \quad (12)$$

4.2.8 Membrane flux and flux decline mechanisms

A permeate flux decline occurs during concentration with a nanofiltration membrane. This can be attributed to increased osmotic pressure, fouling of the membrane, concentration polarization or compaction of the membrane. An increase in solute concentration results in an osmotic pressure increase. Consequently, it is necessary to supply a higher trans-membrane pressure to maintain the permeate flux as shown in equation (6), where ΔP is the trans-membrane pressure and $\Delta \pi$ the osmotic pressure difference between the feed and permeate side.

$$J_v = A_w (\Delta P - \Delta \pi) \quad (13)$$

A detailed overview of the mechanisms has been given in previously reported studies [13-15]. The ratio of the pure water flux observed with the membrane prior to concentration to the flux after prehydrolysate concentration was used as a measure of flux decline. The contribution of each of the prehydrolysate components to the flux decline mechanism has been shown in an earlier study [7]. The fouling tendency of a membrane is due to the combined effect of the pollutants in the solution, the membrane surface and pore characteristics and the operating conditions. Fouling is inevitable, although it can be reversible in some cases, it cannot be completely eliminated but only reduced [16]. A consequence of fouling is an increase of operation and maintenance (O&M) costs [17, 18]

4.3 Results and Discussion

4.3.1 Membrane screening

A comparison of the six membranes shown in Table 4.3 was carried out to determine the most suitable for concentrating the prehydrolysate solution. The criteria for selecting a suitable membrane were the energy requirement for concentration, fouling potential and the retention of desired components (sugars, acetic acid and furfural). Component retention is the most important criteria because it indicates which of the membranes should be used for recovering the sugars in the prehydrolysate. The energy requirement and fouling potential are secondary criteria for selecting between membranes with similar component retention. In addition the fouling extent indicates the durability of the membranes.

4.3.1.1 Membrane power consumption

The power consumption of a nanofiltration membrane system can be attributed mainly to the high pressure pump. The power consumption (W) of the pump is a function of the feed flow rate (Q_f), feed pressure (P_f), and efficiency of the pump (η). The design feed pressure is a sum of the driving pressure, pressure on the permeate side, pressure drop in the system and osmotic pressure of the solution. The pump efficiency comprises the electrical motor efficiency and the impeller efficiency.

$$W = \frac{Q_f P_f}{\eta} \quad (14)$$

The operating pressure versus permeate flow curves was plotted for each of the membranes as shown in Figure 4–3. An equivalent pure water permeate flow rate (30 mL/min) that lies within the operating pressure range for all the membranes was used to determine the operating pressures for the screening experiments.

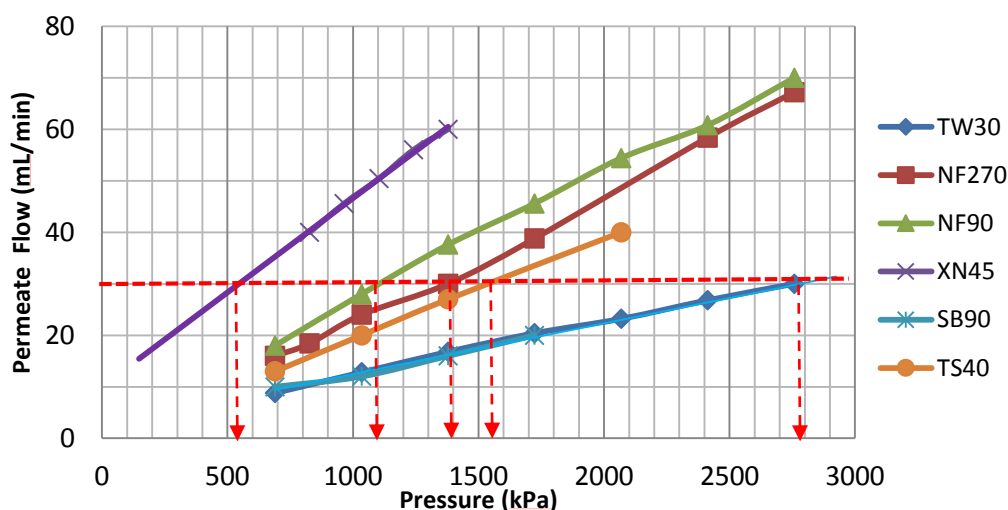


Figure 4–3: Pure water permeate flux and equivalent pressures for component retention screening

The permeate flow for the Trisep SB90 and Dow TW30 membranes overlap. Their power requirement is proportional to the operating pressure and lowest for the XN45 membrane. The determined order of their power requirements are TW30~SB90 > TS40 > NF270 > NF90 > XN45. The membrane polymers have different structure but this trend could be explained by the looseness of the membranes, which is indicated by their Molecular Weight Cut Off (MWCO).

The determined pressure corresponding to a permeate flow rate of 30 mL/min was used for the filtration runs to determine component retention.

4.3.1.2 Component retention

The second screening criterion was the component retention. Closed loop filtration runs to determine the retentions of the main prehydrolysate components (sugars, acetic acid, furfural and phenols) were carried out at the predetermined equivalent pressures for each membrane to enable comparison at the same permeate flow rate. Analysis of the permeate and concentrate streams gave the percentage retentions of each component and the results are given in

Figure 4–4.

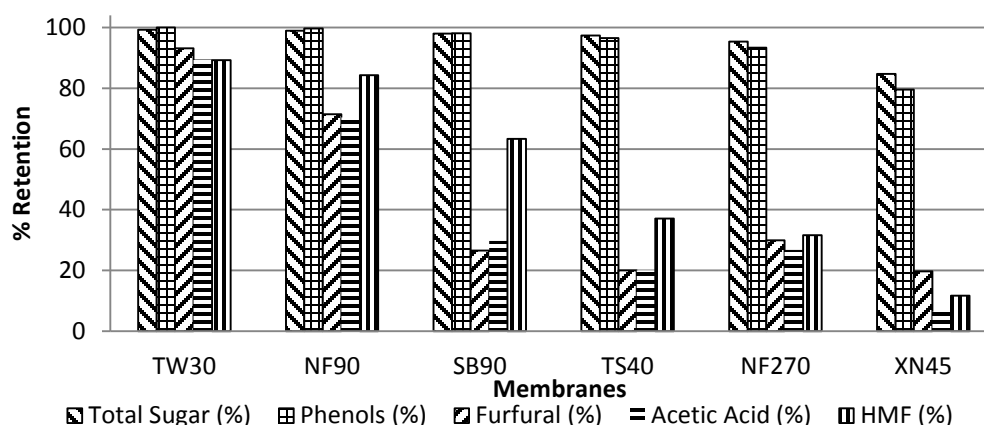


Figure 4–4: Retentions of the main components by each membrane from highest to lowest

High sugar retentions were exhibited by the TW30 (99%), NF90 (99%), SB90 (98%) and TS40 (97%) membranes respectively. In addition, the TW30 and the NF90 also produced the highest acetic acid and furfural retentions. A high retention of acetic acid is important because it produces a low pH that catalyzes sugar conversion into furfural. A membrane with high furfural retention will increase the recovery of furfural present in the prehydrolysate. The retention exhibited by a membrane is due to the interaction between three set of factors [19]: 1. The membrane characteristics (molecular weight cut off, electrostatic charge and hydrophobicity) 2. The characteristics of the prehydrolysate solution (size, electrostatic charge, geometry and hydrophobicity of the solute molecules as well as the ionic strength and pH of the solution) 3. Operating conditions and parameters (cross flow velocity, transmembrane pressure, flow channel

configuration). However, the mechanisms that govern the retention of the organic compounds are considered to be complex and limited knowledge is available [20]. Therefore, data on retention for organic compounds are derived mainly from experimental observation in industrial process applications [21]. This applies to the prehydrolysate solution due to the constituent numerous organic compounds.

4.3.1.3 Flux decline

The feasibility of membrane filtration application depends on the ability to operate the system over long periods at acceptable permeate flux levels. However, a permeate flux decline is always observed. It is caused by compaction of the membrane under pressure, membrane fouling (deposition of organic or inorganic materials on the membrane surface) or increased osmotic pressure of the feed solution. The flux reduction observed after continuous operation of the membrane system over 6 hours were classified as either physically reversible or chemically reversible for each membrane as shown in Figure 4–5. Physically reversible flux decline refers to the relative pure water permeate flux before use to the flux after it has been used for concentration and subsequently cleaned with distilled water only. Chemical reversible decline is the relative pure water permeate flux after use and subsequent cleaning with a NaOH solution at a pH of 11.

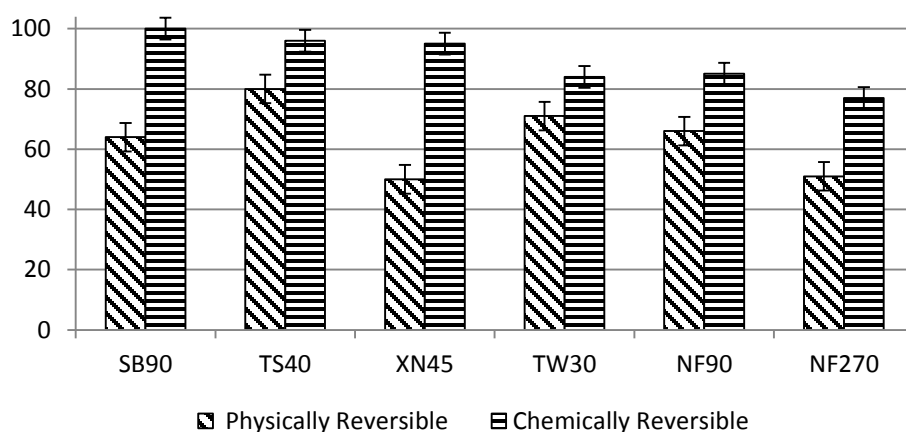


Figure 4–5: Relative pure water flux after concentration followed by physical and chemical cleaning of membranes (indexed to virgin membrane)

It was observed that the relative flux after chemical cleaning was lower for the polyamide membranes (TW30, NF90 and NF 270) than for the cellulose acetate (SB90) and polypiperazine

amide (TS40 and XN45) membranes. It is therefore important to determine if the irreversibility is due to fouling, compaction of the membrane for a membrane to be used for concentration. The results, which show that compaction can explain this observation, is discussed in section 4.3.2.

4.3.2 Membrane selection

On the basis of total sugars rejection, only the XN45 membrane was eliminated because its component retention was inferior to 95%. The highest acetic acid and furfural retention were observed for the TW30 and NF90 membranes respectively, both membranes also exhibited a similar degree of fouling. The NF90 was more suitable for concentration from an energy standpoint because the sugar retention is comparable to that of the TW30 but the power requirement is only about 1/3 that of the TW30 membrane. The NF90 membrane was judged to be the most suitable membrane based on the results from the three screening criteria (component retention, flux decline and power consumption).

To determine whether the flux decline exhibited by the NF90 despite chemical cleaning can be attributed to compaction of the membrane, confirmatory tests were carried out. The tests required continuous operation of the membrane filtration over a period of 4.5 hours. Distilled water was filtered to ensure that the effect of the other flux decline mechanisms (fouling, concentration polarization and osmotic pressure increase) were eliminated while the feed conditions were similar to that of the prehydrolysate screening runs. It was observed that the flux recovery in all cases were in the same range as shown in Figure 4–5. Hence, it can be concluded that compaction plays an important role in the flux decline after membrane use but the decline can be compensated for by using a larger membrane surface area during the design phase of the membrane concentration system.

4.3.3 Prehydrolysate concentration

The selected membrane (NF90) was used in all the subsequent experiments. The experimental design shown in was used to investigate the effect of varied operating pressure and cross velocities at a constant temperature on the component retention and permeate flux decline.

Table 4.4. Test conditions to determine the influence of operating conditions on component separation

Expt	Pres. (kPa)	Cross Vel. (m/s)	Temp (°C)
1	2100	0.66	40
2	3500	0.66	40
3	2100	0.45	40
4	3500	0.45	40

The observed components retention are shown in Figure 4–6. The sugars retention was 99% in all 4 experiments. The total phenolics retention also exhibited the same tendency in all 4 experiments.

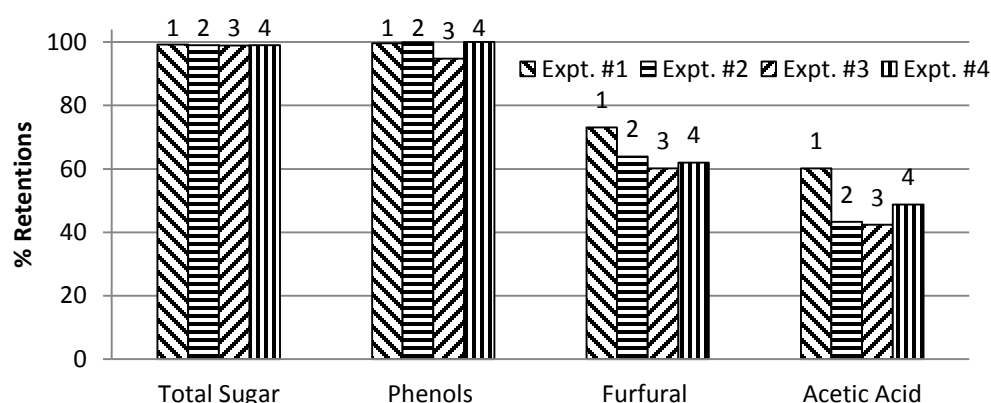


Figure 4–6: Comparison of component retentions for the four experiments (%)

On the other hand, the furfural and acetic acid retentions were similar for all experiments except experiment #1, where they were slightly higher. This could be due to the high cross velocity at the low pressure range of the experiments. The observed permeate flux trend for the 4 test conditions are shown in Figure 4–7. Although the initial permeate flow in experiment #2 was higher than for the other experiments (10 vs ~6 ml/min), they all tend to converge at a concentration factor of 5. The total duration of the concentration runs were #1 (8 hours), #2 (7 hours), #3 (10 hours) and #4 (12 hours). The experiments at a high cross velocity (#1 and #2) required a shorter time to reach a concentration factor of 5. It was also observed that the viscosity increase of the feed is more pronounced at a concentration factor of 5. Hence, only concentrating to a factor of about 4 can be useful in reducing the fouling of the membrane. Furthermore, the

observed equivalent permeate flux of about 12 L/m²h at this concentration factor, can be considered acceptable for a pilot scale system.

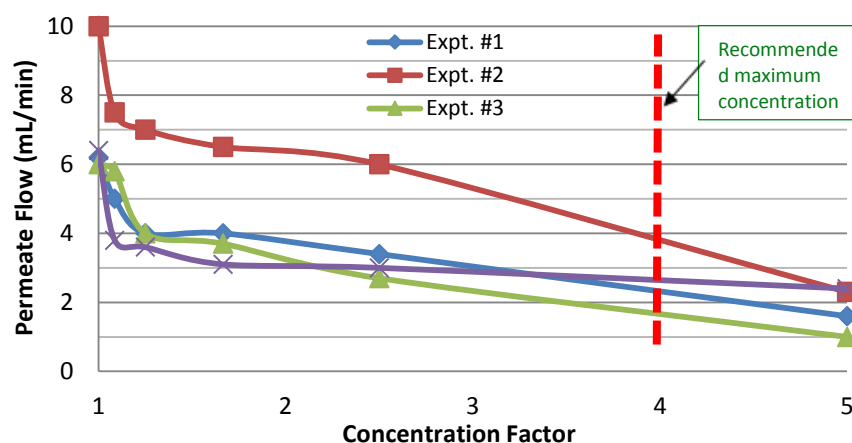


Figure 4–7: Permeate fluxes as a function of concentration factor for Exp. 1-4

The results confirm that it is technically feasible to concentrate the prehydrolysate solution up to a volumetric concentration factor (VCF) of 5. Sugars retention of 99% can be achieved while average acetic acid retention of 50% was observed. In all cases the pH of the prehydrolysate dropped from 3.7 to about 2.9 after concentration, this is in the range expected for acetic acid retentions approaching 100%. Hemicellulosic sugars concentration is technically feasible but the economic feasibility will depend on the possibility to obtain a sufficiently high permeate flux and to minimize the flux decline during prehydrolysate concentration. A permeate flow that is higher than 3mL/min (12 L/m²h) would be suitable at an industrial scale. The frequency of cleaning for an industrial membrane system could range between 7 to 180 days while the life of the membrane element could be between 1 to 5 years. A low flux decline will prevent the need for frequent cleaning and replacement of the membrane elements.

4.3.4 Response surface optimization of membrane life and operating conditions

To determine the most suitable operating conditions for prehydrolysate concentration, it is necessary to establish the relationships between the initial permeate flux and the operating conditions, and the operating conditions that would result in a low flux decline. This was achieved using the response surface model Box–Behnken experimental design (RSM-BBD)

described in section 4.2.6. The RSM-BBD consisted of 15 experiments with 3 levels for pressure, cross velocity and temperature with their coded values shown in Table 4.5. The coding notations are: -1 (minimum), 0 (central) and 1 (maximum).

Table 4.5. Coded variables levels for the Box-Behnken design (BBD)

Controlling Factors	Coded Levels			Units
	-1	0	1	
X ₁ (Pressure)	1050	1500	2050	kPa
X ₂ (Cross Velocity)	0.45	0.56	0.66	m/s
X ₃ (Temperature)	22	30	40	C

The design matrix and the measured results for the 15 experimental runs are shown in Table 4.6.

Table 4.6. RSM-BBD design matrix and experimental results

Exp. Nr.	Input Variables			Response	
	X ₁	X ₂	X ₃	Y ₁	Y ₂
1	1	0	-1	9.5	1.9
2	0	1	1	10.0	2.8
3	1	-1	0	10.5	2.1
4	0	0	0	8.0	2.1
5	-1	0	-1	5.0	1.9
6	0	0	0	7.6	2.0
7	1	0	1	10.5	2.4
8	0	-1	1	7.0	2.3
9	0	-1	-1	7.0	1.9
10	0	1	-1	7.5	1.9
11	0	0	0	7.6	2.1
12	-1	1	0	5.5	1.8
13	-1	0	1	5.5	2.5
14	-1	-1	0	5.0	2.1
15	1	1	0	11.0	1.9

Y₁: Initial permeate flow;
Y₂: Initial permeate flow / final permeate flow

Based on the results, it was found that the relationship between the initial permeate flux and the three input parameters, feed pressure (X_1), cross velocity(X_2) and temperature (X_3) in terms of the coded values can be fitted to a simple first order equation with the corresponding significant coefficient estimates shown in Table 4.7:

$$Y_1 = 7.90 + 5.14 X_1 + 1.20 X_2 + 0.97 X_3 + 1.30 X_2 * X_3 \quad (15)$$

The predicted values of initial permeate flux were compared to the experimental value from equation 8 and showed to be in agreement.

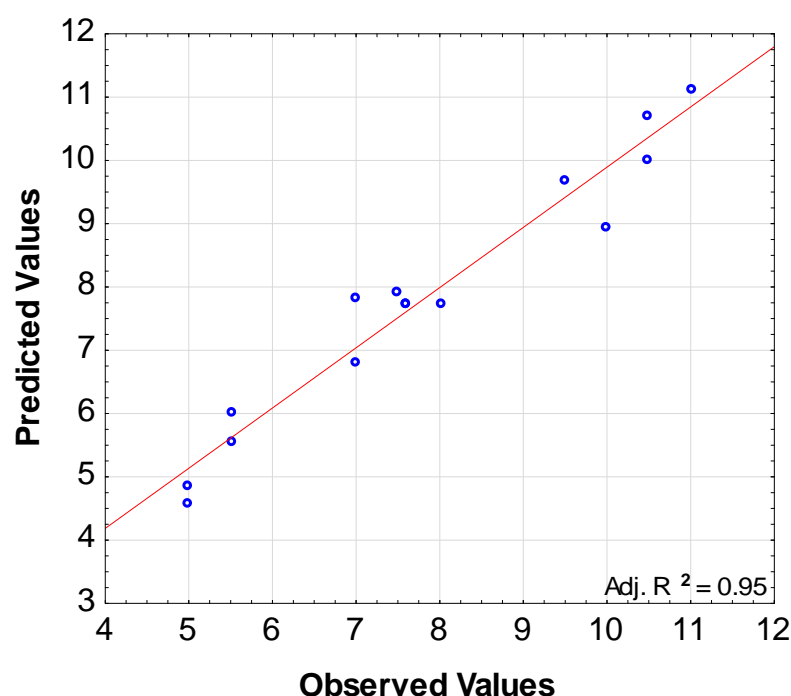


Figure 4–8: Observed initial permeate flux versus the values predicted by equation 8

The retained terms in the equation suggests that the pressure followed by the cross velocity and temperature had a linear effect on the initial flux. This is confirmed in Figure 4–9, that shows the change in permeate flux corresponding to the pressure, cross velocity and temperature. The interaction between the cross velocity and pressure at a temperature of 30°C is illustrated in Figure 4–9A. As expected, the pressure has the dominant effect on the initial permeate flow because the permeate flux is pressure driven. The same trend is shown in Figure 4–9B, in which the effect of the feed pressure was superior to that of the temperature.

The significance of the pressure effect shows that it is important to start concentration at feed pressures less than 1050 kPa so that the flux decline can be compensated by increasing the pressure.

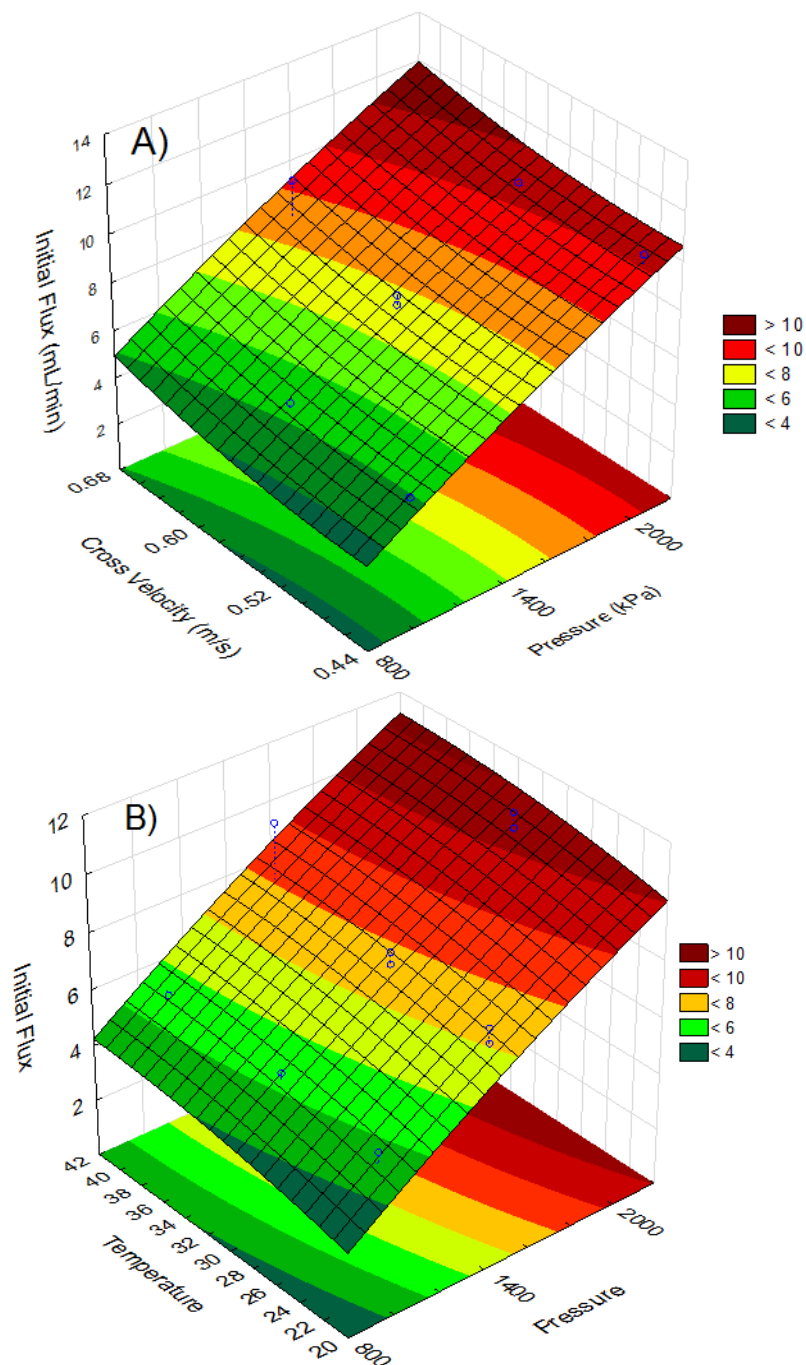


Figure 4-9: Response surface of the combined effects of A) Cross velocity and pressure B) Feed temperature and pressure on initial permeate flow

4.3.4.2 Permeate flux decline during concentration

Given that the prehydrolysate from a Kraft dissolving pulp mill will be available to a furfural biorefinery at a temperature of 80°C or higher, it must be cooled down prior to concentration because the maximum temperature that can be tolerated by the organic membranes is 45°C. Although it must be cooled to less than 45°C, the cooling must be minimized because the prehydrolysate must be again reheated after concentration to a temperature of about 200°C for the conversion of the pentose sugars into furfural. In addition, it was also observed during handling of the prehydrolysate that cooling resulted in increased precipitation that became pronounced at temperatures lower than 20°C. The response surface model could be used in this case to determine the maximum tolerable prehydrolysate temperature that will minimize the decline of permeate flux during concentration. Analysis of Variance (ANOVA) was also used to determine the fitness of the model, the parameters (linear or quadratic) from equation (1) and their corresponding interaction terms to be used for fitting the response surface model in equation (9). The ANOVA results are illustrated in Figure 4–10. The pareto chart shows magnitude and the importance of the effect each term that can be included in the response surface model. Only the first three terms with acceptable p-values ($p \leq 0.1$) were included in the response surface model. They were the temperature linear term (X_3), temperature quadratic term (X_3^2) and the interaction between the temperature and cross velocity ($X_2 * X_3$).

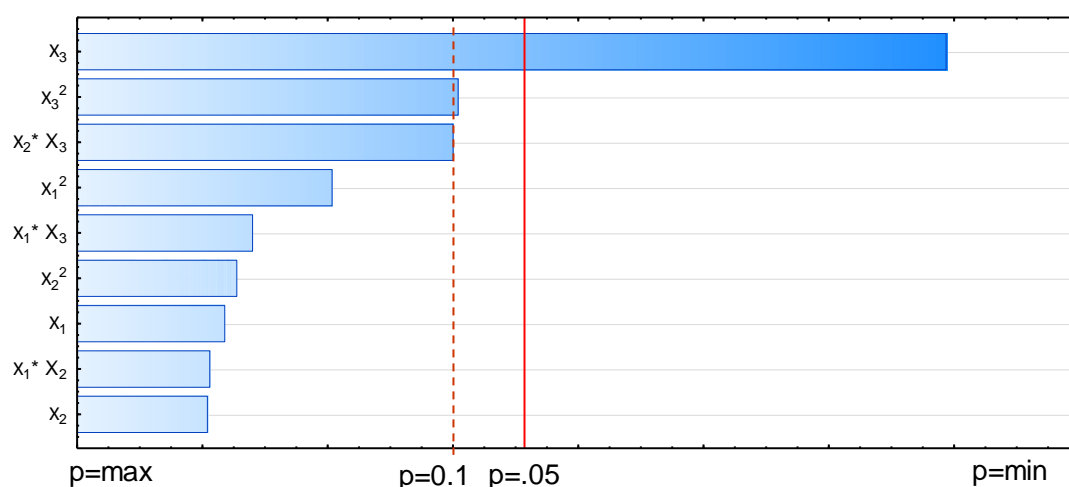


Figure 4–10: Pareto chart of standardized effects for permeate flux decline

The temperature had the highest impact on the flux decline and thus the useful life of the membrane within the range of feed conditions considered for the prehydrolysate. It was found

that the relationship between the initial permeate flux and the three input parameters, feed pressure (X_1), cross velocity(X_2) and temperature (X_3) can be fitted to the second order polynomial equation (9):

$$Y_2 = 2.14 + 0.58 X_3 - 0.147 X_3^2 + 0.275 X_2 * X_3 \quad (16)$$

The response model had an R^2 value of 0.91 and an adjusted R^2 of 0.74. The Adjusted R^2 value was considered a sufficient measure of fit because there are other factors related to the prehydrolysate that could also contribute to flux decline, such as increased osmotic pressure, fouling and concentration polarization.

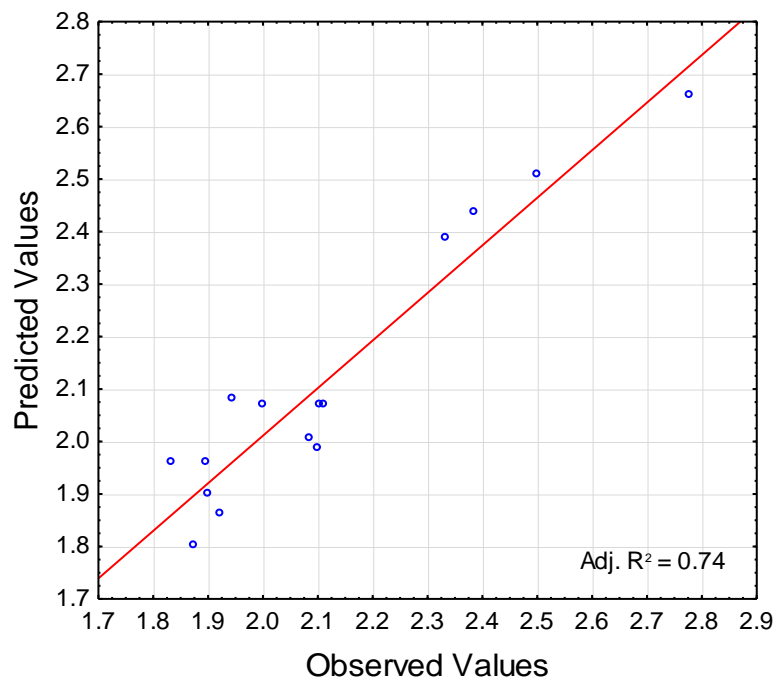


Figure 4–11: Observed initial permeate flux versus the values predicted by equation 9

The response surfaces in Figure 4–12 showing the flux decline variation with the feed temperature, pressure and cross velocity is based on equation 9. The nonlinear effect of pressure on the flux decline is seen in the contour lines in Figure 4–12A while a linear effect was observed for cross velocity in Figure 4–12B.

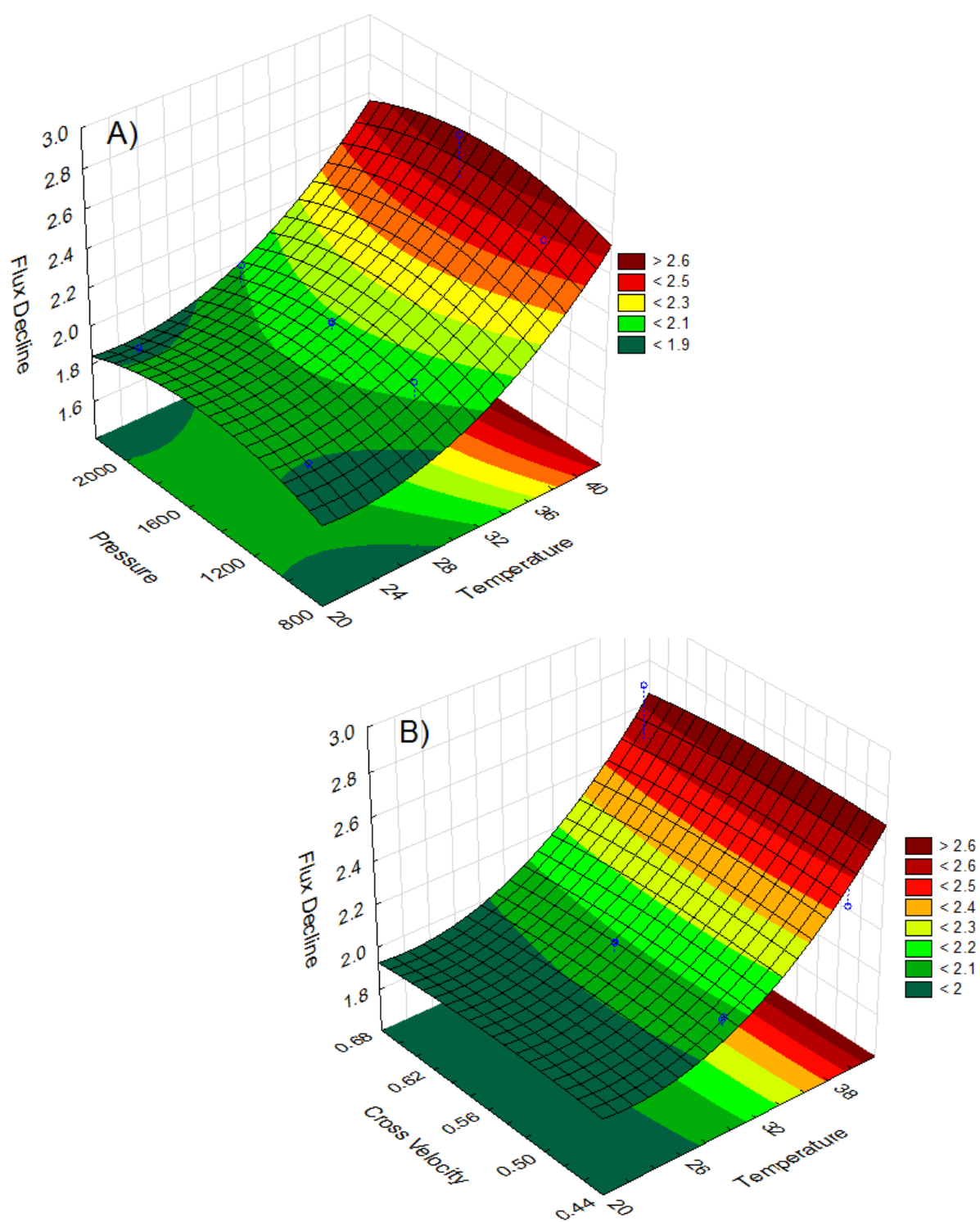


Figure 4-12: Response surface of flux decline, the combined effects of A) feed pressure and temperature B) cross velocity and temperature

Obviously, Figure 4–12A and Figure 4–12B show that the temperature plays the dominant role in the flux decline. It can also be seen that the flux decline at a temperature of 32°C is only about 10 % higher than the flux decline at 20°C. The maximum recommended temperature for limiting the flux decline due to the operating conditions in both response surfaces are in agreement. The effect of temperature was confirmed by two pure water filtrations tests conducted at a cross velocity of 0.45 m/s and a feed pressure of 3450 kPa. The feed temperature was kept at 22°C during the first test and at 40°C for the second test. It was observed that despite the high feed pressure applied over 4.5 hours, the flux decline was less than 12% for the filtration run at 22°C whereas it was as high as 36% when the temperature was raised to 40°C. It can thus be concluded that high temperature could result in flux decline through irreversible membrane compaction. The effect of temperature could be further compounded when the membrane is subjected to high pressure.

The selected nanofiltration membrane (NF90) produced high sugars retention (99 %) and a suitable permeate flux (12 L/m²h) during the concentration of the prehydrolysate solution by a factor of 5. The total sugars concentrations increased from 21 to 103 g/L. Operating the membrane system at a pressure inferior to 1050 kPa allows for compensation of flux reduction during concentration.

4.4 Conclusions

Six organic membranes that differ in MWCO and polymer material were evaluated for their ability to concentrate hemicellulosic sugars, organic acids and furfural in a prehydrolysate solution from a Kraft dissolving pulp mill. The experiments provided strong indications that nanofiltration can be applied to a wide range of hemicellulose prehydrolysate solutions in the forest biorefinery context. The membrane selection results can provide data for similar biorefinery processes involving a chemical conversion of the sugars. Results from this study also clearly demonstrate that RSM is an effective method for optimizing membrane filtration systems. It was used to determine the feed conditions that will lead to a long membrane life and at the same time reduce the energy required to reheat the prehydrolysate after concentration. Future research should include pilot scale experiments to enable a detailed economic analysis of the membrane system in a biorefinery process.

4.5 Acknowledgment

This research was supported by the Natural Sciences and Engineering Research Council of Canada University and College I2I program and BioFuelNet Canada. The authors are grateful to Prof. Jean Paris his valuable contributions to this work and to FPIInnovations for providing the hemicelluloses prehydrolysate.

4.6 References

- [1] J.-P. Lange, E. van der Heide, J. van Buijtenen, and R. Price, "Furfural—A Promising Platform for Lignocellulosic Biofuels," *ChemSusChem*, vol. 5, pp. 150-166, 2012.
- [2] S. Dutta, S. De, B. Saha, and M. I. Alam, "Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels," *Catalysis Science & Technology*, vol. 2, pp. 2025-2036, 2012.
- [3] L. Christopher, *Integrated forest biorefineries*: Royal Society of Chemistry, 2012.
- [4] J. A. Johnson, S. S. Walse, and J. S. Gerik, "Status of Alternatives for Methyl Bromide in the United States," *Outlooks on Pest Management*, vol. 23, pp. 53-58, 2012.
- [5] O. Ajao, M. Rahni, H. Chadjaa, M. Marinova, O. Savadogo, and J. Paris, "Hemicelluloses concentration and recovery using Reverse Osmosis (RO) membrane: Application to an integrated biorefinery for furfural production.," presented at the 63rd Canadian Chemical Engineering Conference, Fredericton, New Brunswick, 2013.
- [6] K. Lamminpää, J. Ahola, and J. Tanskanen, "Kinetics of Xylose Dehydration into Furfural in Formic Acid," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 6297-6303, 2012/05/09 2012.
- [7] O. Ajao, M. Rahni, M. Marinova, H. Chadjaa, and O. Savadogo, "Concentration of hemicelluloses prehydrolysate by membrane filtration: Feasibility and effect of composition on flux decline mechanisms," *Separation and purification technology*, vol. Submitted, 07 May 2014 2014.
- [8] T. Radiotis, X. Zhang, M. Paice, and V. Byrne, "Optimizing Hardwood Prehydrolysis for Simultaneous Production of Bioproducts and Biomaterials," *Journal of Bioprocess Engineering and Biorefinery*, vol. 1, pp. 69-76, // 2012.

- [9] V. L. Singleton and J. A. Rossi, "Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents," *American Journal of Enology and Viticulture*, vol. 16, pp. 144-158, January 1, 1965 1965.
- [10] I. P. Wood, A. Elliston, P. Ryden, I. Bancroft, I. N. Roberts, and K. W. Waldron, "Rapid quantification of reducing sugars in biomass hydrolysates: Improving the speed and precision of the dinitrosalicylic acid assay," *Biomass and Bioenergy*, vol. 44, pp. 117-121, 9// 2012.
- [11] Y. Mo, L. Zhao, Z. Wang, C.-L. Chen, G.-Y. A. Tan, and J.-Y. Wang, "Enhanced styrene recovery from waste polystyrene pyrolysis using response surface methodology coupled with Box–Behnken design," *Waste Management*, vol. 34, pp. 763-769, 4// 2014.
- [12] M. Tian, H. Park, and K. H. Row, "Optimization of Synthesis Amounts of Polymers with Two Monomers by Different Methods Based on Response Surface Methodology," *Advances in Polymer Technology*, vol. 33, pp. n/a-n/a, 2014.
- [13] S. Stade, M. Kallioinen, A. Mikkola, T. Tuuva, and M. Mänttari, "Reversible and irreversible compaction of ultrafiltration membranes," *Separation and Purification Technology*, vol. 118, pp. 127-134, 10/30/ 2013.
- [14] K. M. Persson, V. Gekas, and G. Trägårdh, "Study of membrane compaction and its influence on ultrafiltration water permeability," *Journal of Membrane Science*, vol. 100, pp. 155-162, 4/14/ 1995.
- [15] S. Déon, P. Dutournié, P. Fievet, L. Limousy, and P. Bourseau, "Concentration polarization phenomenon during the nanofiltration of multi-ionic solutions: Influence of the filtrated solution and operating conditions," *Water Research*, vol. 47, pp. 2260-2272, 5/1/ 2013.
- [16] J. I. Marriott, "Detailed modelling and optimal design of membrane separation systems," University of London, 2001.
- [17] Q. Zhang and C. D. Vecitis, "Conductive CNT-PVDF membrane for capacitive organic fouling reduction," *Journal of Membrane Science*, vol. 459, pp. 143-156, 6/1/ 2014.
- [18] M. T. M. Pendergast, J. M. Nygaard, A. K. Ghosh, and E. M. V. Hoek, "Using nanocomposite materials technology to understand and control reverse osmosis membrane compaction," *Desalination*, vol. 261, pp. 255-263, 10/31/ 2010.

- [19] Y.-L. Lin and C.-H. Lee, "Elucidating the Rejection Mechanisms of PPCPs by Nanofiltration and Reverse Osmosis Membranes," *Industrial & Engineering Chemistry Research*, vol. 53, pp. 6798-6806, 2014/04/23 2014.
- [20] A. De Munari, A. J. C. Semiao, and B. Antizar-Ladislao, "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter–pesticide complexation and solute–membrane interactions," *Water Research*, vol. 47, pp. 3484-3496, 6/15/ 2013.
- [21] C. Bellona, J. E. Drewes, P. Xu, and G. Amy, "Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review," *Water Research*, vol. 38, pp. 2795-2809, 7// 2004.
- [22] P. Qiu, M. Cui, K. Kang, B. Park, Y. Son, E. Khim,*et al.* ., "Application of Box-Behnken design with response surface methodology for modeling and optimizing ultrasonic oxidation of arsenite with H₂O₂," *Central European Journal of Chemistry*, vol. 12, pp. 164-172, 2014/02/01 2014.

CHAPTER 5. ARTICLE 3: FURFURAL PRODUCTION IN AN INTEGRATED FOREST BIOREFINERY: PROCESS DEVELOPMENT AND TECHNO-ECONOMIC ASSESSMENT

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ABSTRACT

Hemicellulosic sugars from a Kraft dissolving pulp mill can be valorized through the integration of a biorefinery for furfural production. Furfural is a multipurpose platform chemical, with derivatives that can replace many organic compounds currently produced from fossil resources. A novel process for furfural production from biomass, with a Kraft mill prehydrolysate stream used as feedstock is proposed. A simulation model for the process has been developed. The furfural biorefinery consists of three steps, prehydrolysate concentration, sugars conversion and product purification, and has a production capacity of 47 t/d. To reduce the energy consumption of the biorefinery, an optimized heat exchanger network and an absorption heat pump for implementation were designed. The energy and material integration of the biorefinery is feasible and the utility demands can be supplied by the receptor mill. A techno-economic evaluation of the developed process showed that it is economically feasible and a return on capital employed (ROCE) as high as 36 % can be obtained.

METHODOLOGY

- A novel process for furfural production from hemicellulose prehydrolysate is proposed
- The process is energy efficient and its energy demand is lower than for existing furfural processes
- The integration of the process with a Kraft dissolving pulp mill was demonstrated
- The process is economically feasible and can be implemented

KEYWORDS

Kraft mill, Integrated Biorefinery, Furfural Process, Process simulation, Biorefinery Optimization

5.1 Introduction

The integration of biorefining technologies into Kraft pulp mills has been the focus of several reported studies. An integrated forest biorefinery (IFBR) utilizes woody biomass, for the production of Kraft pulp and co-products such as biofuels or biochemicals. This is advantageous because woody biomass is one of the most abundant non edible biomass resource globally [1] and does not compete with arable land for food and animal feed production [2]. It is also a sustainable feedstock that can contribute to the lowering of greenhouse gases emission [3]. Woody biomass comprises four main classes of components: cellulose, hemicellulose, lignin and extractives. An important characteristic of an IFBR is that the Kraft pulp is the main product despite the production of co-products [4]. The hemicelluloses can be extracted prior to chemical delignification of the wood chips with a prehydrolysis step [5, 6] while the lignin can be extracted from the black liquor in the chemical recovery loop of the Kraft pulp mill after pulping [7, 8]. Hemicellulose extraction via a prehydrolysis step is practiced in some Kraft pulp mills for dissolving pulp production but the extracted hemicelluloses are typically combusted for energy together with the black liquor that contains the lignin fraction. Modifications can be made to such mills to redirect the hemicelluloses stream (prehydrolysate) to a biorefinery as the extraction process is well developed. The energy production capacity of the mill will not be significantly affected if the prehydrolysate stream containing the hemicelluloses is diverted to a biorefinery for conversion into value added products because its heating value is only about half that of lignin [5]. Furthermore, it is also beneficial for liberating pulp production capacity (debottlenecking the recovery boiler) in mills that have their production capacity limited by the recovery boiler.

Furfural is a bioproduct that can be produced via a chemical conversion pathway from the C₅ hemicellulose sugars. It is a platform chemical that can be used directly as nematocide, industrial solvents or precursor for resins and polymers or further converted into biofuels [9]. Currently, the established processes for its production are standalone processes that utilize agricultural residue such as corncobs or bagasse [10]. The processes are characterized by high energy intensity and their integration other existing processes where hemicellulose sugars are already produced has

been proposed as a potential means of lowering the production cost [11, 12]. An integrated biorefinery process with Kraft pulp mill as a receptor thus offers an opportunity for lowering the cost of furfural production and increasing the revenue for the receptor mill. Such a biorefinery process must not only have a minimum impact on the energy balance of the mill but the material and energy integration with the receptor mill must be technologically and economically feasible. It is also important that the pulp yield and quality not be deteriorated after integration of the biorefinery. To the author's knowledge, no process for producing furfural in an integrated forest biorefinery has been reported in scientific literature although it is well known that C₅ sugars can be converted into furfural. This paper aims at achieving the following objectives:

- Develop and propose an innovative furfural process for an IFBR
- Optimize the energy consumption of the biorefinery
- Assess the potential of integration in a receptor mill
- Carry out a techno-economic evaluation of the process.

5.2 Kraft pulping process as a receptor mill of an IFBR

5.2.1 Kraft pulping process

Pulping is the separation of cellulose fibres that are fixed in wood or plant matrices from the other components (mainly hemicelluloses and lignin). It entails the rupture of bonds that exist within the wood structure. The existing pulping methods could be broadly classified as thermal, mechanical, chemical driven. Some pulping methods are a combination of the different classification. Kraft pulping, a full chemical process, is the predominant pulping method in use globally [13]. Its advantages include, (i) the pulp produced has a high quality (stronger than from other methods), (ii) most of the chemicals consumed in the process can be recovered efficiently and economically and (iii) substantial amounts of energy is produced in the recovery boiler. Two kinds of pulp can be produced using the Kraft process, paper and dissolving pulps. Dissolving pulp has a higher cellulose purity ($\geq 96\%$) than Kraft paper pulp ($<90\%$) and the higher cellulose purity is achieved through a prehydrolysis step to extract hemicelluloses prior to pulping [6]. Dissolving pulp is a precursor for consumer products such as rayon textiles, packaging materials and retardant agents. A dissolving pulp mill process is illustrated in

Figure 5–1. Examples of prehydrolysis methods that can be used for extracting hemicellulosic sugars from lignocelluloses include hot water, steam, sodium hydroxide, organic solvents, sulfite pre-treatment, ammonia-fiber expansion and acid catalyzed treatment [14]. The methods all have different costs, level of technological maturity, and amount of sugars extracted and feasibility of integration with a Kraft dissolving pulp mill. A main constraint on the choice of the prehydrolysis method in an IFBR is that a selected method must not lead to the deterioration of the pulp quality or lower the pulp yield. A combination of steam and hot water has been shown to be suitable for an IFBR [15], it also has the advantage of not requiring the addition of chemical agents.

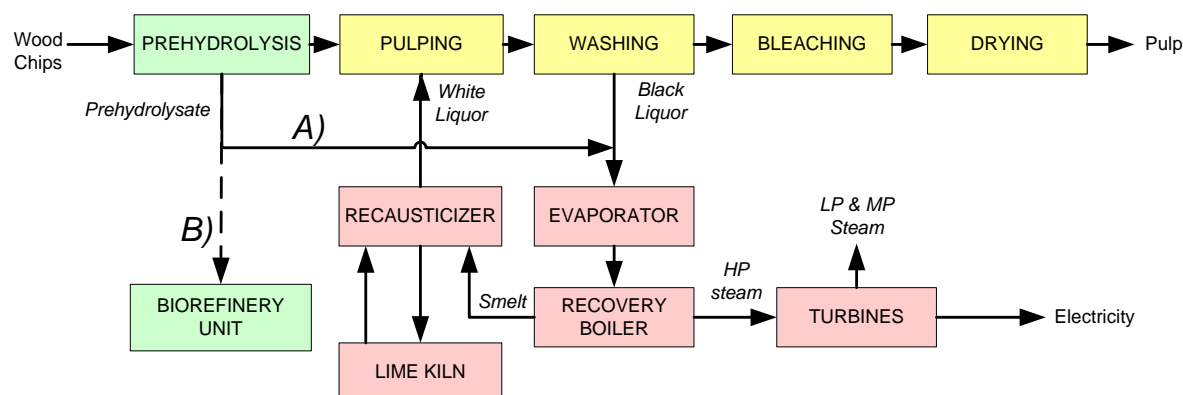


Figure 5–1: Simplified block diagram of Kraft dissolving pulp mill with A) prehydrolysate sent for combustion in the recovery boiler B) prehydrolysate diverted to a biorefinery unit

After hemicellulose extraction by hot water and steam in the prehydrolysis step, the prehydrolysate stream containing the extracted hemicellulosic sugars can be withdrawn and sent to a biorefinery unit. The pretreated wood chips are sent for chemical delignification using white liquor, a mixture of sodium sulfide and sodium hydroxide, to separate the lignin and the residual hemicellulose from the cellulosic fibres (pulp). The pulp is then washed, bleached and dried. Black liquor, the spent liquor from delignification, is separated from the pulp in the washing step, concentrated and sent to the recovery boiler where it is combusted to produce steam for the Kraft mill and for electricity generation. The inorganic chemicals are recovered from the recovery boiler as a smelt and sent to the recausticizer where white liquor is regenerated using lime produced in the lime kiln. Several modern Kraft mills produce about 70% of their total energy demand onsite and in most cases using renewable resources such as biomass residue or bark [16]

5.3 Furfural feedstock, production processes and derivatives

5.3.1 Furfural feedstock

Furfural is a reddish brown liquid with a solubility of 8.3 % wt in water at 25°C. It forms an azeotrope with water at 35% weight. It is typically produced from pentosan rich feedstock of agricultural origin. The pentosan compositions for several potential feedstocks are shown in Figure 5–2.

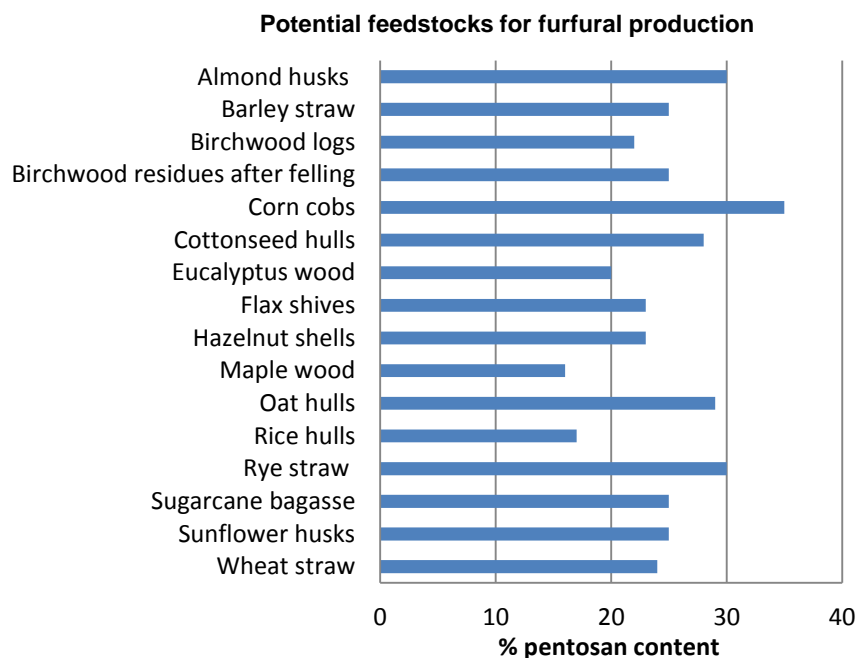


Figure 5–2: Pentosan content of plants and agricultural residues for furfural production [17]

Two subsequent reactions occur during furfural production. First, the hydrolysis of the penstosan into pentoses takes place in the presence of an acid catalyst.



In the second reaction, the pentoses are dehydrated through the liberation of three molecules of water from a pentose molecule to form furfural. The stoichiometric yield is 73g of furfural per 100 g of the pentosan. Low yields can be caused by two types of loss reactions, the reaction of

furfural with itself resulting in a polymer (furfural resinification) and a reaction with an intermediate (furfural condensation) [18].

5.3.2 Furfural production processes

Several existing and recently proposed furfural production schemes have been discussed in the published scientific literature [11, 18-21]. An overview of some production processes is given in Table 5.1. The furfural production processes can be classified as industrial, pilot or laboratory scale. The processes at the laboratory level are characterized by attempts to improve the furfural yield, reduce the energy consumption. The use of solid catalysts to lower costs, organic acids to reduce mineral acid consumption or use of biphasic systems with organic solvents to enhance furfural purification have also been investigated at laboratory scale. Based on the residence time for the conversion reaction is shortened by high temperatures (170 - 220 °C) and pressures of (1800 - 2200 kPa). Carrying out the reactions at high temperatures can also be used to minimize the furfural losses because the loss reactions are slower than furfural formation [22].

Table 5.1: Selected furfural production processes and main characteristics

	Feedstock	T (°C)	P (kPa)	t (mins)	Catalyst	Yield (%)	Status
Batch Process	Corn curbs	140 - 180	607	300	H ₂ SO ₄	35-50	Industry
Biofine (2 steps)	Paper Sludge and MSW	210-220, 190-200	2533, 1420	0.2 , 20	H ₂ SO ₄	70	Pilot
Quaker Oats	air dry oat hulls	-	~1013	60	H ₂ SO ₄	~ 55	Industry
Supratherm ®	Chopped Bagasse	200-240	2026- 3039	-	H ₂ SO ₄	~70	Pilot
Verdenikov	Foliage wood	188	-	-	H ₂ SO ₄	~ 75	Pilot
MTC	Straw	180	1000	25	H ₂ SO ₄	86	Pilot
Current case Study	Prehydrolysate	170-220	1820 - 2230	< 5	H ₂ SO ₄	~ 75	Concept

The industrial furfural processes were developed mainly for the production of furfural from solid biomass and the use of mineral acids as catalysts is predominant. In view of the fact that the feedstock available in the integrated forest biorefinery is aqueous hemicellulose prehydrolysate, a novel energy efficient process is required to make the biorefinery technically and economically feasible.

5.3.3 Furfural derivatives and applications

Furfural is valued as a chemical due to its versatile use; it can be used in direct applications or converted into derivatives. A list of some of the potential derivatives and direct applications is given in Figure 5–3. About 60% of the furfural produced worldwide is converted into furfural alcohol for further transformation into foundry resins, this makes it the most important derivative of furfural [4]. It is produced by the hydrogenation of furfural using copper chromium as catalyst. Furans can be produced by the decarboxylation of furfural and can be further converted into other important bioproducts. Furoic acid is used in the pharmaceutical and agricultural industry and it can be produced either through the oxidation of furfural or a canizzaro reaction. Furfurylamines used in the automotive, pharmaceuticals, industrial chemicals and can be produced via reductive amination of furfural.

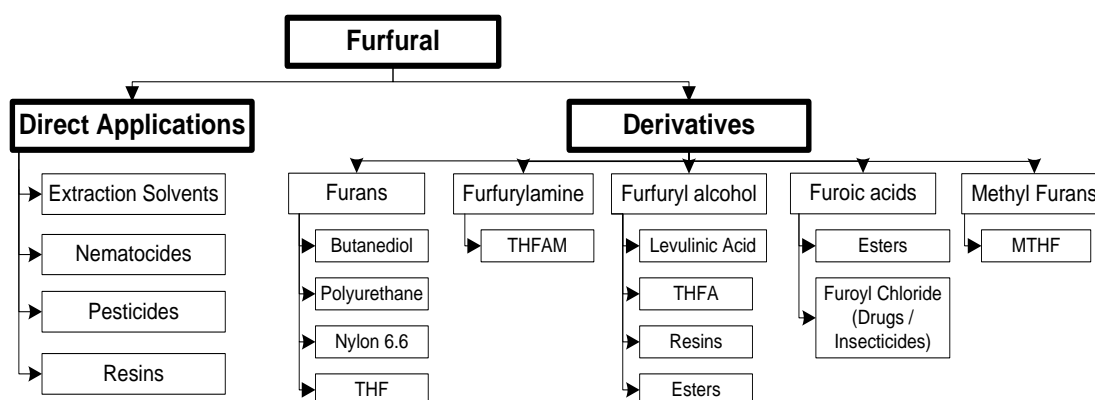


Figure 5–3: Family tree showing some potential furfural direct applications and derivatives

An emerging application of furfural is via the methyl furans derivatives route. 2-methylfuran and methyltetrahydrofuran are considered as fuel precursors, they are promising components of gasoline that have already been tried in extensive road tests [12].

5.4 Methodology for process design and economic analysis

The methodology for the development of an integrated forest biorefinery for furfural production is illustrated in Figure 5–4. Input data for the development of the biorefinery were obtained from literature, previously published reports and the simulation software database (Aspen Plus®). Data was also generated from experiments for process steps with no previously reported data.

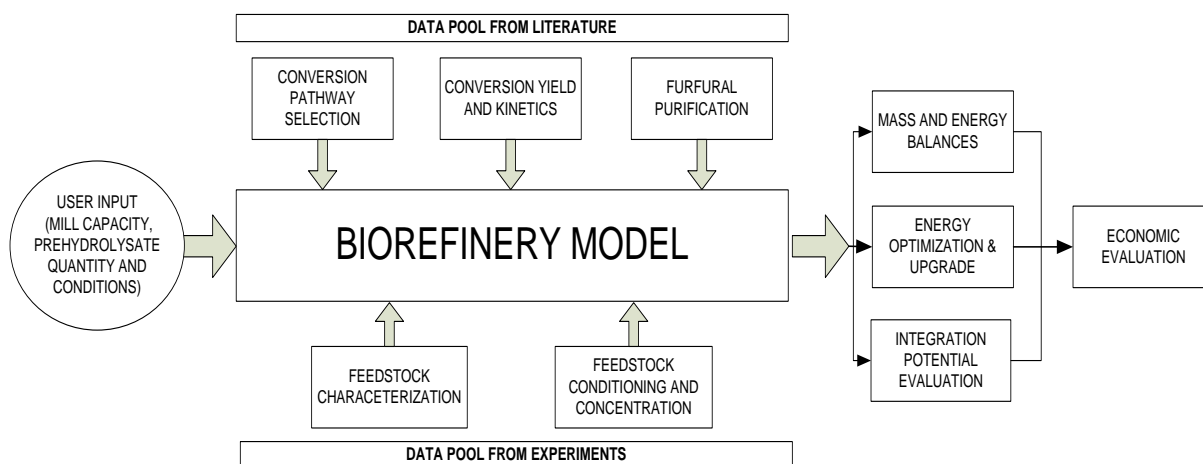


Figure 5–4: Overview of methodology for the furfural biorefinery development

The developed biorefinery model is flexible and can be adjusted to different prehydrolysate composition, and flow rates. A simulation of the furfural process on Aspen Plus® V7.2 simulator was used to compute detailed mass and energy balances. The data were subsequently used for assessing the hot and cold utility requirements and to optimize the heat exchangers network (HEN) using Aspen Energy Analyzer. Energy upgrading through absorption heat pump (AHP) was evaluated as an alternative for improving the energy of the process. The degree of integration between the furfural plant and the receptor mill was determined. The dimensions and cost of the process equipments were estimated. The cost of the standard process equipments such as heat exchangers, pumps and distillation columns were obtained from literature, updated by means of cost indices and scaled up where necessary using the six-tenths factor rule [23]. Estimates of the costs required for the modification of the receptor mill were obtained from a published report [24].

5.5 Proposed biorefinery configuration for furfural production

5.5.1 Identification of alternatives, selection and design of process steps

The feedstock in the proposed biorefinery is hemicellulose prehydrolysate extracted from a receptor Kraft dissolving pulp mill. The prehydrolysate composition was obtained from pilot plant experiments at FPInnovations (Canada) using steam and hot water hydrolysis at 170°C /800 kPa and dry wood chips to water weight ratio of 1:4 and [25]. The composition of the prehydrolysate considered is shown in Table 5.2

Table 5.2: Composition of hemicelluloses prehydrolysate

Components	Mass Flow (t/d)
Water	4800
Acetic Acid	17
Furfural	3
Lignin	15
Pentose	83
Hexose	17

The prehydrolysate had a low sugar concentration (<2 % wt), to reduce the energy requirement and size of the downstream biorefinery process units (hemicelluloses conversion and furfural purification), the implementation of a concentration step is essential. A concentration method that retains the acetic acid fraction is also a means for lowering the pH and thus reducing the organic acid requirement.

Different state of the art alternatives were identified for the following biorefinery process steps:

- prehydrolysate concentration,
- sugars conversion
- furfural purification

Alternatives that would lead to an energy efficient and environmentally friendly process were selected.

5.5.1.1 Prehydrolysate concentration

Two alternatives for prehydrolysate concentration were compared: the use of nanofiltration membranes or multi effect evaporators. The feasibility of concentration with membranes has been reported in an earlier publication [9]. It was shown that a reduction in permeate flux during concentration can be compensated for by increasing the pressure. Furthermore, a permeate flux of 12 L/m²h which is feasible at an industrial scale can be obtained during a volumetric concentration by a factor of 5. The energy demand of the membrane system comes mainly from pumping to supply the pressure gradient between the feed and permeate sides and can be calculated by equation 3.

$$W = \frac{Q_f P_f}{(\eta - L)} \quad (19)$$

The power consumption (W) of the pump is related to the feed volumetric flow rate (Q_f), feed pressure (P_f), efficiency of the pump (η) and pressure loss adjustment (L). The power requirement for the pump is 300 kW at the design conditions, a prehydrolysate volumetric flow rate of 0.06 m³/s, feed pressure of 3500 kPa, total pump efficiency of 80% and pressure losses of 10%.

Another well-known alternative for concentrating the prehydrolysate is the use of multi-effect evaporators. The amount of water to be evaporated to reach a volumetric concentration factor of 5 can be calculated from equation 4.

$$\dot{m}_{evaporated} = \dot{m}_{feed} \left(1 - \frac{\text{initial sugar concentration}}{\text{final sugar concentration}} \right) \quad (20)$$

The amount of water that must be evaporated (45 kg/s) can be further used in equation 5 to calculate the minimum amount of energy (Q_{evap}) that must be supplied to a multi-effect evaporator with the number of effects $N_{t,eff}$ of 4. The latent heat of evaporation (λ) of water is 2,270 kJ/kg.

$$Q_{evap} = \frac{\lambda \cdot \dot{m}_{evaporated}}{N_{t,eff}} \quad (21)$$

A comparison of both alternatives was made given that the membrane cleaning frequency is 7 days with a lifetime of 2 years while the price of steam is 3.3 \$/ ton. The results are shown in Table 5.3.

Table 5.3: Comparison of nanofiltration membranes and multi-effect evaporators

	Membrane System	Multi-effect Evaporator
Purchased Equipment Cost (M\$)	0.42	0.67
Installed Equipment Cost (M\$)	3.3	0.94
Energy requirement * (MW)	0.3	26
Yearly Operating cost (M\$/a)	0.8	2.7
* Electricity for membranes system and steam for evaporator		

A detailed economic analysis of the membrane filtration system and the sensitivity of the concentration costs to the membrane cleaning frequency and useful life are presented in section 5.5.5.

5.5.1.2 Sugars conversion

Existing furfural production processes generally require the fractionation of the biomass feedstock before furfural production. An overview of some furfural processes (pilot or commercial scale) is given in Table 5.1. Although the processes are not directly comparable due to the difference in feedstock, operating conditions and substrate concentration, it can be concluded that the conversion of the pentoses in the prehydrolysate into furfural will require a shorter resident time because the sugars have been broken down into a mixture of oligomers and monomers, during the prehydrolysis step. Furthermore, the kinetics of oligomeric sugar conversion into monomers is much faster than the transformation of the monomers into furfural. For the conceptual design in this case study, it was taken that temperatures between 170 – 210 °C and a pressure of 1800 – 2250 kPa would be sufficient to obtain conversion as high as 75 % of the theoretical yield and a short residence time which would minimize the furfural loss reactions. Upon concentration of the prehydrolysate, the pH is reduced from 3.5 to 2.9 due to the acetic acid

concentration but additional acid catalyst is required to further reduce the pH in the reactor from 2.9 to ~1.5. Sulphuric acid was selected as the catalyst because its use and efficiency have been validated in several publications. The conditions used for the design in this case study are 170°C, 2100 kPa and sulfuric acid concentration of 1.8% wt.

5.5.1.3 Furfural purification

The product stream from the sugars conversion step will contain less than 6% wt of furfural. This is in the same range as all known conversion processes [18]. It must be purified to obtain high quality furfural. The use of a simple distillation for the recovery of furfural is however impossible because furfural forms an azeotrope with water at 35 % wt. The azeotrope formed is a positive azeotrope with its boiling point (97.8°C) lower than that of water (100°C) and furfural (126 °C). A common practice in existing furfural processes is to make use of two distillation columns with a decantation step between the two columns as shown in Figure 5–5A. Furfural is recovered at just below its azeotropic point at the top of the first column and then fed into a decanter where the mixture spontaneously splits into furfural rich and furfural lean phases. The furfural rich phase is withdrawn and sent to the secondary distillation column where furfural at 99% purity can be recovered from the bottom of the column. An alternative method for the purification of azeotropic mixtures is extractive distillation shown in Figure 5–5B. It requires the introduction of a solvent which can alter the relative volatility of the furfural-water mixture. Water and the acid from the product stream can be recovered from the first column while furfural is recovered with the second column and the solvent recycled for use in the first column.

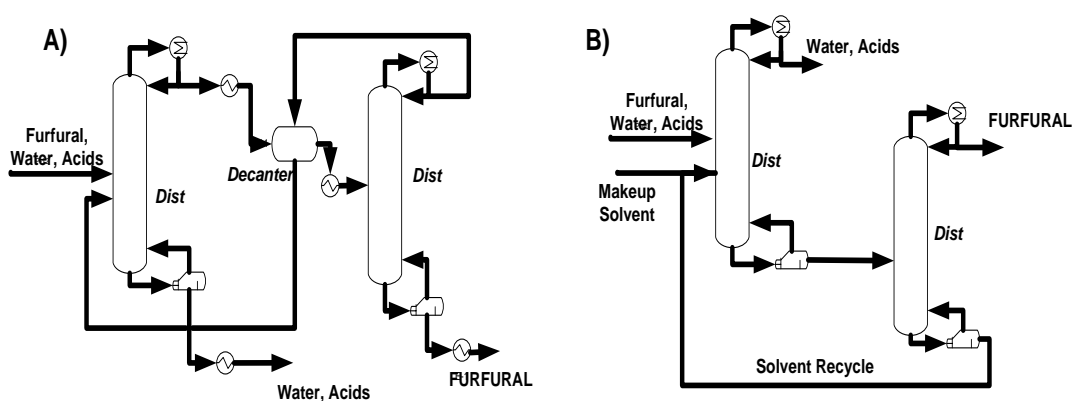


Figure 5–5. Process diagrams illustrating A) conventional furfural distillation B) extractive distillation

Aspen Plus® V7.2 azeotrope search function was used to evaluate the possibility of utilizing several entrainer solvents available in published literature for extractive distillation [26]. It was discovered that most of the solvents are not suitable; they all result in the formation of other azeotropes (in addition to water – furfural) except for trichlorobenzene.

Table 5.4. Entrainer solvents evaluated for the extractive distillation of furfural

Entrainer Solvent	BP (°C)	Azeotropes*
Trichloroethane	73.9	1
Diethylbenzene	180.9	3
Dipropylbenzene	210.5	3
N-Butylbenzene	182.9	2
Tetraline	207.6	2
Isophorone	215.2	2
Dichlorobenzene	173.1	2
Dibromobenzene	218.0	1
Trichlorobenzene	213.0	0
Carbon-Tetrachloride	76.6	1
Ethyl-Acetate	77.1	1
N-Octyl-Acetate	211.3	1

* Azeotropes formed other than water - furfural

It was determined that the energy requirement for furfural distillation can be reduced by as much as 30% with the use of trichlorobenzene. However, it is not a sustainable entrainer from an environmental standpoint since trichlorobenzene is currently classified as a hazardous chemical with restricted use [27, 28]. The design of the furfural purification step in this work was based on Figure 5–5A.

5.5.2 Proposed biorefinery process

The selected receptor Kraft mill produces about 670 odt/d (odt = oven dried tons) of dissolving pulp from hardwood in eastern Canada. The mill employs a series of batch digesters for the

removal of the hemicelluloses from the wood chips. Steam is used in the prehydrolysis step and the wood chips are neutralized with alkali liquor prior to pulping. The mill produces high pressure (HP) steam using a recovery boiler and a bark-bunker oil power boiler. Electricity, medium pressure steam (MP) and low pressure (LP) steam are produced from the HP steam in the cogeneration system. A detailed analysis of the receptor mill using an innovative optimization methodology for the energy and water consumption of the mill was previously done [29].

It was shown that steam consumption (250 MW), water consumption (2480 m³/h) could be reduced by 27 and 38 % respectively. In its current state, the neutralization liquor that is used to neutralize the chips after prehydrolysis degrades the sugars. Modification to the mill is required to recover and redirect the prehydrolysate stream from the recovery loop to the biorefinery. Subsequently, dilute prehydrolysate from the receptor mill will be supplied to the furfural plant at 80 °C. A process flow diagram for the proposed biorefinery for the production of furfural from prehydrolysate is shown in Figure 5–6. The process was simulated using Aspen Plus® V7.2, to obtain the energy and mass balances. The biorefinery process contained several chemical compounds that are not available in the software database. The properties of these compounds were obtained from the National Renewable Energy Laboratory (NREL) physical property database for biofuels components [30] and imbedded into Aspen Plus®.

The composition of the feedstock the retention and flux characteristics of the membrane system and the compositions of stream 1 to stream 6 were obtained from experimental data [9]. The membrane system allows increases the total hemicellulosic sugars concentration from 21 g/L up to 103 g/L. It was modeled as a split separator in the Aspen Plus® module. The concentrated prehydrolysate stream is subsequently sent to the conversion reactor. The reactor was modeled as a stoichiometric reactor in Aspen plus.

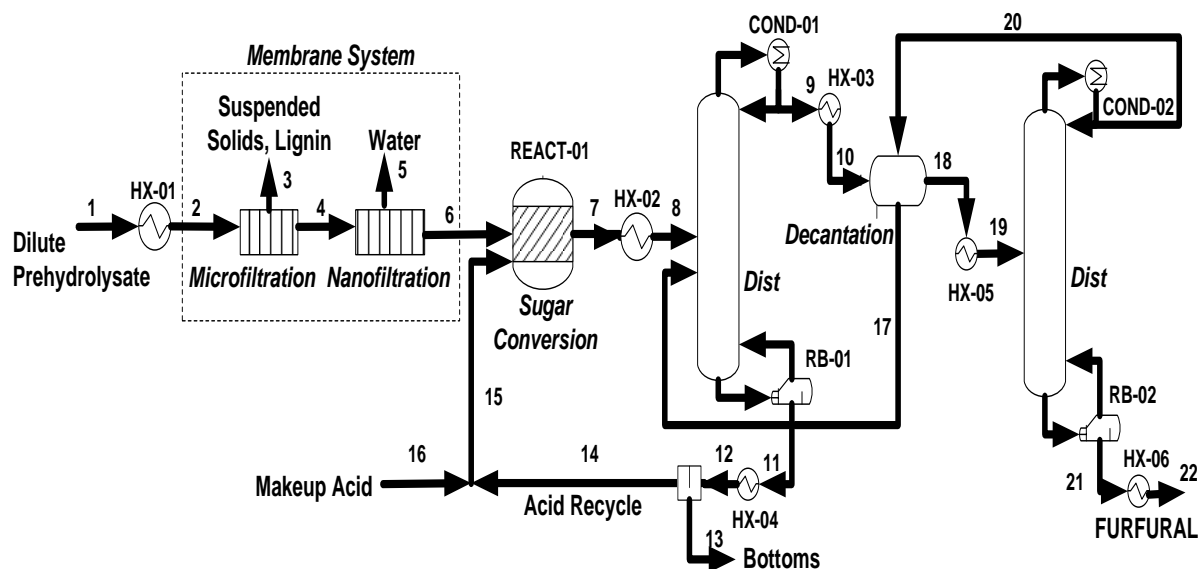


Figure 5–6. Process flow diagram of the furfural biorefinery

A pentose conversion of 100% is achieved with 75 % into furfural and 25 % into other degradation products that remain in the aqueous phase. The azeotrope distillation train is then used to purify the furfural to 99 % wt of furfural. The distillation sequence was modeled using a rigorous distillation Aspen Plus® module. The preliminary values for the specification of the columns were determined graphically with the Mcaabe-Thiele diagram. Extensive sensitivity analysis simulations were performed to determine the number of stages, the feed stage, reflux ratio and distillate to feed ratios.

Recovery of the spent acid is proposed as a part of the biorefinery process. Pressure losses were considered to be negligible in the heat exchangers and columns. The properties for the main process stream are given in Table 5.5. The base case simulation is designed to process 4940 t/d of hemicellulose prehydrolysate from the receptor mill with a furfural production of 47 t/d.

Table 5.5. Data for key process streams

	Streams								
	1	6	7	9	11	17	19	20	21
T (°C)	80	31	170	97	100	20	98	97	131
P (kPa)	100	2100	2100	100	100	100	150	100	100
Total flow (t/d)	4940	616	618	154	569	105	52	5	47
Water (t/d)	4818	494	508	103	504	99	3	3	1
Total C₅ sugars (t/d)	82.4	82.4	23.0	-	23.0	-	-	-	-
Total C₆ Sugars (t/d)	16.7	16.7	17.4	-	17.4	-	-	-	-
Furfural (t/d)	3.3	3.3	47.5	50.7	-	3.2	48.5	1.8	46.8

5.5.3 Energy requirement minimization and upgrading

The total heating requirement (14.2 MW) for the biorefinery stems mainly from the furfural purification step (70 %) while the conversion of the pentoses into furfural constitutes only 30% of the total requirement. The total cooling requirement (25.6 MW) is evenly split between the cooling of the prehydrolysate and the furfural purification step. Approaches that have been used for the energy optimization of integrated forest biorefineries based on pulp and paper mills can be categorized in 2 groups:

- Independent energy optimization of the receptor mill and the biorefinery with the objective to liberate enough energy from the receptor mill for an optimized biorefinery process [29]
- Site wide optimization which simultaneously optimizes the energy requirement of the receptor mill and the biorefinery process [31].

This work favours an independent optimization of the receptor mill and biorefinery process because the product mass flow of the biorefinery is 1% of the prehydrolysate mass flow into the biorefinery process. Furthermore, in terms of output mass flows, the furfural production rate is less than 7% of the pulp production. It is therefore not likely to require extensive modifications to the energy and water network of the receptor mill in order to host a biorefinery process that constitutes only a small fraction of the total site energy requirement. Independent optimization is supported by a previous case study of the same receptor mill which showed that

total steam savings as high as 27% can be achieved [29]. This savings can be obtained by implementing a small number of low risk and low cost energy saving projects.

5.5.3.1 Heat exchanger network optimization

The heat exchanger network optimization of the furfural process was carried out with the pinch analysis technique in the software Aspen Energy Analyzer. Pinch analysis is a well-established method to set energy savings target and design heat exchanger networks in industrial processes [32]. As a first step, all the hot and cold process streams were identified followed by data extraction from the simulated model for the process heating and cooling duties, mass flows and temperature gradient. The data were then used to plot composite curves of hot and cold process streams on a single T-H diagram in order to determine the minimum heating and cooling requirements. A temperature difference (ΔT_{\min}) of 10°C between the hot and cold sides of the process was selected. The pinch point was found to be 105°C , the minimum cooling requirement 21.6 MW and the minimum heating requirement 10.2 MW as shown in Figure 5–7.

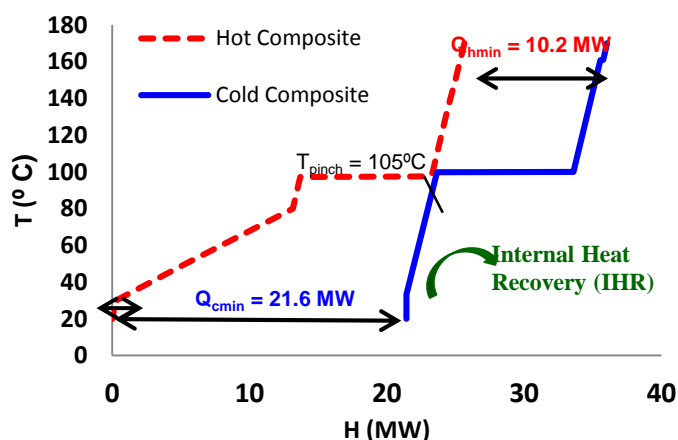


Figure 5–7: Thermal composite curve for the furfural biorefinery

An optimized heat exchanger network was developed to reduce the heating and cooling requirements of the process. Two heat exchangers were added to recover heat from the exchanger after the furfural conversion reactor (HX-02) and the condenser of the main distillation column (COND-01) in Figure 5–6. The liberated heat was used to preheat the input stream (6) for the conversion reactor. This led to an increase of the total heat exchanger surface area by 23%. Nevertheless, the heating and cooling requirement were reduced down to 11.0MW (-22%) and 23.4 MW (-9 %) respectively.

5.5.3.2 Energy upgrade

The furfural biorefinery is a small capacity unit with limited energy optimization potential by heat exchanger network design. However, the availability of low temperature heat was an opportunity to improve the thermal energy efficiency of the process by implementation of an absorption heat pump. An AHP is a heat driven device for upgrading heat liberated from a process at a low temperature to a higher temperature. The steps used for implementing the absorption heat pump can be summarized as:

- Identification of available heat sources for upgrade after the development of an optimized heat exchanger network (HEN)
- Selection of the AHP working fluid ($\text{H}_2\text{O}/\text{LiBr}$), and specification of the AHP on the $\text{H}_2\text{O}/\text{LiBr}$ phase diagram
- Simulation of the AHP and integration with the biorefinery process on Aspen Plus

The AHP implementation in the main distillation column of the furfural biorefinery is illustrated in Figure 5–8. Heat is supplied to the AHP evaporator (E) and generator (G) from the condenser of the distillation column at 97°C and liberated at a higher temperature (145°C) by the absorber (A) and at a lower temperature (30°C) by the condenser (C).

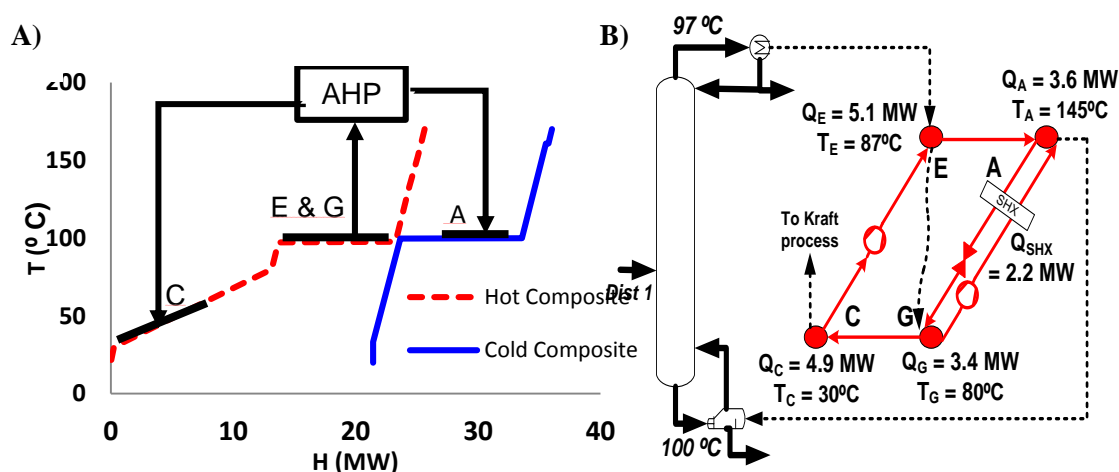


Figure 5–8: Positioning of absorption heat pump illustrated in A) the composite curve B) distillation column

The coefficient of performance (COP), which is the ratio of heat supplied to heat upgraded, for the AHP is taken to be 42 %. After HEN optimization and AHP integration, the heating

requirement for the biorefinery is reduced to 7.4 MW (48 %) and the cooling requirement is reduced to 19.7 MW (23 %), as shown in Table 5.6. The reductions would facilitate the implementation of the biorefinery unit into a Kraft pulping mill without the need for additional steam and hot water production capacity.

Table 5.6: Energy requirement minimization after HEN design and AHP implementation

	BASE CASE	OPTIMIZED HEN	OPT. HEN + AHP	SAVINGS (%)
Heating Requirement (MW)	14.2	11.0	7.4	48
Cooling Requirement (MW)	25.6	23.4	19.7	23

The introduction of an absorption heat pump could make the process control system for the distillation column more complex and challenging to implement but nevertheless, the significant energy savings justifies its use.

5.5.4 Integration with the receptor mill

The potential mass and energy integration between the biorefinery unit and the receptor Kraft pulp mill is illustrated in Figure 5–9. The biorefinery process has a heat demand of 7.4 MW, which constitutes only 11 % of the potential steam savings that can be obtained at the receptor mill (67.5 MW) through the application of steam and water efficiency enhancements projects [29]. The steam required by the biorefinery can be supplied by the receptor mill. The cooling requirement can be met using fresh water available from the utility system. The water recovered by the membrane system could also be redirected to the hot water tank of the mill. The sulfuric acid required to lower the pH of the concentrated prehydrolysate can be supplied by the spent acid from the mill chemical preparation department after recovery and purification with established technologies such as the Generator Acid Purification (GAP™) system developed by FPIInnovations [33, 34]. The same method can be subsequently applied for the regeneration of the used acid from the furfural process.

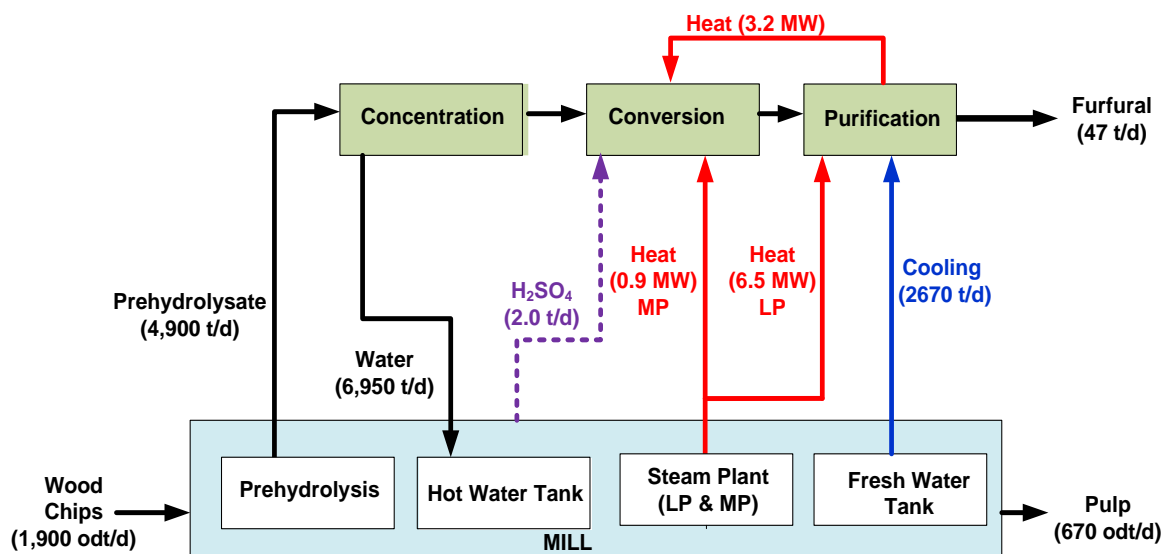


Figure 5–9: Process scheme for biorefinery integration with receptor mill

Specifically, the potential integration considers the following aspects:

- **Energy Integration:** The biorefinery plant will require 0.9 MW of medium pressure steam for the sugar conversion reactor. About 6.3 MW of the total low pressure steam demand (6.5 MW) would be used to drive the reboiler of the main distillation column. The cooling requirement is met by using 2670 t/d fresh water to cool down hot streams at the condensers of the distillation columns and AHP and the prehydrolysate prior to membrane concentration.
- **Water:** The furfural plant has no direct water consumption. However, 6950 t/d of water comprising 4280 t/d recovered with the use of membrane filtration and 2670 t/d cooling water will be sent back to the hot water tank of the Kraft process.
- **Chemicals:** About 2 t/d of sulfuric acid would be required to start up the biorefinery; this can be either purchased or recovered from the spent acid in the Kraft process. The acid would be subsequently recycled to reduce the sulfuric acid consumption. Only make up acid from the Kraft process will be required by the biorefinery after furfural production has started.

The energy and material integration of the furfural process with the receptor Kraft pulp mill is feasible for the designed process.

5.5.5 Economic analysis

A detailed economic analysis of the process was carried out to evaluate the economic profitability of the process. The cost of conventional equipments were based on cost engineering models available in literature [23], the cost of the membrane filtration unit under different scenarios was estimated using the online GE RO tool™ [35] the installed cost for the absorption heat pump is based on a previous study [36]. The cost of modifying the mill to divert the prehydrolysate to a biorefinery unit instead of combusting it and the global plant operating costs were obtained from a published report [24]. The costs were scaled using the six-tenths factor rule where necessary and the original costs were updated to the reference year (2014) values by means of cost indices. All costs are given in US \$. It was necessary to treat the economic implications of the membrane system in detail because it is a novel membrane technique on which there are only limited published data.

A minimum total membrane surface area of 15200 m² is necessary to recover 182000 L/hr of permeate at a flux of 12 L/m²h. The required number of membrane elements (N_E) can be calculated using equation 6.a A membrane element with a surface area of 37 m² can be purchased.

$$N_E = \frac{Q_p}{S_{Ef}} \quad (22)$$

Thirty extra membrane elements were taken into account for the periodic cleaning and replacement of some elements. The preliminary economic evaluation for the membrane filtration system is based on the data given in Table 5.7. The total investment cost for the membrane filtration systems is 3.3 M\$.

Table 5.7: Parameters and values used for economic evaluation of the membranes

Investment cost (\$/m ² membrane area)	200
Membrane bare element area (m ²)	37
Total Number of elements required	440
Number of pressure vessels (8 elements / vessel)	50
Membrane bare element cost (\$/m ²)	26
Membrane element life time (years)	1 – 5
Cleaning frequency (days)	7-180
Electricity price (\$/kWh)	0.07
Pump efficiency (%)	0.7

The total annual cost (C_t) of the membrane system consists of components given shown in equation 7. C_a indicates the amortization cost over the useful life, C_e the electricity cost and C_{op} the operating cost for cleaning and replacing the membrane elements.

$$C_t = C_a + C_e + C_{op} \quad (23)$$

A straight line amortization over a useful life of 20 years is assumed in this case and gives a C_a of 163 k\$/y. The electricity cost (C_e) was calculated to be 168 K\$/y for 8000 hour of operation per year and consumes 300kW of electricity at a unit price of 0.07 \$/kWh. The operating costs for the membrane filtration system were estimated using the online GE RO tool™ [35]. Key input data for the program include the number of hour of operation and the manpower requirement, cost of utilities, cost of chemicals and cleaning agents, size of the cleaning tank and the membrane replacement and cleaning frequency. The sensitivity of the operating cost to the cleaning frequency and the lifetime of the membrane element were determined and is shown in Figure 5–10.

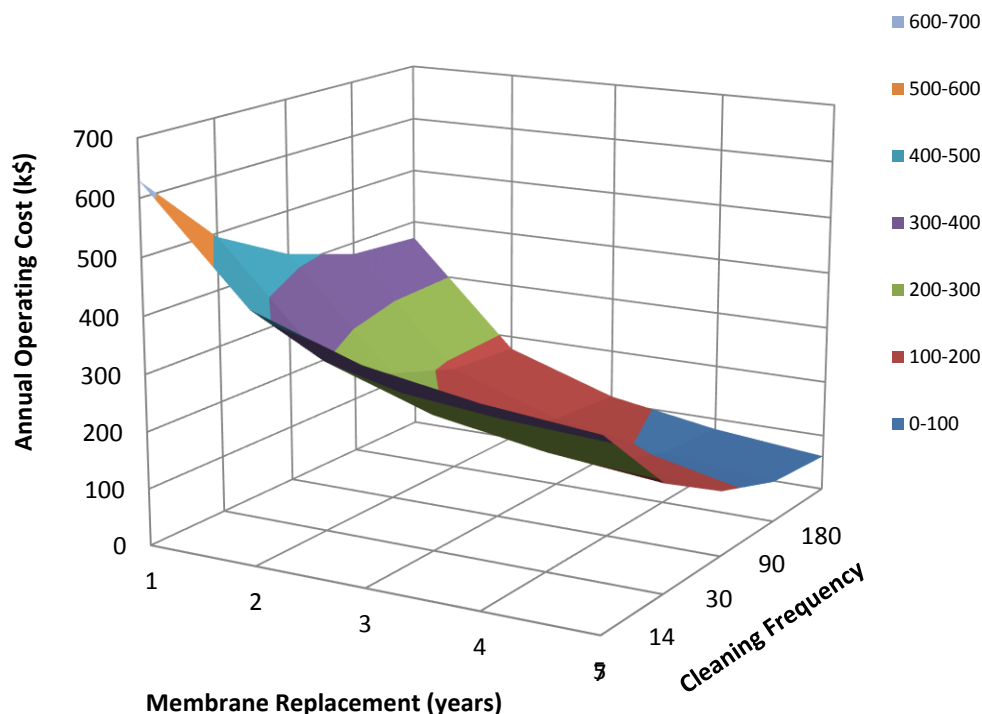


Figure 5–10: Sensitivity of annual operating cost (k\$) to membrane replacement and cleaning frequency

The operating cost (C_{op}) was estimated to be 438 k\$/y, for a replacement interval of 2 years and weekly cleaning of the system, which was considered to be realistic for the prehydrolysate concentration (personal communication). The total annual cost of the membrane filtration system (C_t) is thus 769 k\$/y. This corresponds to 23\$/t of sugars and 45 \$/t of furfural. The costs associated with the other equipments were estimated by using process data from Aspen Plus, cost functions and the material selection was based on previous study [11]. The calculated purchased equipment costs are shown in Table 5.8.

Table 5.8: Overview of the installed equipment costs excluding the membrane system

EQUIPMENT	DESCRIPTION	MATERIAL	COST (k\$)
Reactor System	Jacketed reactor, steam injection, $V = 4 \text{ m}^3$	SS316	350
Heat Exchangers	12 Exchangers (Reb. & Cond. Incl) $A = 160 \text{ m}^2$	SS304	254
Tower 1	$h = 13 \text{ m}$, $d = 1.8 \text{ m}$, 14 trays	SS304	378
Tower 2	$h = 5.5 \text{ m}$, $d = 0.5 \text{ m}$, 4 trays	SS304	45
Decanter	$h = 1 \text{ m}$, $d = 1 \text{ m}$, $V = 3 \text{ m}^3$	CS	10
Heat Pump	356 \$/kW of upgraded heat		890
Total cost for installed equipment			1,927

The installed equipments costs were used to scale the total fixed investment costs as shown in Table 5.9. The membrane system constitutes 34 % of the estimated cost. This cost fraction is however justified by the consequent savings in energy requirement and process equipment dimensions.

Table 5.9: Estimated fixed capital investment for furfural plant

Components	Cost (k\$)	% of FCI
Direct costs excl. membrane system		
Installed Equipment	1927	21
Piping	771	9
Instrumentation and Control	385	4
Electrical	193	2
Buildings	128	1
Yard Improvement	128	1
Service Facilities	257	3
<i>Total direct costs</i>	<i>3790</i>	<i>42</i>
Indirect costs excl. membrane system		
Engineering and Supervision	835	9
Construction and fee	642	7
Contingency and fee	450	5
<i>Total indirect costs</i>	<i>1927</i>	<i>21</i>
Membrane system installed cost	3300	37
Total Fixed Capital Investment (FCI)	9017	100

Modifications to the receptor mill will be required to recover the sugars instead of the typical practice of using a neutralization liquor that damages the sugars prior to combustion in the recovery cycle. The cost for modifying the prehydrolysis method in order to recover and redirect the hemicellulosic sugars to the furfural process is estimated at 10.7 M\$. The fixed capital investment for the furfural plant is estimated at 9.0 M\$ and the working capital 3.0 M\$. The working capital is the provision required for the daily operation of the biorefinery and it was set at 15% of the fixed capital investment for the modification and for the furfural plant. The total

capital expenditure for the biorefinery is estimated to be 22.7 M\$. The economic feasibility of the biorefinery was evaluated using the return on capital employed (ROCE).

Two case studies were compared in the economic analysis. Case 1 is the potential integration previously mentioned and illustrated in Figure 5–9. For Case 2, it was estimated that there would be a reduction in the steam production in the recovery boiler (~10%) of the receptor mill due to the lower mass flow of black liquor after to hemicelluloses recovery and transformation in the furfural process. This debottlenecking effect could be used to increase the pulp production capacity by 10 %. The wood chip consumption at the mill would consequently increase to about 2100 odt/d, while the evaporator load and energy production by the recovery boiler would be kept at its full capacity (same as without any hemicelluloses extraction). The furfural production capacity would also increase to 52 t/d. The energy and material integration of the biorefinery with the Kraft dissolving pulp mill is feasible in both cases

The variables for calculation include.

- Unit price of furfural: \$1200 /t
- Interest on capital: 10%
- Margin on increase pulp production: \$100/t
- Tax rate: 30 %
- Useful life: 20 years
- Number of hours of operation : 8000 h

The ROCE for Case 1 and Case 2 is shown in Table 5.10.

Table 5.10: Economic analysis of the furfural biorefinery

	CASE 1	CASE 2
	(k\$)	(k\$)
Total capital expenditure	22,700	24,036
Revenue for sale of furfural	20,736	22,810
Revenue for increased pulp production	-	2,484
Net Revenue	20,736	25,294
Operating cost	8,590	9,096
EBIDTA	12,146	16,198
Depreciation	1,135	1,202
EBIT	11,011	14,996
Tax rate	3,303	4,499
Interest	1,135	1,202
Net Income	6,572	9,295
Other costs*	2,908	3,079
ROCE	26%	34%

* includes costs for maintenance, receivables and inventory

The ROCE indicates that the biorefinery is economically feasible and the production of additional pulp can increase the profitability by 8 % for case 1. To better understand the range of economic feasibility of the biorefinery, the sensitivity of the ROCE to the price of furfural, the margin on increased pulp production, and the amount of additional pulp were estimated and shown in Figure 5–11. At low furfural prices the IFBR would still be profitable with a ROCE of 20%. The net gains from the production of additional dissolving pulp could also contribute significantly to the profitability of the IFBR, especially at high dissolving pulp prices. The investment cost for the membrane filtration systems had a minor effect compared to the other variables within the studied range. The IFBR for furfural production is profitable and can successfully increase the revenue stream for the receptor Kraft dissolving pulp mill.

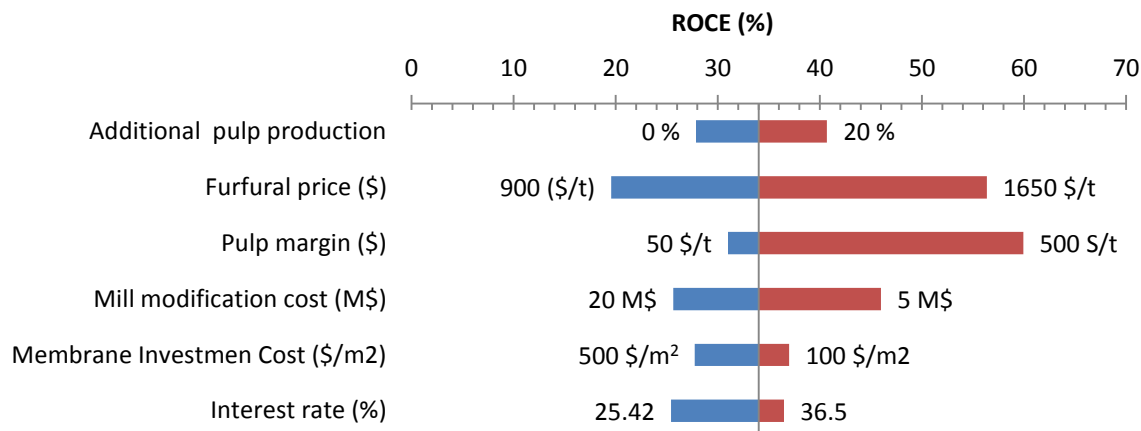


Figure 5–11: Sensitivity of return on capital employed (ROCE) for the biorefinery

5.6 Conclusion

A novel integrated biorefinery process configuration for the production of furfural has been proposed. It comprises prehydrolysate concentration using nanofiltration membranes prior to sugars conversion and furfural purification. A simulation model for the process was developed and applied to a heat exchanger network design and the implementation of an absorption heat pump for energy upgrade. The minimization of the heating and cooling requirements led to a highly energy efficient process. The integration of the biorefinery in an operating Canadian receptor pulp mill was evaluated and it was demonstrated that the energy, water and chemicals requirement of the furfural process can be supplied by the mill. Economic analysis confirmed that the feasibility of the biorefinery is enhanced by the low thermal energy consumption for the added furfural process, which is 13.4 GJ/ton, and represents only 31% of the energy requirement in existing processes for furfural production. Also, concentration of the prehydrolysate prior to conversion makes it possible to reduce the dimensions of the process units; this also translates into cost saving for the biorefinery. It was shown that the biorefinery is economically feasible even at low furfural prices. Such a biorefinery can be a first step towards the production of sustainable biochemicals and increased revenues for dissolving pulp mills.

5.7 Acknowledgment

The authors acknowledge the support provided by University and College Idea to Innovation (I2I) program of the Natural Sciences and Engineering Research Council of Canada program and by BioFuelNet Canada. The authors are grateful to Mr. Hassan Chadjaa and Mohamed Rahni of CNETE for their help during the experiments on nanofiltration membranes and Mr. Raynald Labrecque of Hydro-Quebec for reviewing the techno-economic evaluation of the prehydrolysate concentration step.

5.8 References

- [1] M. F. Demirbas, M. Balat, and H. Balat, "Potential contribution of biomass to the sustainable energy development," *Energy Conversion and Management*, vol. 50, pp. 1746-1760, 2009.
- [2] A. Limayem and S. C. Ricke, "Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects," *Progress in Energy and Combustion Science*, vol. 38, pp. 449-467, 8// 2012.
- [3] M. Pourbafrani, J. McKechnie, T. Shen, B. A. Saville, and H. L. MacLean, "Impacts of Pre-treatment Technologies and Co-products on Greenhouse Gas Emissions and Energy Use of Lignocellulosic Ethanol Production," *Journal of Cleaner Production*, 2014.
- [4] L. Christopher, *Integrated forest biorefineries*: Royal Society of Chemistry, 2012.
- [5] M. Marinova, E. Mateos-Espejel, N. Jemaa, and J. Paris, "Addressing the increased energy demand of a Kraft mill biorefinery: The hemicellulose extraction case," *Chemical Engineering Research and Design*, vol. 87, pp. 1269-1275, 2009.
- [6] E. Mateos-Espejel, T. Radiotis, and N. Jemaa, "Implications of converting a kraft pulp mill to a dissolving pulp operation with a hemicellulose extraction stage," *Tappi Journal*, vol. 12, pp. 29-38, 2013.
- [7] M. Benali, Z. Périn-Levasseur, L. Savulescu, L. Kouisni, N. Jemaa, T. Kudra, *et al.* ., "Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment," *Biomass and Bioenergy*, 2013.

- [8] M. Kannangara, M. Marinova, L. Fradette, and J. Paris, "Lignin recovery by acid precipitation in a Kraft mill: an energy perspective," *Journal of science and technology for forest products and processes*, vol. 2, pp. 28-32, 2012.
- [9] O. Ajao, M. Rahni, M. Marinova, H. Chadja, and O. Savadogo, "Hemicelluloses prehydrolysate concentration by nanomembrane filtration: Feasibility and effect of operating conditions," presented at the 5th Nordic Wood Biorefinery Conference, Stockholm, Sweden, 2014.
- [10] H. E. Hoydonckx, W. M. Van Rhijn, W. Van Rhijn, D. E. De Vos, and P. A. Jacobs, "Furfural and Derivatives," in *Ullmann's Encyclopedia of Industrial Chemistry*, ed: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- [11] G. Marcotullio, "The chemistry and technology of furfural production in modern Lignocellulose-Feedstock biorefineries," Ph.D Thesis, Process and Energy Department, TU Delft, Delft, 2011.
- [12] J.-P. Lange, E. van der Heide, J. van Buijtenen, and R. Price, "Furfural—A Promising Platform for Lignocellulosic Biofuels," *ChemSusChem*, vol. 5, pp. 150-166, 2012.
- [13] M. Marinova, E. Mateos-Espejel, and J. Paris, "From kraft mill to forest biorefinery: An energy and water perspective. II. Case study," *Cellulose Chemistry and Technology*, vol. 44, pp. 21-26, 2010.
- [14] J. Y. Zhu and X. J. Pan, "Woody biomass pretreatment for cellulosic ethanol production: Technology and energy consumption evaluation," *Bioresource Technology*, vol. 101, pp. 4992-5002, 2010.
- [15] T. Radiotis, X. Zhang, M. Paice, and V. Byrne, "Optimizing Hardwood Prehydrolysis for Simultaneous Production of Bioproducts and Biomaterials," *Journal of Bioprocess Engineering and Biorefinery*, vol. 1, pp. 69-76, // 2012.
- [16] H.-J. Huang, S. Ramaswamy, W. W. Al-Dajani, and U. Tschirner, "Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: A comparative study," *Bioresource Technology*, vol. 101, pp. 624-631, 2010.

- [17] C. M. Cai, T. Zhang, R. Kumar, and C. E. Wyman, "Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass," *Journal of Chemical Technology & Biotechnology*, pp. n/a-n/a, 2013.
- [18] K. J. Zeitsch, *The Chemistry and Technology of Furfural and its Many By-Products*: Elsevier, 2000.
- [19] W. De Jong and G. Marcotullio, "Overview of biorefineries based on co-production of furfural, existing concepts and novel developments," *International Journal of Chemical Reactor Engineering*, vol. 8, pp. 1–25, 2010.
- [20] M. Dashtban, A. Gilbert, and P. Fatehi, "Production of furfural: overview and challenges," *Journal of science and technology for forest products and processes*, vol. 2, pp. 44-53, 2012.
- [21] L. Montastruc, O. Ajao, M. Marinova, C. B. d. Carmo, and S. Domenech, "Hemicelluloses biorefinery for furfural production, energy requirement analysis and minimization," *Journal of Science and Technology for Forest Products and Processes*, vol. 1, pp. 48-52, 2012.
- [22] R. Xing, W. Qi, and G. W. Huber, "Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries," *Energy Environ. Sci.*, vol. 4, pp. 2193-2205, 2011.
- [23] M. S. Peters, K. D. Timmerhaus, R. E. West, K. Timmerhaus, and R. West, *Plant design and economics for chemical engineers* vol. 4: McGraw-Hill NY, 2003.
- [24] T. Browne, R. Gilsenan, D. Singbeil, and M. Paleologou, "Bio-energy and Bio-chemicals Synthesis Report," FPInnovations, Pointe-Claire 2011.
- [25] O. Ajao, M. Rahni, M. Marinova, H. Chadja, and O. Savadogo, "Retention and flux characteristics of nanofiltration membranes during hemicellulose prehydrolysate concentration," *Chemical Engineering Journal*, vol. Submitted, 07 July 2014 2014.
- [26] D. J. Medeiros and M. B. Burnett, "Furfural process," 1985.
- [27] M. Ostoich, A. Critto, A. Marcomini, E. Aimo, M. Gerotto, and L. Menegus, "Implementation of Directive 2000/60/EC: risk-based monitoring for the control of dangerous and priority substances," *Chemistry and Ecology*, vol. 25, pp. 257-275, 2009.

- [28] S. Lin, G. Su, M. Zheng, M. Jia, C. Qi, and W. Li, "The degradation of 1,2,4-trichlorobenzene using synthesized Co_3O_4 and the hypothesized mechanism," *Journal of Hazardous Materials*, vol. 192, pp. 1697-1704, 9/15/ 2011.
- [29] M. J. Keshtkar, "Steam and Water Combined Analysis, Integration, and Efficiency Enhancement in Kraft Pulping Mills," École Polytechnique de Montréal, 2013.
- [30] R. J. Wooley, V. Putsche, and N. R. E. Laboratory, *Development of an ASPEN PLUS physical property database for biofuels components*: National Renewable Energy Laboratory Golden, CO, 1996.
- [31] T. Rafione, M. Marinova, L. Montastruc, S. Domenech, B. Srinivasan, and J. Paris, "Optimization of Water and Energy Consumption in an Integrated Forest Biorefinery," *Journal of science and technology for forest products and processes*, vol. 2, pp. 54-59, 2012.
- [32] I. C. Kemp, "Pinch analysis and process integration," *A user guide on process integration for the efficient use of energy*, 2007.
- [33] W. Bucher, J. Lockhart, J. Wearing, and D. Carwile, "Commercial recovery of ClO_2 Generator sesquisulfate by-product," presented at the TAPPI Engineering, pulping & environmental conference, Memphis, Tennessee, 2009.
- [34] NORAM Engineering and Constructors Ltd. (2014, 06.08.2014). *GAP Plus™: chlorine dioxide generator waste acid recovery*. Available: <http://www.noram-eng.com/groups/pulp-group-overview.html>
- [35] GE water and process technologies. (2014, 06.08.2014). *RO Tools™ Home - cost of operations*. Available: <http://www.gewater.com/rotools/access.jsp>
- [36] B. Bakhtiari, L. Fradette, R. Legros, and J. Paris, "Retrofit of absorption heat pumps into manufacturing processes: Implementation guidelines," *The Canadian Journal of Chemical Engineering*, vol. 88, pp. 839-848, 2010.

CHAPTER 6. ARTICLE 4: CONCENTRATION AND DETOXIFICATION OF KRAFT PREHYDROLYSATE BY COMBINING NANOFILTRATION WITH FLOCCULATION

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Abstract

The prehydrolysate stream from a Kraft dissolving pulp mill can be valorized by fermentation of the hemicellulosic sugars into biofuels or bioproducts such as ethanol or butanol, instead of the typical practice of combustion to produce energy. A precondition to ensure the survival of the fermentation microorganisms and to have high fermentation yields is to remove the inhibitors present in the prehydrolysate such as organic acids, furans and phenolic compounds. Concentration of the prehydrolysate is also necessary to reduce the size of the processing equipments and lower energy cost. The purpose of this study was to develop a strategy for the concentration and detoxification of hemicelluloses prehydrolysate to lower the production costs of biofuels. Laboratory experiments were conducted to screen and select suitable organic membranes among 7 samples of reverse osmosis, nanofiltration and ultrafiltration membranes. Three membranes (Dow NF270, Trisep TS40 and Trisep XN45) produced the highest sugar

retentions relative to inhibitors removal. They were however not efficient for the removal of the phenolic compounds. It was also observed that flocculation with ferric sulfate as coagulant could be utilized as a secondary detoxification step that can be combined with nanofiltration. The optimization of the flocculation step with a jar test showed that the highest phenolics removal ($\approx 80\%$) can be obtained when the ratio of ferric ions to phenols is 1 g/g, and the pH is between 6.5 and 7.5. A process concept for the detoxification and concentration has been developed based on these experimental results.

Keywords

Membrane filtration, Prehydrolysate detoxification, Concentration, Inhibitors removal

6.1 Introduction

Lignocellulosic biofuels have gained wide attention in recent times because they can be manufactured from a broad range of non-food feedstock such as agricultural residue, forest residue and municipal solid wastes. Furthermore, they are sustainable and provide an avenue for reducing greenhouse gas emissions. A forest by-product that can be converted into biofuels is the prehydrolysate from a dissolving Kraft pulp mill that is normally concentrated and combusted to produce energy [1, 2]. It is a dilute stream comprising hemicellulosic sugars that can be fermented into ethanol or butanol. In addition to the sugars, the prehydrolysate also contains lesser quantities of organic acids, phenolic compounds and furans that can inhibit fermentation. A pulp mill with an added process for biofuels production on its site with which it exchanges materials and energy streams constitutes an integrated forest biorefinery [3]; it could lead to increased revenue for existing pulp and paper mills. The production cost of the biofuels in the IFBR should be cost competitive with biofuels made sugar cane or starch crops. Two important steps to enhance the economic feasibility of the integrated forest biorefinery based on the integrated forest biorefinery are:

- Concentration of the dilute prehydrolysates to reduce the process equipments size and energy cost
- Removal of the toxic compounds that can inhibit the growth of the fermentation microorganisms and lead to low sugar conversion yields

The inhibitory compounds are degradation products of the different classes of wood components (cellulose, hemicellulose and lignin) that are formed during the extraction of the hemicellulose sugars from wood chips in the Kraft process. The amount of inhibitors formed depends on the severity of the prehydrolysis (pH, pressure and temperature), type of biomass, presence of catalysts and duration of the reaction. The pathways for the formation of the main inhibitory compounds are shown in Figure 6–1.

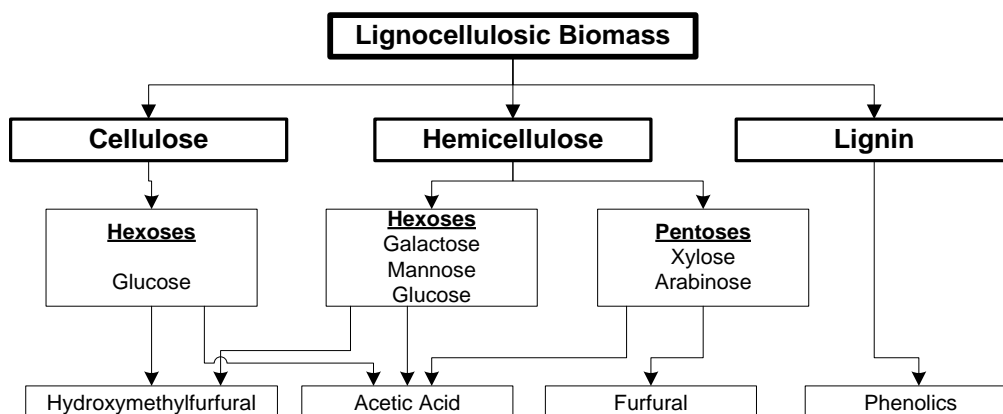


Figure 6–1: Sources of the main inhibitory compounds produced during prehydrolysis

Methods that have been used for the detoxification of hydrolysate solutions include alkali treatment with ammonium hydroxide or by over liming [4], with activated carbon [5], ion exchange resins [6], nanofiltration membranes [2] and evaporation [7]. Only membrane filtration and evaporation are capable of concentrating the prehydrolysate amongst the methods listed. Although evaporation is efficient for removing the volatile inhibitors, its use is ineffective to remove the non-volatile lignin degradation products [8]. It also requires a high amount of energy for the evaporation of water. To avoid these drawbacks, the use of membranes is recommended. The reported studies showed that neutralization with an alkali is efficient for acetic acid removal but less efficient for furfural and phenolic compounds, while activated carbon is efficient for phenols removal only. Evaporation and membrane filtration are efficient for furfural and acetic acid removal. A detoxification strategy for conditioning hemicelluloses prehydrolysate from a Kraft dissolving pulp mill can be developed by combining two or more methods to attain the following objectives:

- Simultaneous detoxification and concentration of the prehydrolysate,
- Minimal loss of hemicellulosic sugars,

- Limited wastes generation,
- Low energy requirement,
- short residence times,
- No production of residual metal salts that can also inhibit fermentation.

The phenolic compounds are more difficult to eliminate so a detoxification strategy should comprise of two different steps.

A comparison of different detoxification methods has been reported [9]. The application of published results to this case study is however not feasible because the reported detoxification tests were carried out on solutions generated using different lignocellulosic biomass and a wide variety of hydrolysis methods and conditions. Our objective has thus been to:

- 1 Identify and select a commercially available membrane for inhibitors removal and concentration
- 2 Screen different methods and select the most suitable to complement membrane filtration
- 3 Optimize the operating conditions to ensure high inhibitors removal
- 4 Propose a strategy for concentration and detoxification of hemicelluloses prehydrolysates

Several commercially available organic membranes with Molecular Cut Off Weights (MWCO) between 100 and 3500 Da were tested using prehydrolysate generated in a pilot plant from a wood furnish similar to that of an eastern Canadian dissolving pulp mill. The Dow NF270, Trisep TS40 and Trisep XN45 were identified as the most promising for concentration and detoxification depending on the sugar monomer fraction of the prehydrolysate. It was however discovered that a secondary detoxification step is required to remove the phenolic compounds. The method appropriate for this step was identified by comparing activated carbon adsorption and flocculation with ferric sulfate, alum and chitin. It was shown that the use of ferric sulfate provided the highest phenolic compounds removal relative to sugar losses. The optimum conditions for flocculation were determined and the results have been used to design and propose a detoxification strategy that could be applied to biorefineries.

6.2 Materials and Methods

6.2.1 Materials

The two sets of prehydrolysate solutions used in the experiments were generated in a pilot digester. The first solution was prepared with steam at 700 kPa, 170 °C for 110 minutes followed by hot water treatment for 15 minutes [10]. A mixture of aspen (60%) and maple (40%) wood chips was used for the prehydrolysate solution. The second solution was prepared by using hot water only. Water was added to the digester and it was heated indirectly with steam to 170 °C in 50 minutes. The digester was maintained at 170 °C for an additional 65 minutes. The compositions of the generated prehydrolysate solutions are given in Table 6.1.

Table 6.1: Composition of prehydrolysate used for the experiments

Component	Concentration (g/L)	
	Solution 1	Solution 2
Total sugars	21,8	39.0
Total phenols	4.7	4.6
Acetic Acid	3.8	6.3
Sugar monomers	3.1	6.5
Total solids	3.4	4.5
Furfural	0.7	0.7
Hydroxymethylfurfural	0.1	0.1
K	0.04	-
Na	0.02	0.01
Ca	0.15	0.16
Fe	0.00	0.00

Solution 1 was used in the preliminary experiments while solution 2 was used to validate the efficiency of the strategy with a different solution.

Activated carbon was purchased from Jacobi Carbons Ltd, alum powder from Bulk Barn Ltd, Canada and ferric sulfate from Mallinckrodt analytical reagents. The Folin & Ciocalteu's phenol reagent and 3,5-Dinitrosalicylic acid were purchased from Sigma Aldrich. Potassium sodium tartrate (Rochelle salt) came from MP Biomedicals and sodium hydroxide from Laboratoire

MAT. Sulfuric acid was purchased from Caledon Laboratories Ltd and Chitin originated from ABK-Gaspésie Inc. All materials were used as received without further purification.

6.2.2 Membranes and filtration procedure

The SEPA CF II, cross-flow flat-sheet membrane from GE OSmonics that was used in this study has been described in a previous publication [11]. The membrane test unit can accommodate various flat sheet membranes. A fresh membrane sheet was used in each experiments. As illustrated in Figure 6–2 A), the prehydrolysate in the tank was fed to the membrane unit at a predetermined volumetric flow rate and pressure. Samples of the permeate and concentrate streams were taken for analysis at regular intervals after the flows reached steady state. The same procedure was repeated in all the membranes screening experiment.

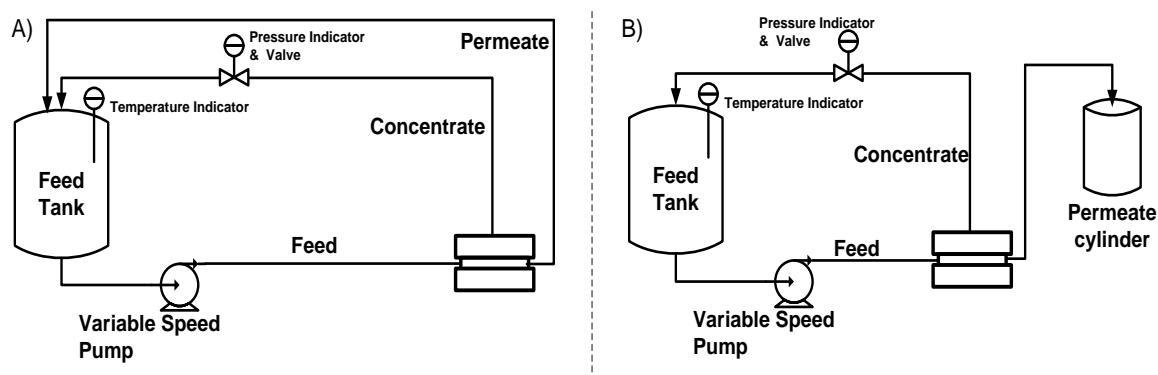


Figure 6–2: Schematic of membrane system for A) membrane selection B) prehydrolysate concentration

The observed retention (rejection) of the main components was used as a measure of detoxification efficiency and was determined using equation (1), where C_f represents the concentration of the component in the feed and C_p the concentration in the permeate.

$$R = 100 * (C_f - C_p) / C_f \quad (24)$$

Concentration trials with the selected membranes were performed by discharging the permeate stream to a reservoir as shown in Figure 2B). The volumetric concentration factor (VCF) obtained can be calculated by equation (2).

$$VCF = V_i / V_f \quad (25)$$

In this equation, V_i is the initial feed volume and V_f the final feed volume. The VCF is 1 during the membrane selection run when no concentration is performed. The characteristics of seven commercial organic membranes were evaluated. The retention and flux characteristics for six of the membranes with molecular weight cut off (MWCO) between 100 and 500 have been previously reported [10]. The seventh membrane, an ultrafiltration membrane with a MWCO of 3500 was compared in order to broaden the experimental range.

6.2.3 Activated Carbon (AC) adsorption

Two types of adsorption tests were carried using activated carbon. The first was a batch series of experiments in which 5g, 10g and 15 g of activated carbon was mixed with 150 mL of prehydrolysate at room temperature in a magnetically stirred flask. A treated sample (1 mL) was taken for analysis after 45 minutes and the stirring was continued for another 45 minutes before the final sample was taken. The treated prehydrolysate was collected and filtered through a 0.45 μm membrane. The second test was a continuous experiment run in which activated carbon was introduced into a 4 cm diameter burette. Prehydrolysate was then fed into the burette and allowed to pass through the activated carbon layer. Treated prehydrolysate was collected in a graduated cylinder and passed through a 0.45 μm filter before analysis.

6.2.4 Flocculation

Preliminary flocculation tests were carried out in beakers. Calculated doses of the flocculants (chitin, ferric sulfate - $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$, and Alum - $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) were added to 500 mL of the prehydrolysate solution, this was followed by the addition of sodium hydroxide to bring the pH to 6. The beakers were stirred using a magnetic stirrer for 30 minutes and left to settle. Treated prehydrolysate were analyzed with and without passing the samples through a 0.45 μm filter. After a flocculant had been selected, optimization experiments for the coagulant dosage, pH, and choice of alkali for pH adjustment were carried out with a jar test apparatus. The jar was agitated for 15 minutes upon addition of the flocculant at a speed of 150 rpm. The speed was then reduced to 50 rpm after adjustment of the pH for another 30 minutes.

6.3 Analyses

6.3.1 Sugars analysis

Sugar monomers composition in the prehydrolysate was measured using a Dionex DX600 ion chromatograph equipped with a pulsed amperometric detector and Carbopac PA1 column [12]. The oligomeric sugars content was determined by hydrolysis using 2.5 % wt/vol of sulphuric acid for 120 minutes in an autoclave prior to analysis. The dinitrosalicylic acid (DNS) colorimetric method [13] was adapted for determining the total reducing sugars before and after filtration and flocculation experiments.

6.3.2 Furans analysis

Furfural and hydroxymethylfurfural composition were measured by HPLC (Agilent Technologies, Germany) using a 280 nm diode array detector (DAD) and a Nucleosil C18 column. The eluent used was a mixture of acetonitrile, water and acetic acid [11].

6.3.3 Phenols analysis

The total phenols composition was measured by a UV-Visible colorimetric method using a Folin–Ciocalteu reagent method adapted from Singleton and Rossi [9]. A volume of 500 μL of diluted samples, a blank sample and standard solution were pipetted in separate tubes, 3800 μL of water and 200 μL of Folin-Ciocalteu reagent were added. After 3 minutes, 500 μL of NaOH 6% (wt/vol) was added, the tubes were vortexed and the samples were placed in the dark to stabilize. The absorbance was measured at 725 nm and the total phenol content was calculated as gallic acid equivalents. A HPLC analysis method that is capable of measuring gallic acid, catechol, vanillin and syringaldehyde was developed. The previously described HPLC was equipped with a 280 nm DAD for gallic acid and catechol detection and a 313nm DAD detector for vanillin and syringaldehyde. In both cases, a Nucleosil C18 column (150 x 4.6 mm) was used. The eluent used was a mixture of acetonitrile and 0.1% wt/wt of phosphoric acid solution (CH_3CN 15%, phosphoric acid solution 85%) and it was fed to the column at 17000 kPa and 25°C at a flow rate of 0.8 mL/min.

6.3.4 Organic acids analysis

Organic acids concentrations were measured using the same HPLC. It was however equipped with A 210 nm diode array detector (DAD) and an Inertsil ODS-3 (150 X 4.6 mm) column. The method was adapted to determine the concentrations of acetic, lactic, propanoic and butyric acids.

6.3.5 Physico-chemical characteristics

The metal ions were measured with an Optima 4300 DV Inductively coupled plasma atomic emission spectroscope (PerkinElmer Inc., USA). An Accumet AB250 pH/ISE Meter (Fisher Scientific, USA) and an Orion 3-Star Benchtop Conductivity Meter (Thermo Scientific, Canada) were used to measure the pH and conductivity respectively.

6.4 Results and discussion

6.4.1 Membrane selection

The measured retention of sugars and phenolic compounds was in the same range for all the membranes. The objective of the detoxification step is to identify a membrane that displays a wide gap between the retention of sugars and inhibitors (phenolic compounds included). The sugars and phenolics retentions decreased with increasing membrane MWCO and the highest retention was produced by a reverse osmosis membrane (TW30) with a MWCO of ~150 Da, while the lowest sugars and phenolic compounds retention was obtained with the UA60 membrane, a tight ultrafiltration membrane with a MWCO of 1000 – 3500 Da. The other inhibitors did not follow a similar trend and this implies that the factor governing the retention is not only the size of the molecules in the prehydrolysate. Electrostatic repulsion could also play a role as each membrane has different charge characteristics. The seven membranes that were compared and their degree of relative retention of components are shown in Figure 6–3. Membranes TW30 and NF90 retained most of the inhibitors and were excluded from the list of potential detoxification alternatives. The other membranes with various degrees of inhibitors removal were retained as possible concentration alternatives except for the UA60, which produced the highest sugar losses. A final choice of membrane can be made based on the fraction of sugar monomers present in the prehydrolysate. Another criterion can be employed if the membranes exhibit similar sugar retention and inhibitor removal is the energy requirement. The

energy implications of the membranes have already been reported by Ajao et al [10]. In cases where membranes exhibit comparable component retentions, the membrane that requires a lower pressure (power requirement) for an equivalent pure water flux rate should be chosen. The XN45 and NF270 membrane were selected as alternatives for all further detoxification experiments in this case study.

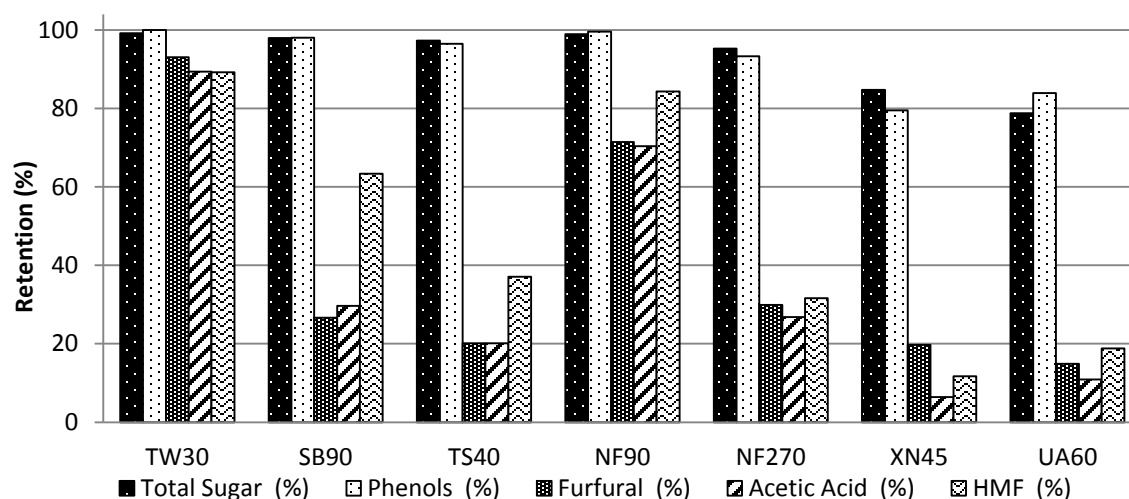


Figure 6–3: Membranes and observed retentions, in order of increasing MWCO (L-R)

6.4.2 Effect of operating conditions on membrane flux and retention characteristics

The XN45 membrane was subjected to compaction to evaluate whether the sugar losses can be reduced. Compaction is a physical compression of membranes which can alter the flux and retention characteristics of a membrane [14]. It increases with increasing temperature and pressure. A significant reduction in the permeate flux was observed at the beginning of concentration as shown in Figure 6–4.

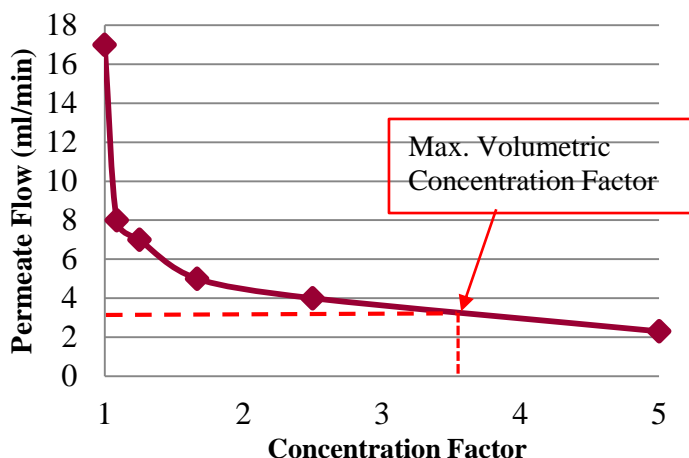


Figure 6-4: Permeate flux decline during concentration

At a concentration factor of 5, changing the feed pressure and cross flow velocity did not result in a change of permeate flow. An industrial feasible permeate flow of 3.5 mL/min (permeate flux of 14 L/m²h) can be produced during concentration as long as the concentration factor does not exceed 3.6. It is also necessary to have concentration conditions that minimize the rapid flux decline at the beginning of concentration. Increasing the feed pressure, cross flow velocity and temperature, from 550 kPa / 0.4 m/s/ 30°C to 2100 kPa / 0.5 m/s/ 40°C to favour compaction revealed that the sugar retention increased from 84 % to 92 % and acetic acid retention was less than 1 % as shown in Figure 6-5 A). An undesired effect was observed, the retention of phenolic compounds also increased in similar manner to the sugars. The combined effect of compaction and pH on the retention of phenolic compounds and sugars was also investigated and the results are shown in Figure 6-5B. Compaction of the membrane was performed prior to filtration using distilled water at two pressure values, 2100 kPa and 3100 kPa. The pressure values that were selected exceeded manufacturer recommended upper pressure limit of the XN45 membrane (1380 kPa). After the compaction, 4 prehydrolysate filtration tests at 750 kPa / 0.4 m/s/ 30°C were performed. The pH was adjusted from 3.5 to 2.8 using hydrochloric acid for two of the four experiments.

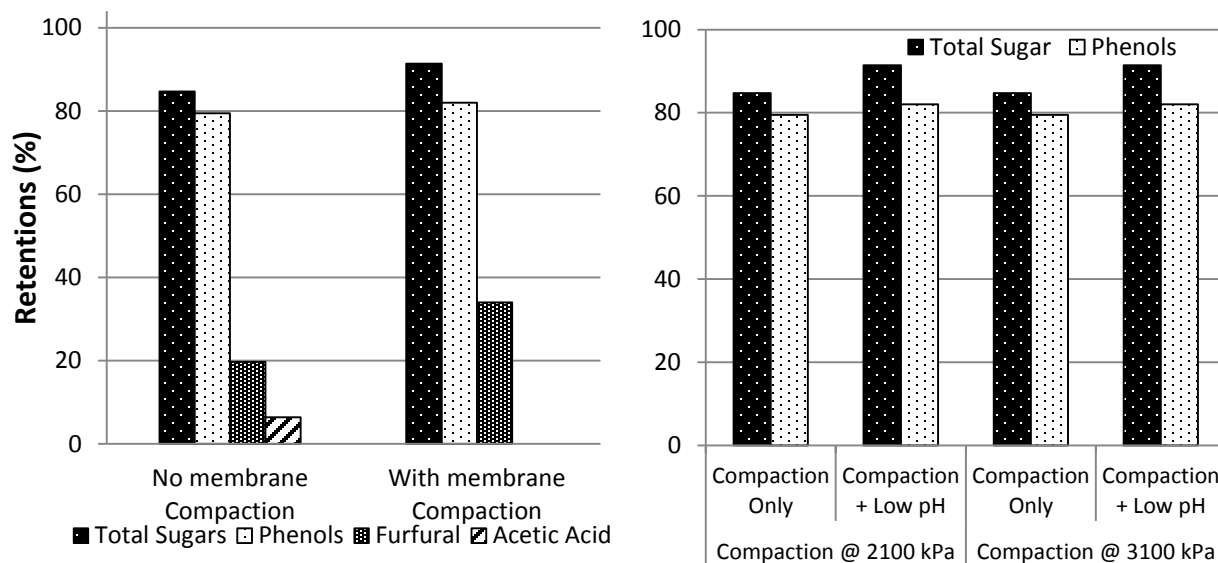


Figure 6–5: Component retentions after A) compaction B) compaction before pH adjustment and filtration

It was observed that the effect of the pressure at which compaction with distilled water was carried is negligible. No significant difference resulted from compaction of the membrane at 3100 kPa instead of 2100kPa, the sugars and phenolics retention remain unchanged. A lower pH increases the sugars retention in both cases but does not lead to lower phenolic compounds retention. This could be due to the presence of lignin-carbohydrate complexes (LCCs), which exist as a result of chemical bonds between lignin and carbohydrates (sugars). Fractionating the complexes posed a challenge in finding a complementary detoxification method that would enable improved sugar retention and at the same time reduce the retention of the phenolic compounds, this is discussed below.

6.4.3 Secondary detoxification method selection

6.4.3.1 Screening and identification

Several methods were evaluated to identify a secondary detoxification method with high phenolic compounds removal and high retention of the hemicellulosic sugars. They include treatment with activated carbon and with common flocculants (ferric sulfate, alum and chitin) as illustrated in Figure 6–6. Activated charcoal is used industrially as an efficient adsorbent. Flocculation, a process for agglomeration of colloids, is widely used for the treatment of drinking water. The

effect of passing the prehydrolysate through a 0.45 μm filter was also evaluated, because samples from flocculation with ferric sulfate, alum and chitin must be passed through a filter before analysis, but it was shown to be negligible. Activated carbon treatment using a column and flocculation with ferric sulfate showed the highest degree of phenolic compounds removal. Activated carbon treatment however had a side effect which was the adsorption of sugars together with the phenolic compounds. It could be concluded that the selectivity exhibited by activated carbon is not suitable because it is not specific enough to target only the phenolic molecules. The higher the phenolics removal the higher was the associated sugar losses, this observation is confirmed by another study on the use of activated carbon to treat spent liquor from a sulfite pulping process [15]. The sugar loss with the use of this method makes it infeasible as a detoxification method on a large scale for biofuels production. In addition, saturation of the activated carbon might pose a challenge as the detoxification will not be effective after a certain period. The highest phenolics removal relative to the retention of sugars was observed when the ferric sulfate supernatant was passed through a 0.45 μm filter.

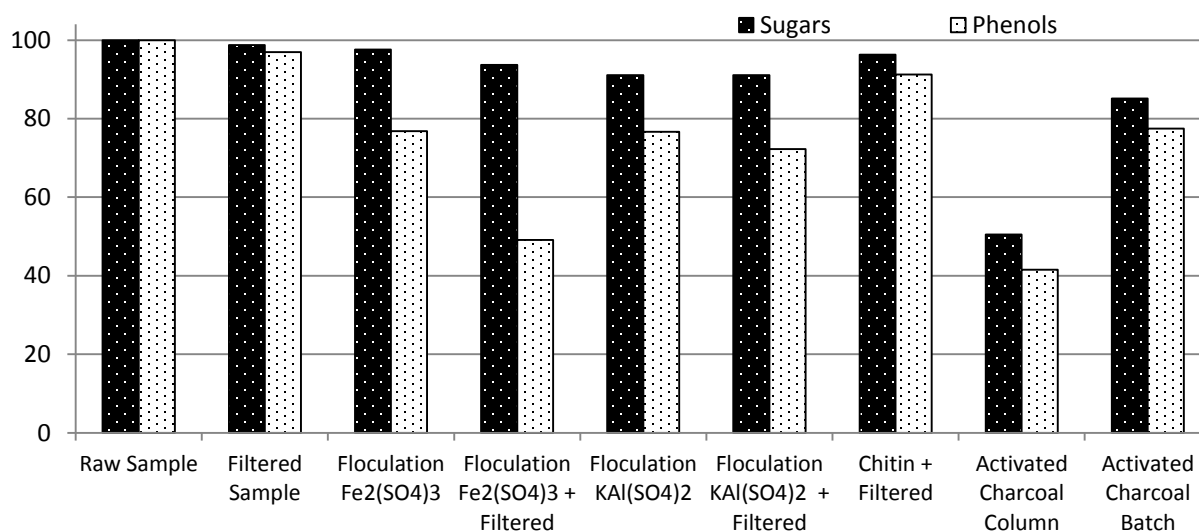


Figure 6–6: Comparison of alternatives for secondary detoxification of prehydrolysate

The use of ferric sulfate was retained as a secondary detoxification step and further experiments to optimize the selectivity during flocculation were performed.

6.4.4 Flocculation with ferric sulfate

6.4.4.1 Optimum flocculant dosage

Iron (III) ions form complexes with various phenolic compounds by a chelation mechanism in which a molecule forms several bonds with a single metal ion [16, 17]. The degree of chelation is a function of pH, the structure of the compounds present and of the quantity of metal ions [18]. Series of experiments were designed to determine the optimum ratio of Iron to phenols $[\text{Fe}]/[\text{Phenols}]$ and pH for flocculation. The prehydrolysate used in the preliminary tests was diluted by a factor of 4 to obtain phenolics concentration of 1 g/L. The coagulant, used for the experiments was a 200 g/L solution of hydrated ferric sulfate $\text{Fe}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with a Iron (Fe^{3+}) ions concentration of 43.97 g/L. A sensitivity study with six different doses of the covering a wide range of Iron to phenols $[\text{Fe}]/[\text{Phenols}]$ ratios between 0.25 and 2 as illustrated in Figure 6–7. The tests were performed at room temperature with the solution stirred at 150 rpm for 15 minutes. The pH was subsequently adjusted to 6 (+/- 2%) in all jars using a 5M NaOH solution and the rotation speed was reduced to 50 rpm and stirring continued for 30 minutes. Flocculation requires a lower mixing speed to promote the agglomeration of the colloids and prevent the break-down of the flocs that are formed.

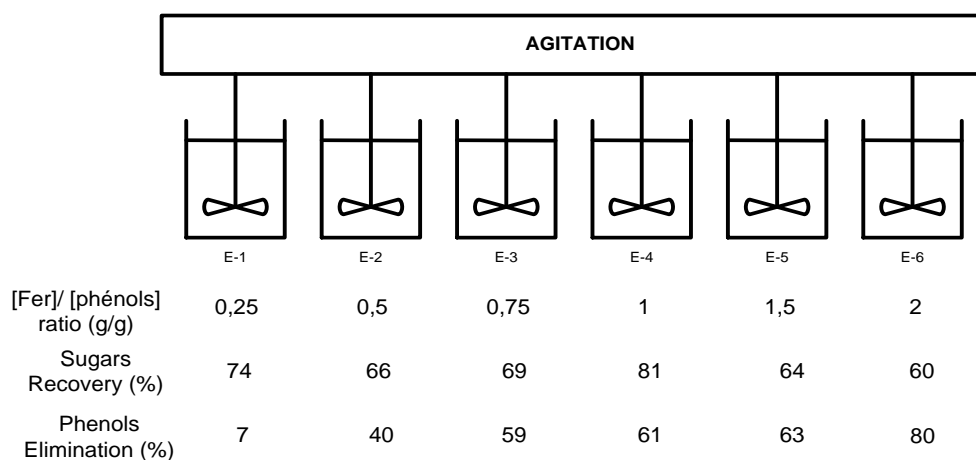


Figure 6–7: Effect of coagulant dosage on the sugars recovery and phenols elimination

It was observed that the highest sugars recovery (81%) can be obtained when the $[\text{Fe}]/[\text{Phenols}]$ ratio is 1. Exceeding this does lead to an increased chemical consumption without any benefit to the recovery of sugars. This dosage also represents a good compromise between sugar recovery

and phenols elimination. Validatory tests were made to confirm the $[\text{Fe}]/[\text{Phenols}]$ ratio using non diluted prehydrolysate and the same results were obtained.

6.4.4.2 Optimum pH for flocculation

The most favourable pH for flocculation was determined by carrying out flocculation studies at the optimum dosage identified earlier ($[\text{Fe}]/[\text{Phenols}]=1$) but with the pH in the jars varying between 4 and 9. The mechanism of flocculation with the use of ferric sulfate is a reduction of electric charge. Positively charged ions (Fe^{3+}) which have an opposite charge to the phenol ions (OH^-) were introduced to the prehydrolysate. The flocculation was further improved and the sedimentation velocity increased by raising the alkalinity of the solution. NaOH was used to adjust the pH. As shown in Figure 6–8, the phenolics retained in the supernatant were at the lowest when the pH was between 6.5 and 7.3. This indicates that the near neutral pH is most favourable for flocculation of the prehydrolysate.

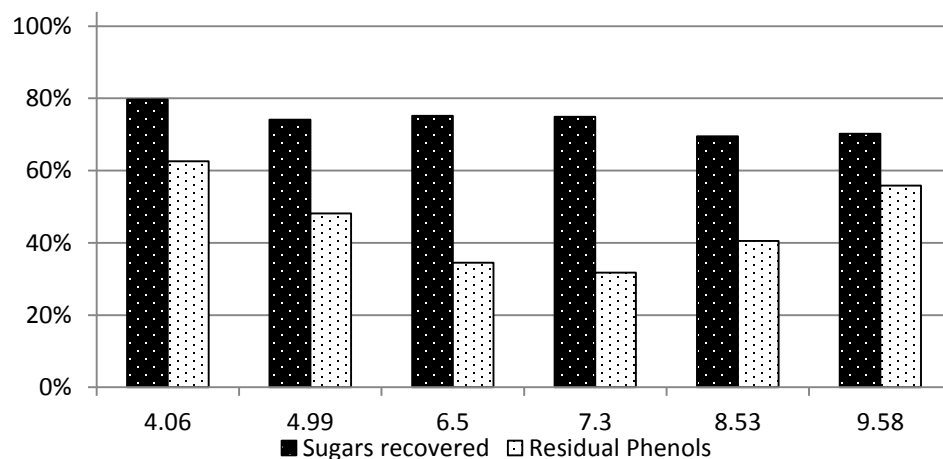


Figure 6–8: Relative amount of sugars and phenols in the supernatant after flocculation

Metal ions in the prehydrolysate could be toxic to microorganisms. The presence of sodium ions has been shown to be a potential cause of fermentation inhibition [19]. An analysis of the supernatant by inductively coupled plasma (ICP) was therefore carried out quantify the metal ions after flocculation. The results showed that the amount of residual iron at a pH between 6.5 (24 ppm) and 8.5 (0 ppm) was low so that there is no likelihood of inhibition effects from iron. A different observation was made for the residual sodium in the supernatant, the measured concentration was about 6 g/L, and high.

Further jar tests in which the pH adjustment was carried out with Ca(OH)_2 instead of NaOH were performed to resolve this problem. The results obtained showed that residual calcium ions concentration was 1/3 that of sodium ion. Furthermore, no reported inhibition effect due to Ca^+ ions was found. The use of lime did not result in any observed change to the sugar recovery and elimination of phenols. It was concluded that the pH rather than the nature of the alkali used plays a more important role. Ultimately, the use of Ca(OH)_2 for pH adjustment is more suitable to prevent the formation of salts which are soluble and can inhibit the growth of microorganisms.

6.4.4.3 Effect of hydrolysis before flocculation on sugars recovery and phenols removal

All previous experiments were carried out using an untreated prehydrolysate solution that contained about 80% oligomeric sugars. However, to determine if the presence of sugar monomers would improve the sugar recovery relative to phenols removal a set of experiments was carried out. Since monomers have a lower molecular weight and higher solubility than the oligomers [20], it was expected that they would be less prone to formation of complexes with iron. Hydrolysis was performed by adding 1.5% wt/wt of sulfuric acid to the prehydrolysate and heating the mixture in an autoclave at 121°C for 1 hour. The optimal coagulant dosage and pH were determined. It was observed that the sugar recovery with the hydrolysate solution was about 10 % higher than with the prehydrolysate at pH between 4 and 9.5. The removal of phenolic compounds was lower between pH of 4 to 6, but slightly higher at pH between 7.3 and 8.5. A higher amount of alkali is required to adjust the pH for the hydrolysate because of the sulfuric acid introduced. This also led to an increase of residual sodium in the supernatant which was 3 times as high as for the prehydrolysate. In contrast to the prehydrolysate where no changes were observed, adjusting the pH during flocculation of the hydrolysate with Ca(OH)_2 instead of NaOH resulted in higher sugars recovery (94% vs 78%) while the phenolics removal remained unchanged (~60%). The removal of phenolics from the hydrolysate solution can be attributed to 3 factors, flocculation with ferric sulfate, neutralization with lime and oxidation of some phenols during acid hydrolysis. Flocculation plays the most important role. The sugars recovery and residual phenolic compounds in the prehydrolysate and hydrolysate are shown in Figure 6–9.

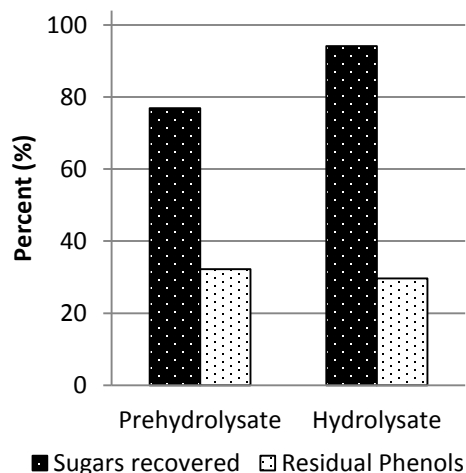


Figure 6–9: Sugars recovery and residual phenolics in the prehydrolysate and hydrolysate after flocculation

The standard Folin-Ciocalteu reagent method cannot be used to quantify the different phenolic compounds present in the prehydrolysate. To determine the selectivity of flocculation to individual phenolic compounds, a HPLC was used to analyze the quantity of the key phenolic compounds (vanillin and syringaldehyde), which are known to have an impact on fermentation. The fractions removed for both compounds were 26 % in the prehydrolysate, 30 and 26% of the vanillin and syringaldehyde were removed from the hydrolysate respectively.

6.4.4.4 Effect of flocculation on other inhibitors

In addition to the elimination of about 70% of the phenolic compounds that has been demonstrated, flocculation also led to the removal of other inhibitors in both the prehydrolysate and hydrolysate solutions. More than 54% of the acetic acid was removed while the removal of furfural and hydroxymethylfurfural was about 15-20%. The fraction of inhibitors removal from the hydrolysate due solely to the alkali pH adjustment was determined for Ca(OH)_2 . It was concluded that pH adjustment alone led to about 15 % of the total removed inhibitors for all compounds (acetic acid, furfural and hydroxymethylfurfural).

6.4.5 Strategies for sugars recovery and detoxification, and future perspectives

Membrane filtration can be used for the removal of some of the inhibitors (acetic acid, hydroxymethylfurfural and furfural) present in the prehydrolysate. As shown in Figure 6–3, the removal of the phenolic compounds by membrane filtration alone is not feasible while concentrating the hemicellulosic sugars up to a factor of 3.5. A additional detoxification step is therefore necessary. Flocculation using ferric sulfate has been shown to be capable of removing up to 70% of the phenolic compounds and recovering more than 75% and 90% of the sugars in the prehydrolysate and hydrolysate respectively. The 3 alternative process configurations that were proposed and evaluated for prehydrolysate concentration and detoxification based on experimental results are illustrated in Figure 6–10. Process comparisons were made using criteria such as minimum sugar losses, amount of inhibitors removed and pH adjustment. The concepts were applied to a prehydrolysate solution with compositions of sugars (39 g/L), phenol (4.6 g/L), acetic acid (6.3 g/L), furfural (0.7 g/L) and hydroxymethylfurfural (0.1 g/L)

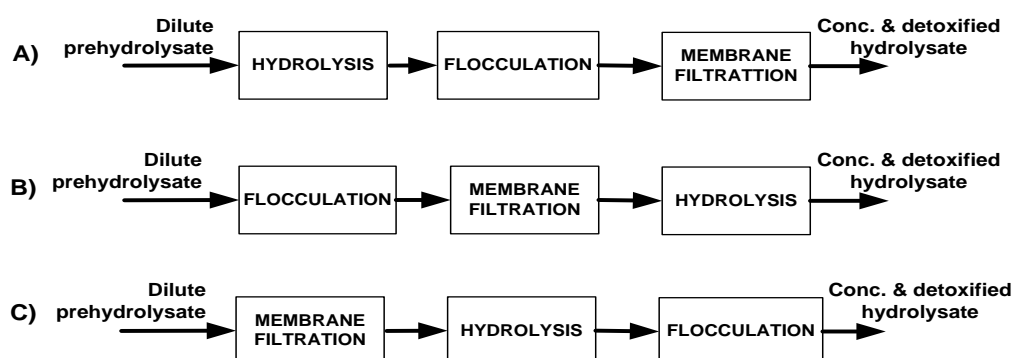


Figure 6–10: Alternative process configurations (A-C) for concentration and detoxification of hemicellulose prehydrolysate

6.4.5.1 Configuration A (Hydrolysis –Flocculation – Membrane filtration)

A hydrolysate solution that had been flocculated was filtered using the XN45 membrane that was shown to have the highest inhibitors removal after hydrolysis. The sugar losses were elevated because the oligoeric sugars had been broken down into simple sugars, which are not easily retained by the membrane. The higher the amount of recovered sugars, the higher the amount of phenols retained in the prehydrolysate. Lowering the pH from 6.2 to 3.0 confirmed that even

though the sugar losses can be reduced from 75% down to 66%, the use of this configuration is not suitable for a biorefinery process.

6.4.5.2 Configuration B (Flocculation – Membrane filtration – Hydrolysis)

Prehydrolysate that had been flocculated was filtered using the XN45 membrane at a cross velocity of 0.45m/s, a temperature of 30°C and a transmembrane pressure of 2100 kPa. Although the sugars had not been broken down into simple sugars, the sugar losses were as high as 40 %. Adjusting the pH from 7 to 3 did not improve the sugars retention. The lower retention of the sugars could be due to a change in the composition of the prehydrolysate induced by the flocculation step. Many compounds and ions form complexes and are decanted. In addition, a 10 % decrease in the total solid content was observed after flocculation. It could be concluded that the composition of the prehydrolysate solution plays an important role in the retention of sugars and phenols that can be achieved. The filtration system was operated at a cross velocity of 0.45m/s, a temperature of 30°C and a transmembrane pressure of 2100 kPa.

6.4.5.3 Configuration C (Membrane filtration – Hydrolysis –Flocculation)

The retention characteristics observed for all the membranes in Figure 6–3 showed that the membrane with the highest degree of inhibitors removal is XN45 and compaction can be used to limit sugar losses. These results are valid for prehydrolysate solutions where the sugar monomers constituted less than 10% of the total sugars in the prehydrolysate. In cases where the sugar monomers make up a larger fraction of the oligomers, a different membrane such as the NF270 or TS40 would be a good compromise between minimum sugar losses and maximum inhibitors removal. This was taken into account during the process configuration evaluation step. A NF270 membrane was also investigated. The prehydrolysate was concentrated by a factor of 3 before being subjected to acid hydrolysis. A diminution of the phenol content (42%) was observed after hydrolysis. Flocculation after hydrolysis was carried out with a dosage ratio of $[Fe]/[phenols]=1g/g$. This resulted in a reduction of the phenols content down to 26% of the original value as shown in Figure 6–11.

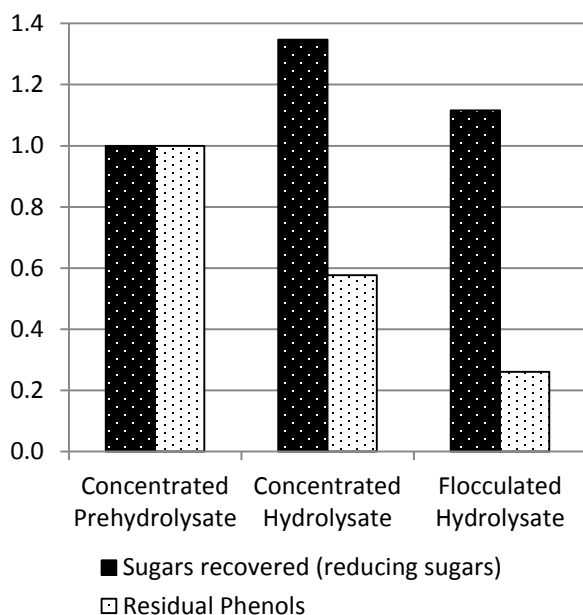


Figure 6–11: Sugar recovery and residual phenolic compounds evolution with configuration C

The increased reducing sugar concentration after hydrolysis can be explained by the increase in number of aldehyde groups that occurs when the sugar oligomers are broken down into monomers. Flocculation however resulted in about 24% loss of the sugars in the hydrolysate. At the same time, the amount of phenols removed during the flocculation and concentration is about 74 %. The final amount of phenolic compounds in the concentrated prehydrolysate was reduced from 15.9 g/L down to 4.1 g/L

6.4.5.4 Proposed Strategy

The objective of the proposed strategy is to concentrate and detoxify the prehydrolysate from a receptor Kraft pulp mill for biofuels production. It has been shown that the use of nanofiltration membranes allows for the simultaneous concentration and partial detoxification of hemicelluloses prehydrolysate. Secondary detoxification by flocculation can be performed after hydrolysis of the concentrated prehydrolysate. As shown in Table 6.2, the use of dilute acid to convert the concentrated prehydrolysate into concentrated hydrolysate decreased the concentration of phenolic compounds but led to an increase of the acetic acid, furfural and hydroxymethylfurfural.

Table 6.2: Evolution of prehydrolysate composition during detoxification (Membrane filtration – Hydrolysis –Flocculation)

Compounds	Prehydrolysate	Concentrated Prehydrolysate	Concentrated Hydrolysate	Flocculated Hydrolysate
Total sugars (g/L)	39	118	155	129
Phenolic compounds (g/L)	4.51	15.59	8.97	4.06
Acetic Acid (g/L)	6.33	12.40	29.90	5.85
Furfural (g/L)	0.66	1.08	1.67	1.17
Hydroxymethylfurfural (g/L)	0.09	0.18	0.29	0.21

Our hypothesis is that the increase in the concentration of inhibitors as a result of acid hydrolysis can be minimized successfully by the use of enzymatic hydrolysis. The use of a compacted XN45 membrane instead of the NF270 membrane could also be used to remove a higher fraction of inhibitors prior to hydrolysis and flocculation. The integration of the proposed conceptual process with a Kraft dissolving pulp mill is illustrated in Figure 6–12.

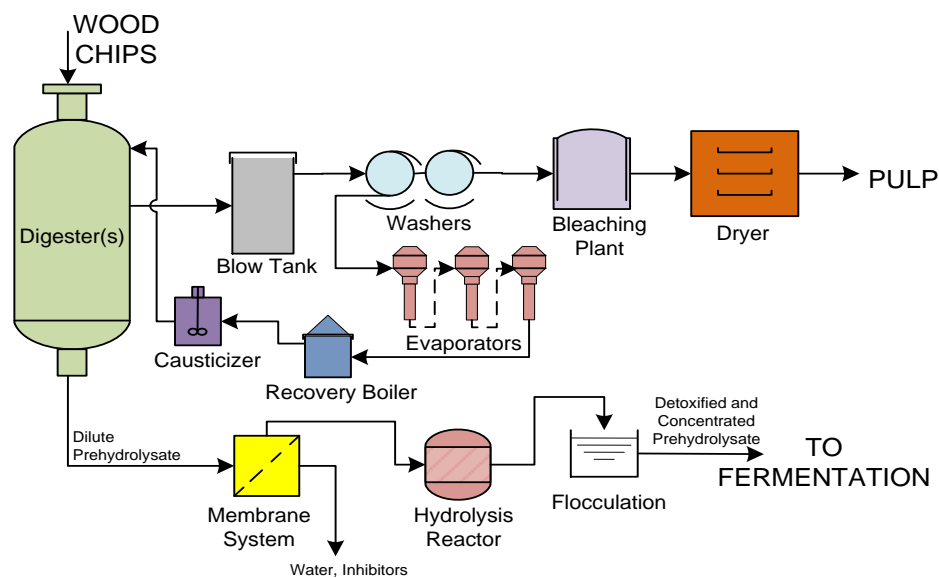


Figure 6–12: Schematic flow sheet of the proposed concept for the concentration and detoxification

The selected sequence of operations (membrane filtration – hydrolysis – flocculation) leads to high sugar recovery and the elimination of a significant fraction of the phenolics.

6.5 Conclusions

A combined concept of nanofiltration and flocculation has been applied to the detoxification and concentration of prehydrolysate from a Kraft dissolving pulp mill. Screening of several commercial organic membranes with molecular cut of weights between 150 Da and 3500 Da showed that the Trisep TS40, Trisep XN45 and Dow NF270 membranes can be successfully applied to concentrate and detoxify hemicelluloses prehydrolysate solutions. The membranes produced high removal of fermentation inhibitors except for the phenolic compounds. The XN45 had the highest degree of phenols removal. Flocculation with ferric sulfate was proven to be an interesting secondary detoxification method for the removal of phenolic compounds. A strategy for concentration and detoxification for integration with a Kraft dissolving pulp mill has been proposed; it is based on laboratory experiments. Pilot scale experiments are mandatory for detailed technical feasibility studies and economic assessment. Some of the envisaged variations to the process include the use of enzymatic hydrolysis instead of acid hydrolysis, identification of other flocculants and regeneration of the flocculant.

Acknowledgment

The support of this research by the Natural Sciences and Engineering Research Council of Canada University and College I2I program and BioFuelNet Canada is appreciated. The authors are grateful to FPInnovations for providing the hemicelluloses prehydrolysate and all the technicians at CNETE, Shawinigan for providing assistance during the experiments. The authors are indebted to Prof. Jean Paris for his valuable contributions to this work.

References

- [1] M. Moshkelani, M. Marinova, M. Perrier, and J. Paris, "The forest biorefinery and its implementation in the pulp and paper industry: Energy overview," *Applied Thermal Engineering*, vol. 50, pp. 1427-1436, 2013.
- [2] Z. Sun and S. Liu, "Production of n-butanol from concentrated sugar maple hemicellulosic hydrolysate by *Clostridia acetobutylicum* ATCC824," *Biomass and Bioenergy*, vol. 39, pp. 39-47, 2012.

- [3] M. Marinova, E. Mateos-Espejel, and J. Paris, "From kraft mill to forest biorefinery: An energy and water perspective. II. Case study," *Cellulose Chemistry and Technology*, vol. 44, pp. 21-26, 2010.
- [4] E. W. Jennings and D. J. Schell, "Conditioning of dilute-acid pretreated corn stover hydrolysate liquors by treatment with lime or ammonium hydroxide to improve conversion of sugars to ethanol," *Bioresource Technology*, vol. 102, pp. 1240-1245, 2011.
- [5] J. M. Lee, R. A. Venditti, H. Jameel, and W. R. Kenealy, "Detoxification of woody hydrolyzates with activated carbon for bioconversion to ethanol by the thermophilic anaerobic bacterium *Thermoanaerobacterium saccharolyticum*," *Biomass and Bioenergy*, vol. 35, pp. 626-636, 1// 2011.
- [6] J. Shen, I. Kaur, M. M. Baktash, Z. He, and Y. Ni, "A combined process of activated carbon adsorption, ion exchange resin treatment and membrane concentration for recovery of dissolved organics in pre-hydrolysis liquor of the kraft-based dissolving pulp production process," *Bioresource Technology*, vol. 127, pp. 59-65, 1// 2013.
- [7] A. Converti, J. Domínguez, P. Perego, S. Da Silva, and M. Zilli, "Wood hydrolysis and hydrolyzate detoxification for subsequent xylitol production," *Chemical Engineering & Technology*, vol. 23, pp. 1013-1020, 2000.
- [8] S. I. Mussatto and I. C. Roberto, "Alternatives for detoxification of diluted-acid lignocellulosic hydrolyzates for use in fermentative processes: A review," *Bioresource Technology*, vol. 93, pp. 1-10, 2004.
- [9] A. K. Chandel, S. S. da Silva, and O. V. Singh, "Detoxification of lignocellulosic hydrolysates for improved bioethanol production," *Biofuel production-Recent developments and prospects*, pp. 225-246, 2011.
- [10] O. Ajao, M. Rahni, M. Marinova, H. Chadjaa, and O. Savadogo, "Retention and flux characteristics of nanofiltration membranes during hemicellulose prehydrolysate concentration," *Chemical Engineering Journal*, vol. Submitted, 07 July 2014 2014.
- [11] O. Ajao, M. Rahni, M. Marinova, H. Chadjaa, and O. Savadogo, "Concentration of hemicelluloses prehydrolysate by membrane filtration: Feasibility and effect of composition on

flux decline mechanisms," *Separation and purification technology*, vol. Submitted, 07 May 2014 2014.

[12] T. Radiotis, X. Zhang, M. Paice, and V. Byrne, "Optimizing Hardwood Prehydrolysis for Simultaneous Production of Bioproducts and Biomaterials," *Journal of Bioprocess Engineering and Biorefinery*, vol. 1, pp. 69-76, // 2012.

[13] I. P. Wood, A. Elliston, P. Ryden, I. Bancroft, I. N. Roberts, and K. W. Waldron, "Rapid quantification of reducing sugars in biomass hydrolysates: Improving the speed and precision of the dinitrosalicylic acid assay," *Biomass and Bioenergy*, vol. 44, pp. 117-121, 9// 2012.

[14] S. Stade, M. Kallioinen, A. Mikkola, T. Tuuva, and M. Mänttari, "Reversible and irreversible compaction of ultrafiltration membranes," *Separation and Purification Technology*, vol. 118, pp. 127-134, 10/30/ 2013.

[15] M. Dashtban, A. Gilbert, and P. Fatehi, "A combined adsorption and flocculation process for producing lignocellulosic complexes from spent liquors of neutral sulfite semichemical pulping process," *Bioresource Technology*, vol. 159, pp. 373-379, 5// 2014.

[16] M. Andjelković, J. Van Camp, B. De Meulenaer, G. Depaemelaere, C. Socaciu, M. Verloo, *et al.* , "Iron-chelation properties of phenolic acids bearing catechol and galloyl groups," *Food Chemistry*, vol. 98, pp. 23-31, // 2006.

[17] S. Khokhar and R. K. Owusu Apenten, "Iron binding characteristics of phenolic compounds: some tentative structure–activity relations," *Food Chemistry*, vol. 81, pp. 133-140, 5// 2003.

[18] M. Kumamoto, T. Sonda, K. Nagayama, and M. Tabata, "Effects of pH and metal ions on antioxidative activities of catechins," *Bioscience, biotechnology, and biochemistry*, vol. 65, pp. 126-132, 2001.

[19] E. Casey, N. S. Mosier, J. Adamec, Z. Stockdale, N. Ho, and M. Sedlak, "Effect of salts on the Co-fermentation of glucose and xylose by a genetically engineered strain of *Saccharomyces cerevisiae*," *Biotechnology for biofuels*, vol. 6, p. 83, 2013.

[20] M. C. Gray, A. O. Converse, and C. E. Wyman, "Sugar monomer and oligomer solubility," in *Biotechnology for Fuels and Chemicals*, ed: Springer, 2003, pp. 179-193.

CHAPTER 7. FEASIBILITY OF INTEGRATING AN ETHANOL PROCESS WITH A DISSOLVING PULP MILL

7.1 Introduction

The cellulose fraction of woody biomass can be purified with a pulping processes to obtain rayon or specialty grade dissolving pulp. Rayon grade dissolving pulp can be further transformed into products such as textiles and flexible packaging material while specialty grade dissolving pulp can be transformed into microcrystalline cellulose (MCC), pharmaceuticals, sausage casings, cigarette filters, transportation hoses and belts [46]. The predominant pulping process worldwide is the Kraft pulping process [1]. The main advantages of the Kraft process are (i) the pulp obtained has a higher strength than other pulping methods (ii) the chemicals used in the process can be recovered [4, 35] A state of the art Kraft dissolving pulping process is the VisCBC technology; its main advantages include a low energy demand, homogenous pulp and short residence time [158]. A disadvantage of this technology is that the steam prehydrolysis of wood chips is followed by a neutralization step that degrades the hemicellulosic sugars and renders them irrecoverable [2]. Usually, the degraded sugars are combusted for energy production. The process can be modified to recover the sugars by carrying a hot water displacement after the regular steam prehydrolysis [159]. Extracting the hemicelluloses would not result in a significant energy deficit for the mill because the heating value of the hemicelluloses is 50% lower than that of lignin, the other combusted wood fraction [5]. One of the proposed alternative uses of the hemicelluloses sugars is for the production of ethanol [132].

Ethanol production is one of the most studied processes in the past decade. The global ethanol production increased from 39 billion litres in 2006 and is expected to exceed 90 billion litres in 2014 [156]. In recent times, the use of forest biomass for biofuels production has gained interest because it is not edible and does not compete for arable land.

A biorefinery process that is implemented on the site of a pulp and paper mill, exchanges material, energy and chemicals with the receptor mill is known as an integrated forest biorefinery (IFBR). The IFBR could lead to the diversification of products and increases the revenues of the pulp mill. In addition, the investment cost is lower due to the existence of facilities on the pulp mill site and an established wood supply chain. Moreover, the pulp production capacity can be

increased if it is limited by the calorific capacity of the recovery boiler where the hemicelluloses is typically combusted.

7.2 Context

The case study reference mill is an eastern Canadian dissolving pulp mill with a production capacity of 670 odt/d (odt = oven dried tons). A batch digester is used for prehydrolysis, followed by pulping. The hypothesis in this study is that hot water displacement is used to recover the hemicellulosic sugars instead of neutralization with alkali liquor prior to pulping. High pressure (HP) steam is produced in the recovery boiler and a power boiler that is fired by wood bark and bunker oil. Steam at high and low pressure as well as electricity is generated in the co-generation system of the mill. The current steam consumption of the mill is about 250 MW and the water consumption is 2480 m³/h. A previous study on the development of a novel methodology for reducing steam and water consumption showed that up to 67.5 MW and 940 m³/h can be saved at the mill [160]. The ethanol process consists of concentration and detoxification, hydrolysis, conversion and purification steps. Opportunities for integration of the ethanol process with a receptor dissolving Kraft pulp mill is shown in Figure 7–1.

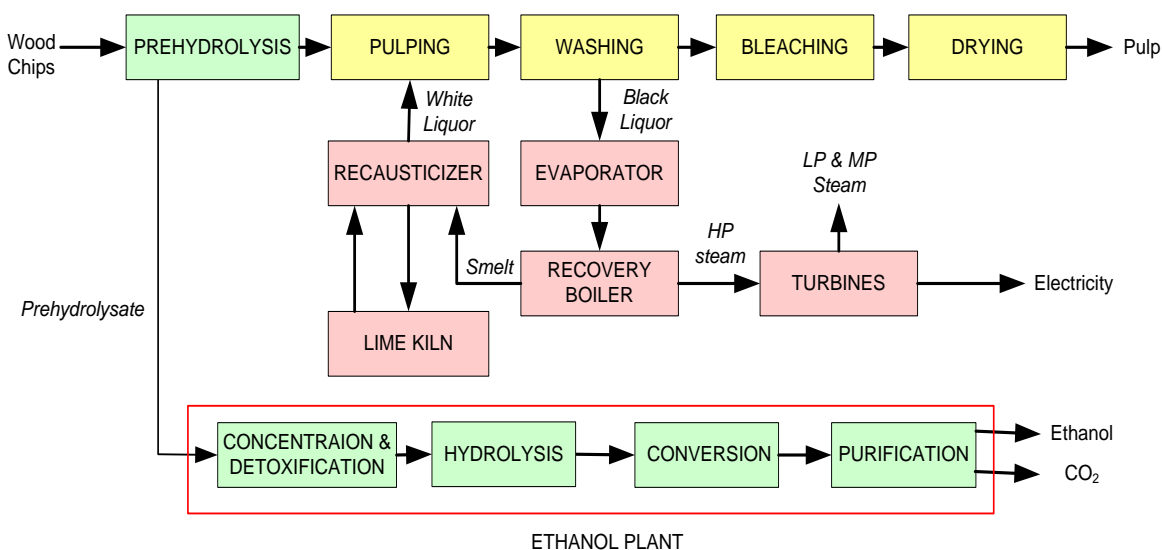


Figure 7–1 Simplified scheme of an integrated forest biorefinery for ethanol production

The composition and mass flow of the prehydrolysate stream was calculated based on results from pilot scale prehydrolysis experiment [80]. A wood furnish similar to that of the receptor mill was used in the experiment. About 80 % of the total sugars are oligomers and the remaining 20% monomers.

Table 7.1: Composition of the ethanol process feed stream

Components	Mass Flow (t/d)
Furfural	3
Lignin	15
Acetic Acid	17
C ₆ sugars	17
C ₅ sugars	83
Water	4800

7.3 Methodology

The methodology used for developing the ethanol IFBR is illustrated in Figure 7–2. The real prehydrolysate solution was used to determine the amount of fermentation inhibitors to be removed from the hemicelluloses prehydrolysate. The prehydrolysate solution had a low sugar composition, concentration is therefore necessary for reducing the size of the process equipments and energy cost. A concentration and detoxification strategy was developed for hemicelluloses prehydrolysate [161]. Input data for the fermentation and purification steps of the biorefinery were obtained from published references and the Aspen Plus[®] (simulation software) database.

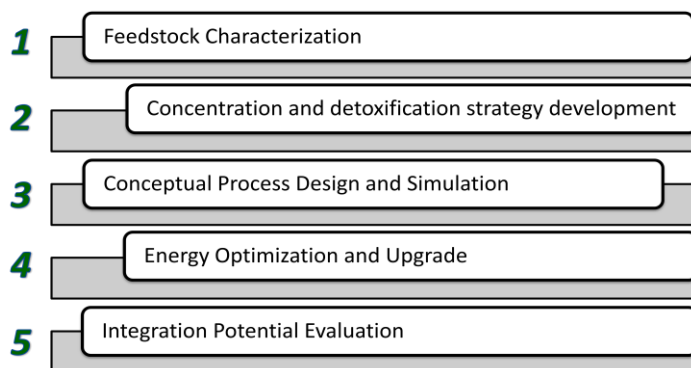


Figure 7–2: Overview of methodology for the ethanol biorefinery development

7.4 Process overview

The process diagram for the ethanol process is illustrated in Figure 7–3. The main steps of the biorefinery can be classified as concentration and detoxification (nanofiltration and flocculation), sugar conversion (hydrolysis and fermentation) and product purification (flash separators, scrubbers, distillation columns and molecular sieves).

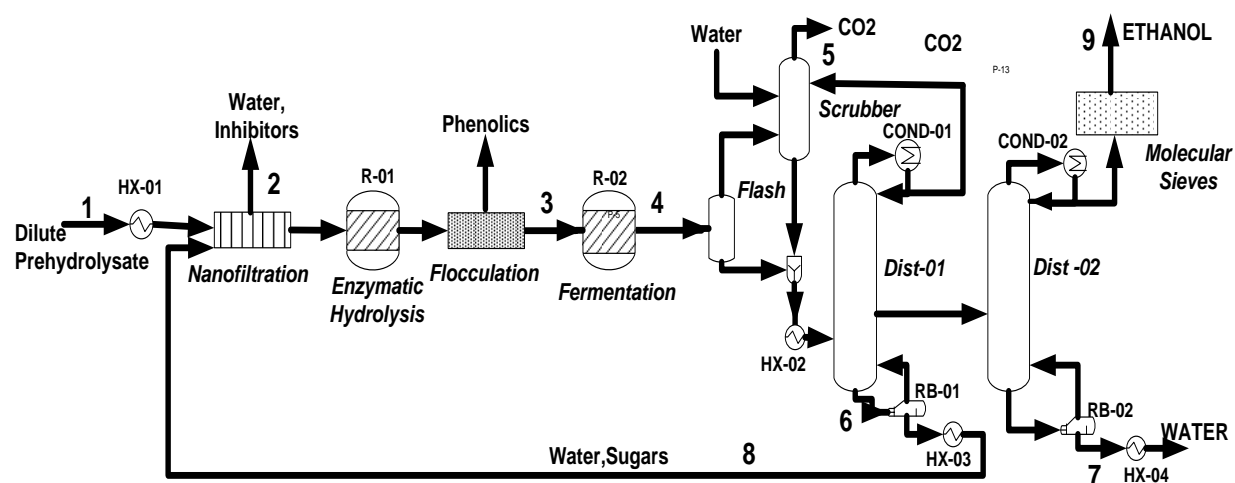


Figure 7–3: Process diagram for ethanol production

The screening of membranes with molecular weight cut offs (MWCO) between 100 and 500 Da to identify the most suitable for simultaneous concentration and detoxification has been reported [80].

Most of the inhibitors could be removed using a membrane except the phenolic compounds. It was necessary to identify a complementary detoxification method. Flocculation with ferric sulfate as coagulant was selected as a suitable method [13].

Enzymatic hydrolysis was used to convert the oligomers into fermentable monomers. It has the following advantages over acid [133, 162, 163]:

- High yield of sugar monomers
- It generates less effluents that must be treated
- It produces less inhibitors

- It can be carried out at mild condition and
- Reduced cost of equipment

The sequence (nanofiltration – enzymatic hydrolysis – flocculation) was used in the proposed process. The development of the detoxification strategy is presented in chapter 6.

Fermentation of sugars can be carried out with several microorganisms such as *E. Coli*, *C. Glutamicum*, *S. Cerevisiae*, *P. Stipitis*, *T. Reesei*, and *A. Niger* [112]. As shown in Table 7.1, the extracted hemicelluloses fraction contains about 80 % of pentose sugars. The lack of organisms that can ferment pentoses with a high yield has been identified as one of the main obstacles for the conversion of hemicelluloses into ethanol or other biofuels [164-166]. The fermentation yields in this case study was based on a proprietary pentose fermenting yeast (personal communication with an ethanol production company). The flash separator, the scrubber and the first distillation column are used to remove carbon dioxide from the ethanol stream. The second distillation column is to purify ethanol up to its azeotropic point (80% weight) before dehydration with molecular sieves.

7.5 Process Simulation

Aspen Plus[®] V7.2 was used to simulate the process and generate the mass and energy balances. Property data for several compounds that were not present in the physical property database of Aspen Plus[®] were obtained from a published report and embedded into the software [167].

The nanofiltration membrane system, flocculation step and the final product dehydration with molecular sieves were modeled as split separators in Apen. The enzymatic hydrolysis reactor was represented as a stoichiometric reactor with 95 % conversion of the oligomers into monomers at 101 kPa and 50°C. The fermentation reactor was also modeled as a stoichiometric reactor with 90% conversion of the hexose monomers and 70 % conversion of the pentose monomers into ethanol respectively. A two outlet flash module was used to represent the flash separator while the scrubber and the distillation columns were modeled as rigorous fractionating columns. Estimates for the starting values of the columns were determined with the McCabe-Thiele graphical method. The stream data for the ethanol process are summarized in Table 7.2.

Table 7.2: Data for key process streams

	Streams								
	1	2	3	4	5	6	7	8	9
T (°C)	80	30	50	30	28	137	120	20	76
P (kPa)	101	327	101	102	91	327	205	327	174
Total flow (t/d)	4940	4775	954	954	55	804	76	804	57
Water (t/d)	4797	4746	794	794	1	754	75	754	1
Total C₅ sugars (t/d)	82	0	135	43	0	43	0	43	0
Total C₆ Sugars (t/d)	17	0	25	7	0	7	0	7	0
Total monomer (t/d)	14	0	156	46	0	46	0	46	0
CO₂ (t/d)	0	0	0	54	54	0	0	0	0
Ethanol (t/d)	0	0	0	56	0	0	1	0	55

7.6 Energy requirement minimization and site integration

The heating and cooling demands for the ethanol process are 8.41 MW and 20.6 MW respectively. Pinch analysis is a well known method for minimizing the heating and cooling demand in chemical processes [24, 39] and it was used to reduce the heating and cooling demands. The analysis was performed by means of the software, Aspen Energy Analyzer. Data for the hot and cold process streams were extracted and used to plot a T-H diagram as shown in Figure 7–4.

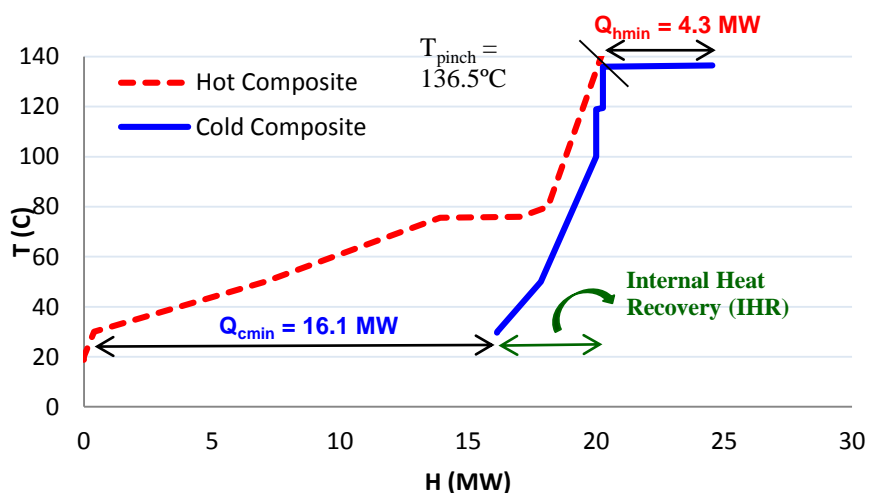


Figure 7–4: Thermal composite curve for the ethanol biorefinery

The principles of the pinch analysis have been explained in details in chapter 5. The pinch point was found to be 136.5°C, the minimum cooling requirement 16.1 MW and the minimum heating requirement 4.3 MW. To reduce the heating and cooling requirements of the process by internal heat recovery, two additional heat exchangers were implemented. Heat can be recovered from the prehydrolysate feed to the biorefinery (HX-01) and used to heat the reactor for enzymatic hydrolysis (R-01). Heat can also be recovered from the recycled stream (HX-03) and used to preheat the feed stream to the first distillation column (HX-02). The HEN design reduced the heating and cooling requirements to 4.6 MW (-45%) and 16.8 MW respectively (-19%)

To further increase the thermal efficiency of the ethanol process, an AHP was implemented. The AHP principles of operation and stepwise methodology for installation have been described in details in chapter 5. Heat can be upgraded from the condenser of the second distillation column (COND-02) and used to drive the reboiler of the first column (REB-01). Heat is also available from the AHP to preheat water in the Kraft process.

The total energy reduction that can be obtained by designing a heat exchanger network and implementing the heat pump is shown in Table 7.3.

Table 7.3: Energy requirement minimization after HEN design and AHP implementation

	BASE CASE	OPTIMIZED HEN	OPT. HEN + AHP	SAVINGS (%)
Heating Requirement (MW)	8.41	4.58	3.31	60 %
Cooling Requirement (MW)	20.6	16.78	15.5	25 %

Considering the fact that up to 67.5 MW of steam and 940 m³/h of fresh water consumption can be saved at mill, the total heating requirement of the optimized biorefinery (3.31 MW) can be supplied by the receptor mill. The cooling requirement can also be met as only 185 m³/h of fresh water will be required to cool process streams in the biorefinery. The water can be returned at about 50°C for direct use at the mill. An additional 201 m³/h of water from the membrane detoxification step can be reused in the receptor mill.

7.7 Conclusions

An ethanol process for integration into a Kraft dissolving pulp mill is proposed. The integration has been shown to be technically feasible. The utility demands of the ethanol plant can be supplied by the mill. In comparison to the production of furfural, the ethanol plant has a lower heating requirement but a higher cooling requirement than the furfural process developed in chapter 5. The fermentation of pentoses still requires technological and scientific developments in the areas of prehydrolysate detoxification and fermentation. This makes it difficult to determine the production cost of ethanol production in the integrated forest biorefinery. A more promising alternative could be the production of butanol or other higher value chemicals from the prehydrolysate stream

CHAPTER 8. HEMICELLULOSES BASED INTEGRATED FOREST BIOREFINERIES: IMPLEMENTATION STRATEGIES

8.1 Introduction

The biorefinery concept is widely accepted as a cost competitive means of lowering greenhouse gas emissions, reducing reliance on fossil fuels and transitioning towards a biobased economy. A Biorefinery can be defined as a process or combination of processes for converting renewable biomass into a wide spectrum of products such as biochemicals, biofuels or biomaterials [46]. Lignocellulosic biomass is one of the most abundant feedstock for biorefineries globally [7] and it is made up of three main classes of polymers: cellulose, hemicelluloses and lignin. The breakdown of the polymers into their constituent monomer before conversion into other value added chemicals is a key step in biorefineries. Each of the polymers has different degrees of recalcitrance to fractionating methods and also different potential end products. Fractionating costs constitute a significant portion of the production cost for biofuels or bioproducts [57, 168]. Integrating a new biorefinery process with an established process where the fractionating of biomass is already practiced could therefore lead to significant cost reductions for biorefineries [132].

A potential receptor process is the Kraft dissolving pulp mill in which the hemicelluloses are separated with a prehydrolysis step prior to pulping. The cellulose fraction is subsequently purified by chemical delignification to obtain pulp while the lignin fraction is mixed with the pre-extracted hemicellulose and combusted to produce energy for the process. The hemicelluloses from the prehydrolysis step can be diverted and used as a feedstock for the biorefinery. The implementation of a biorefinery plant into an existing receptor pulp mill for the manufacture of additional non pulp products (biochemical, biomaterials or biofuels), is known as the Integrated Forest Biorefinery (IFBR). An IFBR would lead to an increase in the onsite energy demand [5] but this can be addressed through intensive energy optimization of the receptor Kraft process [160]. The IFBR is also a means for pulp and paper mills to diversify and increase their revenues in the face of declining pulp and paper commodities demand, intense global competition and high energy prices. In this paper, the concept of hemicelluloses based integrated forest biorefineries

and strategies that can be successfully implemented are presented. It includes an analysis of proposed processes and challenges for their implementation. A list of criteria to guide product selection and biorefinery development has been developed. The valorization of other wood components (lignin and cellulose) is outside the scope of this study and not treated.

8.2 Pulping processes and modifications required for IFBR implementation

Pulping is the separation of fibres that are fixed in wood or plant matrix and it entails the rupture of bonds within the wood structure. The existing pulp making processes can be broadly classified as mechanical, chemi-mechanical, semi-chemical, and chemical pulping [9]. The classifications are in the order of decreasing dependence on mechanical energy and increasing dependence on the use of chemicals to facilitate fibre separation. Although mechanical pulping is very energy intensive, it comes with the advantage that a pulp yield of up to 95% of the dry weight of wood can be obtained [4].

Chemical pulping on the other hand has a lower yield but the strength of the produced pulp is higher and it is possible to recover the chemicals used. Kraft pulping, a chemical process, is the predominant pulping method in use worldwide [169] and about 90% of the global pulp production is via the Kraft process [1]. A brief overview of conventional Kraft pulping and its variant, prehydrolysis-Kraft pulping for the production of dissolving pulp, is given in sections 8.2.1 and 8.2.2.

8.2.1 Kraft paper pulp

A simplified representation of the Kraft process is illustrated in Figure 8–1. Wood chips undergo chemical delignification, the dissolution of hemicelluloses and lignin from the cellulose. Delignification is carried out in a digester in the presence of white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulphide (Na₂S). After delignification, the cellulose fibres (pulp) are washed, bleached and dried. The black liquor, which contains the dissolved wood components and the bulk of the inorganic elements used for digesting, is concentrated by multi-effect evaporators.

The concentrated black liquor is subsequently burnt in the recovery boiler to produce a smelt that is dissolved in water to form green liquor (mainly CaCO₃ and Na₂S). This is followed by

recausticizing, the reaction of the green liquor with lime to regenerate the active chemicals used in the digesting step. This sequence makes up the chemical recovery cycle.

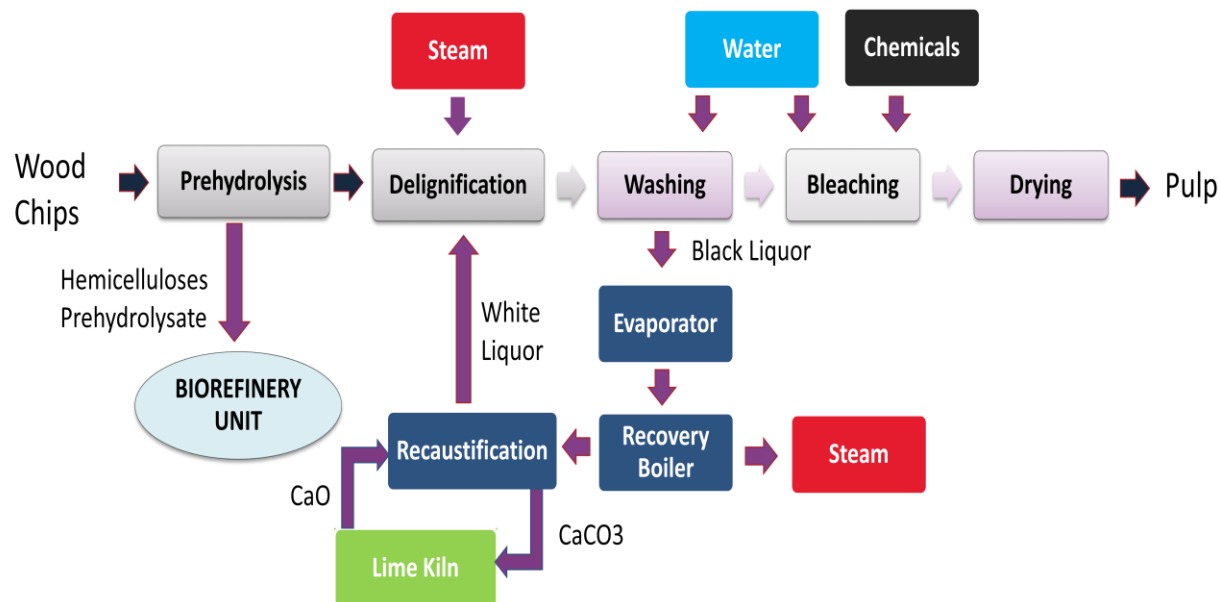


Figure 8–1: Simplified diagram of the Kraft process with a prehydrolysis step for hemicelluloses extraction

8.2.2 Dissolving pulp

Dissolving pulp is a type of pulp that has a high cellulose content ($\geq 96\%$) compared to paper pulp with 72-79% typically [170]. It is used for the production of rayon, cellophane and cellulose nitrates [16]. The higher cellulose purity is obtained by introducing a prehydrolysis step in a Kraft process to remove hemicelluloses prior to delignification. This leads to a lower pulp yield but the higher price of dissolving pulp in comparison to Kraft pulp compensates for this reduction. In addition, an advantage of the prehydrolysis step in dissolving pulp mills is that the extracted hemicelluloses could be used for the production of sugar based chemicals or fuels thus generating additional revenue. A dissolving pulp mill is attractive when the price of wood is low compared to other feedstock for the production of textile or when the dissolving pulp price is high [18]. High dissolving pulp prices have spurred the conversion of several Canadian paper pulp mills into dissolving pulp mills in recent years [2].

8.2.3 Hemicelluloses: composition and extraction

Hemicelluloses rank behind cellulose as the second most abundant natural polymer and are the most complex components in the cell wall of lignocellulosic biomass [54]. Hemicelluloses are heterogeneous polysaccharides comprising of hexoses (galactose, mannose, glucose) and pentoses (xylose, arabinose). They form bonds with other classes of wood components (cellulose and lignin). They have a degree of polymerization (DP) of 80 – 200, compared with cellulose at about 10,000 [55, 56]. As a result of their lower DP, they also exhibit lower chemical and thermal stability and are consequently more soluble and susceptible to hydrolysis than celluloses. Their composition varies with types of feedstock. A comparison of typical compositions of hardwoods and softwoods is given in Table 8.1.

Table 8.1: Typical variation of wood chemical composition (percent) [59]

	Hardwoods	Softwoods
Celluloses	30 -43	40 - 48
Hemicelluloses		
<i>Hexoses</i>	2 - 5	12 -15
<i>Pentoses</i>	17 - 25	7-10
Lignin	20-25	26 - 31
Extractives	1-5	3-8
Ash	0.4-0.8	0.2-0.5

A major difference between hardwoods and softwoods is the distribution of the hemicelluloses fraction between hexoses and pentoses. Hardwood hemicelluloses are principally made up of pentoses while softwood hemicelluloses are made up of hexoses. The bonds between the pentoses are hydrolyzed more rapidly than that of the hexoses and require less severe hydrolysis conditions than the hexoses polymers [1, 57]. Hemicelluloses gives strength to paper pulp and also increases the process yield but are undesired in dissolving pulp which requires a higher degree of purity of the cellulose [146]. A higher amount of hemicelluloses can be extracted in a dissolving pulp process (40%) than in a conventional Kraft pulping process (15 %). The hemicellulose extraction method must be adapted for each process. Extraction methods can be classified as chemical or physical methods. Physical methods include steam explosion, hot water and microwave pre-treatment while acid, alkali, Ammonium Fibre Explosion (AFEX), Ionic

Liquids and ozonolysis pre-treatment are chemical methods. Not all these methods can be utilized in an IFBR, the chemical methods are the most promising.

8.2.4 Receptor Kraft pulp mill modifications

Modifications have to be made to a receptor Kraft pulp mill to transform it into an integrated forest biorefinery. The extent of modifications required depends on the type of mill, intended final products and the current state of the mill. The three following scenarios for modification are envisaged:

- Modifications to an existing Kraft pulp mill with pulp production unchanged
- Modifications to a Kraft pulp mill and conversion into a dissolving pulp mill
- Modifications to an Kraft dissolving pulp mill

In all the scenarios, an optimization of the energy and water network would be necessary to lower emissions and production costs.

8.2.4.1 Existing Kraft pulp mill with no change to pulp production

In the case of an existing mill where the production of Kraft pulp would be maintained, hemicellulose extraction from the wood chips prior to cooking would not be economically feasible because the amount of hemicelluloses that can be extracted without reducing the pulp yield and degrading the fiber would be too low. In addition, the energy requirement for the prehydrolysis step would be high and unjustifiable. On site co-location of a biorefinery process that is only energetically integrated with the receptor mill could be feasible as illustrated in Figure 8–2A. Energy optimization of Kraft pulp mills has been shown to result in steam savings of 25 % or higher [160]. This represents a huge amount of energy that can be liberated to drive a biorefinery plant. The feedstock for the biorefinery would however have to be agricultural residue or other lignocellulosic biomass. Another alternative for the production of bioproducts could be to repurpose the mill so that a small fraction of the cellulose fibers would be diverted for upgrading into a niche product.

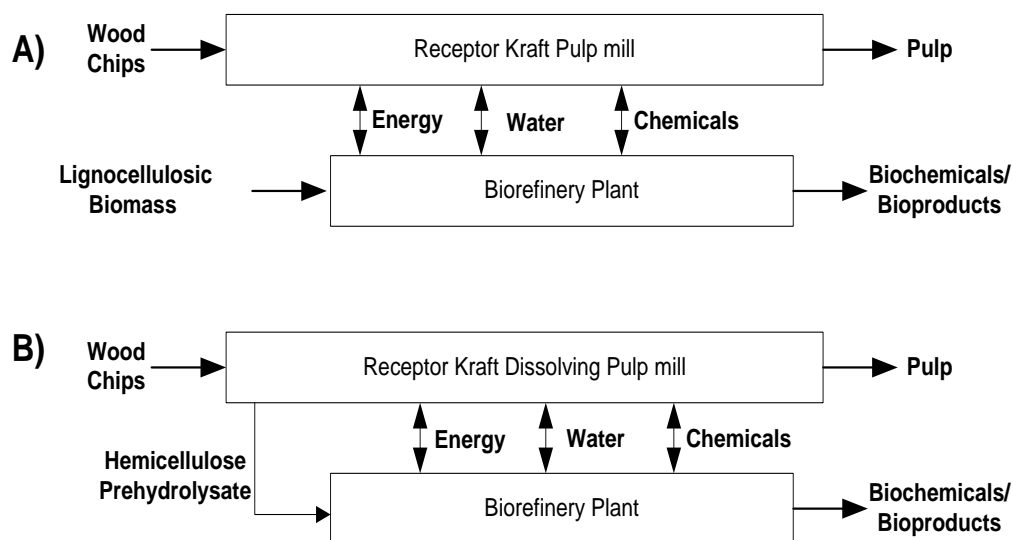


Figure 8–2: Process diagrams for a biorefinery plant integrated with a Kraft A) pulp mill B) Dissolving pulp mill

8.2.4.2 Kraft pulp mill to be converted into a dissolving pulp mill

Kraft pulp mills are prime candidates for conversion into dissolving pulp mills. The major modification required is the addition of a prehydrolysis step for hemicelluloses extraction before the chemical delignification of the wood chips. The choice of extraction method is critical. A suitable method would not reduce the pulp yield and deteriorate its quality. It should also produce a high sugar yield with minimal energy requirement and low cost [65]. The formation of inhibitors (hemicelluloses degradation products) must be at a minimum if the sugars are further transformed by enzymatic hydrolysis and/or fermentation. This should be achieved by optimization of the extraction condition [64]. Each method presents different challenges and opportunities, the amount of sugars extracted and the form in which they will be made available (monomers or oligomers) are different. The most suitable method is receptor mill specific and should be determined by a thorough study. A comparison of some extraction methods is illustrated in Table 8.2.

Table 8.2: Feasibility of integrating some hemicellulose extraction methods with a receptor Kraft pulp mill

Method	Cost	Maturity	Final PH	Sugar Quantity	Integration Potential	State of development
Hot Water	Low	Yes	Yes	High	Yes	Industrially level
Steam	Medium	Yes	Yes	Medium	Yes	Industrially level
Acid Based	Medium *	Yes*	Yes	High	Yes	Proven method
Alkali Based	High	No	No	Low	Yes	Proven method
Organic Solvents	High	No	-	High-	Yes	Potential
Enzymes	Medium	Yes	-	-	No	Not for primary extraction

Acids: HNO₃, H₃PO₄, H₂SO₄, HCl, H₃PO₄, SO₂, CO₂, Alkali: NH₃, NaOH, Ca(OH)₂, Solvents: Organosolv, Ionic liquid, Ozonolysis

*H₂SO₄

It is important that the potential end product be taken into consideration prior to modifying the mill configuration. The nature and duration of the prehydrolysis step would have an impact on the residence time for delignification (digester capacity), amount of cooking chemicals required in the receptor mill and type of digester, pulp yield and bleaching sequence [2]. Consequently, these would determine the energy and water utility savings targets that can be achieved for the mill. The second stage of modification that should be considered is the material, energy and water integration of the biorefinery plant with the receptor mill.

8.2.4.3 Existing Kraft dissolving pulp mill

In a mill that already produces dissolving pulp; the modifications required would depend on whether steam or hot water is used for prehydrolysis. A state of the art process that uses steam prehydrolysis such as the VisCBC[®] has several advantages which include a shorter delignification time, low energy requirements and high pulp quality [171] but it employs an alkaline solution for neutralization prior to pulping. The neutralization liquor degrades the sugars and renders them irrecoverable so they can only be sent to the recovery boiler for combustion to produce energy. Proposed modification to such processes includes a multifunctional alkaline cooking after hemicellulose pre-extraction by using hot water [158]. Displacement with hot water

after steam hydrolysis has also been shown to be effective for hemicelluloses extraction [70]. Obstacles to the industrial application of hot water prehydrolysis include high investment and energy cost, formation of sticky prehydrolysate [172]. In cases where alterations of the mill configuration is not envisaged due to high capital cost, an alternative could be the diversion of a minor fraction of the dissolving pulp for the production of high value biomaterials.

8.3 Energy optimization, upgrade and introduction of renewable energy sources

The optimization of the energy and water consumption of a mill can be carried out using two different approaches.

- Concurrent energy and water optimization of the entire IFBR site, proposed by Rafione et al. [28]
- Independent energy and water optimization of the receptor mill and the biorefinery plant, the energy savings in the receptor mill will be sufficient to supply the requirements of the biorefinery unit, proposed by Keshtkar [160]

A previous study has shown that about 4800 t/d of prehydrolysate solution can be diverted from a mill that produces about 670 odt/d of dissolving pulp from 1900 t/d of hardwood chips by steam and hot water hydrolysis [173]. The total sugars concentration of the prehydrolysate was about 2% wt/wt while total furfural production capacity was 47 t/d. The biorefinery plant production capacity was inferior to 10 % of the receptor mill pulp production capacity. Concurrent energy optimization of the entire IFBR site would be rigorous and disproportionate to the production scale for cases where the biorefinery plant would not be implemented at the same time with the mill modification. A better approach would be the implementation of energy and water savings projects that can be identified through independent optimization approaches. Furthermore, the projects can be carried out in stages. Tools for energy optimization include pinch analysis technique, simultaneous energy and water optimization and mathematical modeling approach. The Kraft process is water based process in which the steam and water systems are interconnected. A reduction of the energy consumption would lead to water consumption reduction and vice versa. The steps for an innovative steam and water combined analysis,

integration and efficiency enhancement in Kraft pulping mills that has been proposed is illustrated in Figure 8–3. The methodology was successfully applied to three case study mills.

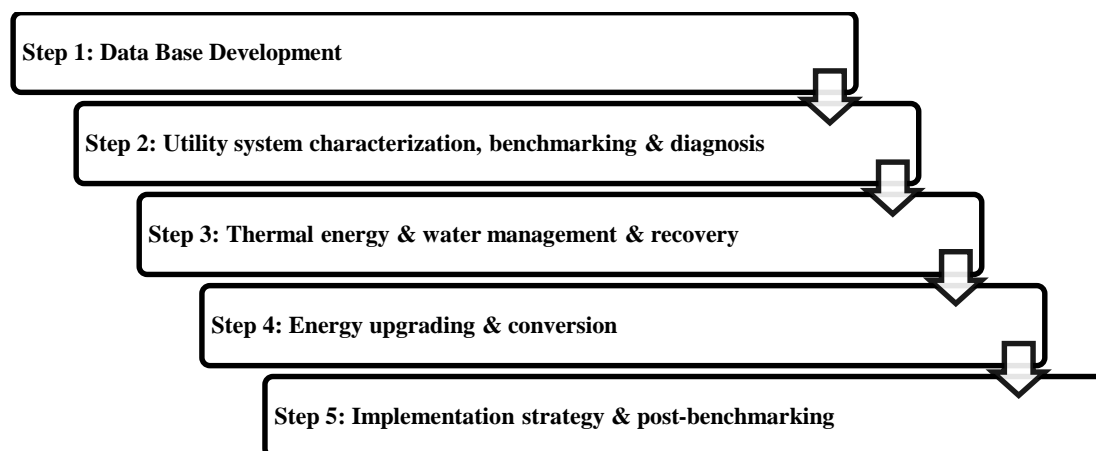


Figure 8–3: Stepwise methodology for innovative steam and water optimization [160]

Concurrent energy optimization is more adapted to the IFBR if the startup of the biorefinery will be at the same time as the mill modification.

Energy available at a low temperature can be upgraded to a higher temperature by using an absorption heat pump (AHP). The use of other renewable energy sources such as solar, geothermal and wind energy should also be explored where applicable.

8.4 Products from hemicelluloses / Applications

Hemicelluloses derived sugars can be used directly, converted into other biofuels, organic acids, sugar alcohols or furans. Some of the direct uses of hemicellulosic sugars include yeast cultivation, enzymes production and polymer films for packaging. The conversion of the sugars can be either through a biochemical (fermentation) or chemical pathway. Some potential derivatives are illustrated in Figure 8–4.

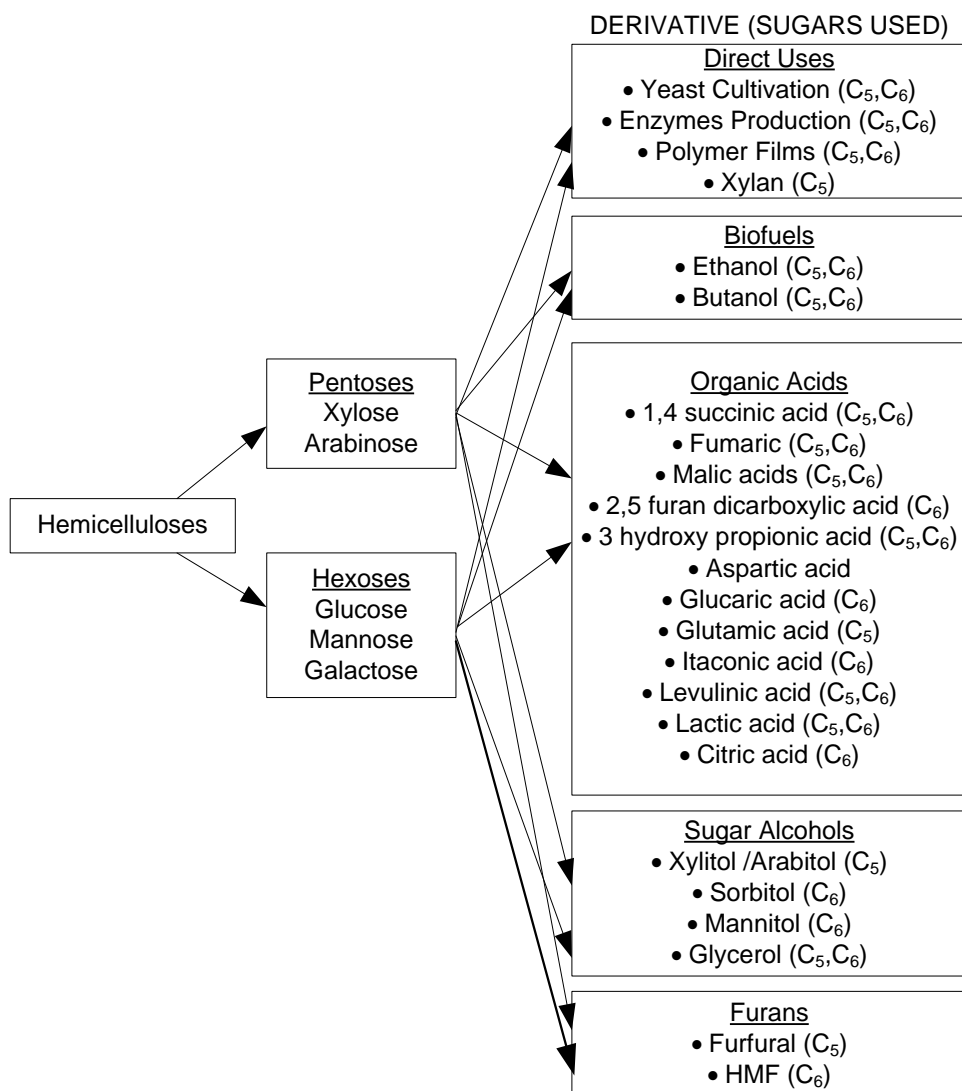


Figure 8–4: Potential applications and products from hemicelluloses prehydrolysates

Most of the listed biochemicals are among the 30 top chemicals that were identified in the National Renewable Energy Laboratory (NREL) list of top valued added chemical from biomass [174]. The list based on strategic criteria has been useful for narrowing down alternative products such as:

- Feasibility of directly replacing existing products,
- Products that can open new market opportunities and,
- Building block intermediates that can be further transformed into a wide spectrum of chemicals.

It is advantageous to select a chemical that can be produced from both pentoses and hexoses to obtain maximum value from the hemicelluloses.

Most of the potential chemicals that can be bio-derived require the development of commercially viable production processes. The profitability of biobased chemicals that can be used as substitute to petroleum based chemicals will depend on oil prices and on the desire for sustainable products by end users. The hemicellulose extraction method also plays a role in the choice of process for the transformation of the sugars. For instance, an extraction method that is capable to partition all oligomers into sugar monomers will require no further finishing hydrolysis with acid or enzymes. The choice of bioproduct in an IFBR is a complex decision that should include not only the technical feasibility but also the market assessment and socio-economic impact.

8.4.1 Product selection strategy

Ideally, the selection of bioproducts for an IFBR should be known prior to making modifications to a receptor mill but preliminary knowledge of the conversion pathway (biochemical or chemical) may be sufficient. Current typical practice is to select bioproducts based on the prehydrolysate composition, and available conversion processes at the industrial or exploratory stage (supply side product selection). The higher the price of the biochemical, the lower is the market size as illustrated in Figure 8–5. The simplest form of product that a biorefinery can export is sugar. This option requires the least amount of capital investment as new process equipments for a biorefinery plant would not be installed. Hardwood derived sugars such as Xylan or its monomer (Xylose) can be used in several applications. There is rising interest in the use of biobased feedstock (sugars) in the chemicals industry due a desire for sustainable chemicals by end users [175]. The downside of sugars production is its low value. Depending on the intended application of the sugars by the user, it could be necessary to achieve a high degree of purity and homogeneity (monomers or oligomers only).

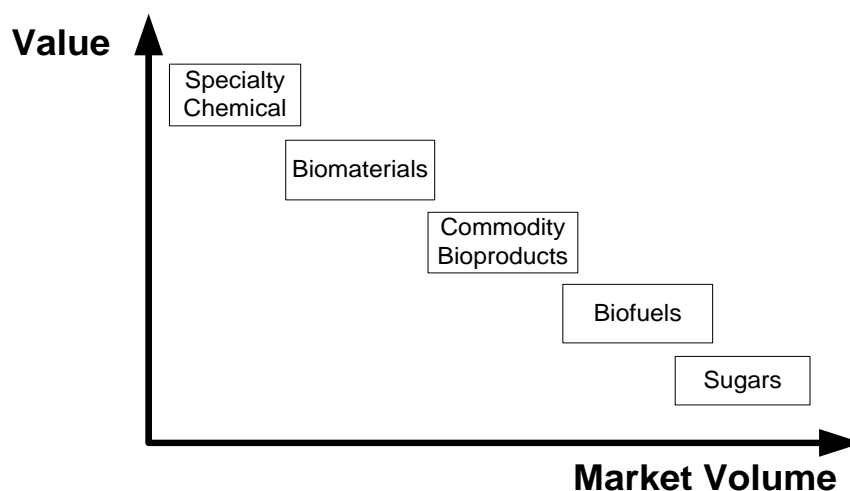


Figure 8–5: Value versus market volume for different bioproducts in an IFBR

Production of biofuel from hemicelluloses has gained wide interest due to the success of first generation biofuels and an established market, the production cost of biofuels from lignocelluloses is however higher than for first generation sources. The value of biofuels is only a fraction of pulp or dissolving pulp, so it would not lead to maximization of revenues for a receptor mill. A better alternative would be to produce other chemicals with a market value that is at least in the same range with pulp or higher. On the other hand, selection of a product with a high but lower market volume also carries the risk that the market could be easily saturated with the production capacity of a few mills and this could lead to a price decline. Other challenges for producing specialty chemicals include the requirement for registration and approval especially if the product is of food or pharmaceutical grade. This could be outside the core competence of a mill and carry a high level of risk. The objective of the products selection step should thus be to identify a unique product for a receptor mill that would offer a good margin between the market value and production cost over a long term. A low volume product must not necessarily be excluded on the basis of market saturation alone. A platform chemical that can be further transformed is an incentive for other users to participate in products development. A competitive product strategy should encompass the demand of the chemical industry. Some companies are interested in the use of sustainable chemicals and an IFBR take advantage of this by producing chemicals in high demand (demand side product selection).

The demand for biobased chemicals has increased over the past years and this is evidenced by the increased number of plants that are being constructed globally. Production of biochemicals that are unique and not substitute for petroleum or natural gas based products should stimulate the growth of biochemicals. However, this is constrained because the chemical industry expects substitute, biobased feedstock or drop in chemicals at a competitive price. The shale gas boom in North America has led to the preference for ethane feedstock in place of naphtha in hydrocarbon cracking plants and consequently the scarcity of C_3 to C_8 based compounds [176]. Biochemical producers should focus on filling the gap for the scarce chemicals and this probably explains why the chemicals with the highest industrial activity at present (commissioned plants, proposed plants, number of companies involved) have C_3 or higher. The top building blocks chemicals are classified based on the level of industrial interest as shown in Table 8.3

Table 8.3: Classification of the top 12 building block chemicals as hot, warm and cold, based on the level of industrial interest [177].

<u>TOP 12 BUILDING BLOCK CHEMICALS</u>		
Hot	Warm	Cold
<ul style="list-style-type: none"> • 1,4 succinic, fumaric & malic acids • 2,5 furan dicarboxylic acid • 3 hydroxy propionic acid 	<ul style="list-style-type: none"> • Levulinic acid • Glycerol- • Glucaric acid • Aspartic acid 	<ul style="list-style-type: none"> • Glutamic acid • Itaconic acid • 3-hydroxybutyrolactone • Sorbitol • Xylitol/arabinitol

From the standpoint of industrial demand, the biochemical of highest interest are currently 1,4 succinic acid its derivative 1,4 Butanediol, Butanol, Hydroxypropanoic acid and its derivative acrylic acid, Maleic acid and tetrahydrofuran (THF). These chemical are essentially drop in chemical that can replace fossil derived chemicals and their profitable production is hinged on the availability of low cost sugars. An IFBR that can successfully develop supply chain partnership with the chemical industry will benefit from these increasing demands. Other IFBRs can still focus on other speciality product segment with projected increase in demand at about 46% between 2014 and 2017 [178].

In summary, a product selection strategy must be developed for each mill and must take into account the market analysis in addition to the technical challenges of productions. IFBR's should produce widely varying products based on their individual business case and the product should be profitable in the absence of subsidies or carbon credits on the long run. It is also important to select a product that is derived from both the hexose and pentose fraction in order to derive maximum value from the hemicelluloses stream. It should be taken into consideration that the co-products could become the main product of the IFBR and cellulose derived products would be needed in the event of pulp production demand decline,

8.5 Biorefinery Clusters

The development of integrated biorefinery would involve capital investment and risks because the biorefining processes are not typical for a pulp and paper mill. The risks and capital investment could be lowered by means of clusters. An industrial cluster refers to the geographical concentration of industries that cooperate with each other to boost growth, competitiveness and performance advantages as a result of their co-location [179].

Some of the benefits of a cluster could include the availability of skilled workers, proximity to training institutions, power and heat generation, market accessibility for final products and established feedstock supply chains. Examples of clusters in the forest sector include the establishment of sawmills close to sites of lumbering activities and cellulosic crop biorefineries in proximity to farms where agricultural residues can be obtained. Some of the potential clusters for the valorization of hemicelluloses prehydrolysate that can be developed can be classified into 3 groups:

- Development of clusters with other pulp mills
- Integration with chemical plants
- Integration with local communities

8.5.1 Development of clusters with other pulp mills

An integrated biorefinery is easier to develop than a standalone biorefinery because it can share resources that are already available on site and this can lead to significant cost reduction.

Nevertheless, some challenges still exist for the development of an IFBR. Specifically, new process operations which are not typical for the pulp and paper industry will have to be installed and operated while capital investment must also be sourced. In the Canadian context, the current scarcity of capital has been identified as a key obstacle for the development of biorefineries by Näyhä et al. [180]. A cluster concept involving several pulp mills is a means to facilitate sourcing for capital investment, lower the risk exposure and to benefit from a larger production scale. A cluster will consist of 2 or more mills having a prehydrolysis stage for the extraction of hemicelluloses. A centralised mill will serve as the base of the cluster where concentrated hemicelluloses prehydrolysate from the satellite mills will be treated and transformed into value added products as shown in Figure 8–6.

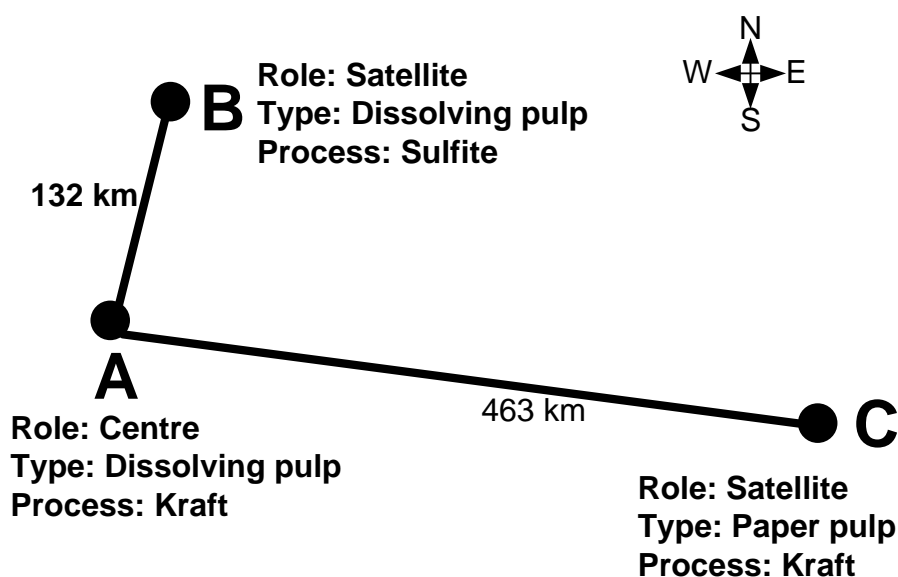


Figure 8–6: Schematic of a biorefinery cluster

Several conditions must be met in order to establish a profitable biorefinery cluster with hemicelluloses extraction and conversion. A cost effective concentration of the prehydrolysate streams at the satellite mills must be achieved. The satellite mills must be energy sufficient and in addition, the cluster base must be able to supply energy for the transformation process. The transportation cost must also be as low as possible. The maximum tolerable distance between the mills must be determined. A previous study showed that for a prehydrolysate with a volume reduction of 80% prior to transportation, the recommended maximum distance between a satellite mill and a receptor mill should be less than 150 km at a transportation cost of 0.2 \$/km when

furfural with a selling price of about 1650 \$/t is produced [181]. The choice of product for a cluster must be mutually acceptable to cluster participants as the ratio of pentoses to hexoses might vary for the mills involved. The proposed cluster concept is based on the premise that pulp mills in proximity to other mills will be willing to collaborate. Another study however recommended that the cluster should be owned by a sole company to avoid extensive negotiations, have a simple supply chain logistics and lower investor risks [182, 183].

8.5.2 Integration with chemical complexes

The production and utilization of drop in chemicals will require the integration of biorefineries with chemical plants or industrial complexes for further processing. Considering the Canadian context, there is great variability in the geographical distribution of chemical companies. As shown in Figure 8–7, most of the manufacturing and production of formulated products, pharmaceuticals and specialty are located in Ontario and Quebec while the production of oil and gas, agricultural chemicals and bulk chemicals is concentrated in Alberta. The main large chemical plant complexes in Canada are the Sarnia chemical valley in Ontario, the Lacombe County and Fort Saskatchewan complexes both in Alberta. This knowledge should guide hemicelluloses IFBR product selection. Producing biobased chemicals as substitutes for established petroleum based products in the Alberta region could be challenging due to the abundance low cost petrochemical feedstock. Product selection strategies should therefore focus on chemicals that are scarce, not easily derived from fossil resources, niche products or those for which there is a proven shift of demand by the consumers for bio derived alternatives. The production of biochemicals in the other regions could be more flexible in locations with less access to low priced petrochemical feedstock.

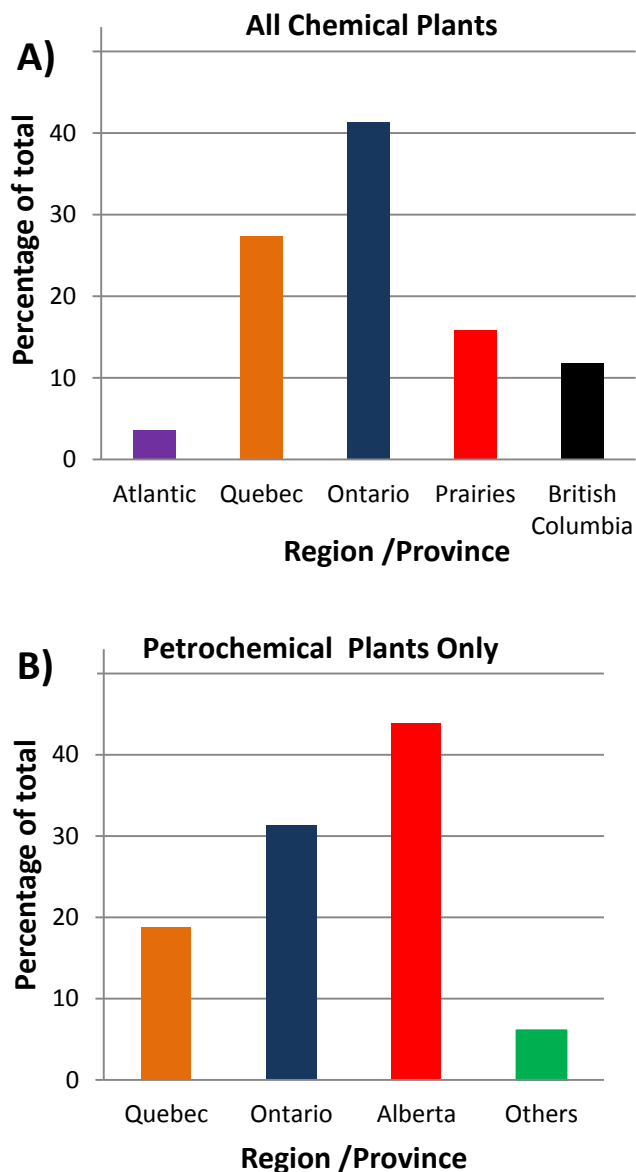


Figure 8–7: Regional distributions of A) Chemical products plants B) petrochemical plants [184]

The transportation of biobased chemicals is also an important factor for integration. Pipelines are existing infrastructure for transportation of large volumes and they can be also used for the transportation of biochemicals, biofuels or other bioproducts. Most of the natural gas and crude oil produced in Canada are currently distributed by pipelines within Canada and to the United States. It could be necessary to utilize pipelines for transportation over long distances due to the size of Canada during the transition to a bioeconomy in which a wide spectrum of products including biofuels would be derived from biomass. The density of existing pipelines however

varies by region in Canada as shown in Table 8.4. This should be taken into consideration because about 50% of the total pipeline infrastructure (115,000 km) is situated in Alberta [185] whereas other provinces like Quebec have less than 1% (912 km of pipeline for natural gas transport and 354 km for liquids).

Table 8.4: Pipeline length in kilometers for some provinces in Canada [185]

Provinces	Pipelines Distances (km)		
	Natural Gas	Liquids	Total
British Columbia	6,485	2,917	9,402
Alberta	34,997	20,746	55,743
Saskatchewan	19,043	7,753	26,796
Manitoba	2,472	2,787	5,259
Ontario	12,821	2,080	14,901
Quebec	912	354	1,266
New Brunswick	597		597
Nova Scotia	422		422
Northwest Territories		751	751
Total	77,749	37,388	115,137

Ultimately, transitioning towards a bioeconomy would require safe, reliable and cost effective means for distributing bioproducts, biochemicals and/or biofuels across cities, terminals or for local distribution. Construction of pipelines could be necessary in the future if existing infrastructure cannot be utilized or if biorefineries are situated at locations without access to existing pipelines.

8.5.3 Integration with local communities / development of eco-industrial complexes

Collaboration between pulping mills and host communities can help to maintain employments and create new jobs. An eco-industrial park can be defined as “a community of businesses that

collaborate with each other and with the local community to efficiently share resources (information, materials, water, energy, infrastructure and natural habitat), leading to economic gains, environmental sustainability and equitable enhancement of human resources for the businesses and the local community” [186]. Pulp and paper mills are typically located in rural communities. The development of biorefineries in rural communities could be a means of revitalizing the local economy: It could lead to jobs creation, reduce emigration and create economic activity [187]. All stakeholders (the receptor Kraft mill, municipal and provincial governments, concerned citizens and educational institutions) in the locality should be involved from the conceptual phase of the cluster development. Biorefinery development strategy must be defined jointly by stakeholders as a function of infrastructure requirements, transportation modes, market opportunities, skilled manpower requirements and synergy with other businesses must be identified. The product selection criteria should be based on local demand, feedstock composition and the socio-economic benefits for the community. The environmental benefits can be maximized by developing a flexible process for transforming various feedstock that are available locally into a wide spectrum of products that can be supplied locally, distributed and sold. Such community based projects can bring government support and the growth of local research clusters that could evolve into centres for innovation.

8.6 Practical guidelines for implementation of an IFBR

The implementation of integrated forest biorefineries is a challenging task that requires a multidisciplinary approach. In most cases, new innovative processes must be developed or adapted. These should lead to products for which a market exist or is emerging and should be economically viable and lead to sustainable social and environmental benefits as illustrated in Figure 8–8. To develop a technical and economically feasible hemicelluloses IFBR, it is important to fulfill the following requirements: determine a prehydrolysis method that produces a recoverable hemicelluloses sugars stream, ensure that the modifications to the receptor pulp mill does not reduce the pulp yield or quality, identify bioproducts or biochemicals that will be most profitable, develop strategies for reducing the energy requirement for the IFBR complex and implement biorefinery clusters where applicable.



Figure 8–8: Requirement for a successful IFBR implementation

Practical strategies for a successful implementation of IFBRs inspired by the previous studies, past and ongoing research, proposed processes and authors experience include:

- 1 Receptor Kraft pulp mills should proactively pursue diversification by biorefinery implementation
- 2 The context must be well defined and reflect the strengths and weaknesses of the receptor mill
- 3 Target products or at least the conversion pathways (bio or chemical) must be identified at an early stage
- 4 Value of new products must be equal or greater than that of pulp
- 5 Practice reverse engineering, let target product influence required modifications to the receptor mill
- 6 High energy efficiency must be achieved through optimization, upgrade and use of other renewable sources
- 7 The potential for energy, material and chemicals integration with the receptor mill must be determined and feasible for any developed process
- 8 Biorefinery clusters should be created where applicable and partnerships should be facilitated
- 9 A phased transition should be used where necessary to lower the risks

- 10 Social, economic and environmental sustainability must be determined
- 11 Continuous research must be carried out on all aspects of the value chain (feedstock to utilization)
- 12 Development efforts should promote short gestation period between laboratory research and commercialization

8.7 Conclusions and implications

Hemicelluloses from Kraft pulp mills are promising feedstock for the production of value added bioproducts, biofuels or biochemicals and the diversification of revenues for Kraft pulp mills. However, knowledge on the commercialization of integrated biorefineries is presently limited. Successful development of hemicelluloses based biorefineries requires that a significant proportion of current research lead to scientific and technological breakthroughs. Furthermore, product selection, potential market assessment and the socio-economic aspects must be considered at an early stage. An analysis of the modifications required to potential receptor Kraft mills, product selection and collaborations to lower cost and enhance sustainability was carried out and the results have been used to develop practical guidelines for the implementation of integrated forest biorefineries for the transformation of hemicelluloses.

CHAPTER 9. GENERAL DISCUSSION

A discussion of the main results of this thesis and their application has been presented as an article entitled “Hemicelluloses based integrated forest biorefineries: implementation strategies” in chapter 8.

This chapter covers the aspects that were not discussed in chapter 8 but are pertinent to synthesis of the results and knowledge generated in this thesis. Two conversion pathways were studied, a chemical pathway for furfural production and a biochemical pathway for ethanol production.

Preliminary tests using model prehydrolysate solutions with different amounts of sugars, furfural, acetic acid and syringaldehyde were used to establish the feasibility of applying reverse osmosis membrane filtration in hemicellulosic biorefineries. It was demonstrated that the composition of the prehydrolysate and the cross flow velocity had less effect on the permeate flux than the feed temperature and pressure, a flux decline was observed in all cases. The mechanisms that led to flux decline were identified to be osmotic pressure increase due to the sugars, concentration polarization by syringaldehyde and fouling by furfural. Cleaning of fouled membranes using sodium hydroxide was shown to be effective. Based on these results, it was concluded that the use of organic membranes is technically feasible for concentrating hemicelluloses prehydrolysate. It also led to the conclusion that despite the high sugar recovery observed, the permeate flux produced by a reverse osmosis would be too low and lead to an economically infeasible membrane application. The use of nanofiltration membranes was proposed to redress this drawback.

In the second phase, prehydrolysate solutions generated from a wood furnish similar to a reference mill were used in experiments. The main components of the solution were sugars (21 g/L), phenol (4.7 g/L), acetic acid (3.8 g/L), furfural (0.7 g/L) and hydroxymethylfurfural (0.09 g/L). A comparison of six organic membranes with molecular cut off weights between 100 and 500 Da was made and a membrane suitable for concentration of prehydrolysate in a furfural biorefinery process was selected. The selection criteria were high sugar retention and requirements for industrial application (low energy consumption and degree of fouling). It was shown that increasing the total sugars concentration from 21 to 103 g/L was possible and 99% of the sugars could be recovered. A response surface modeling approach was developed and used to determine the operating conditions that would minimize flux decline during concentration. The

results and modeling approach can be applied to other biorefinery processes with a chemical conversion of the sugars.

The membrane screening step in the second phase also led to the identification of membranes that could be used for the removal of fermentation inhibitors from the prehydrolysate solution. Most of the inhibitors (furfural, hydroxymethylfurfural, acetic acid), except the phenolic compounds, can be removed by nanofiltration. To identify a complementary detoxification step for the elimination of the phenolics, the use of activated carbon and flocculation with ferric sulfate, chitin or alum as coagulant were evaluated experimentally. Ferric sulfate was shown to have the highest ratio of phenol removal relative to sugar recovery. The optimum coagulant dosage and pH for flocculation were determined using a jar test apparatus. A novel detoxification strategy was developed by combining nanofiltration and flocculation.

The prehydrolysate composition, capacity of the receptor mill and data from the experiments were used as the basis for computer based simulations. Process models were developed for the production of furfural and ethanol. The energy consumption of the processes was minimized by the design of optimized heat exchanger networks and the implementation of an absorption heat pump in the distillation columns. The thermal energy requirement of the furfural process is higher than that of ethanol process. In both cases, the energy and material integration of the biorefinery processes can be supplied by the receptor mill. The implementation of the furfural process is feasible within a short term while further research could be necessary to enhance the feasibility of the ethanol process.

In the last phase, an analysis of possible modifications that can be made to conventional Kraft and dissolving pulp mills was made. The merits of two alternative approaches for product selection were examined. In addition, the potential influence of the receptor mill location on the product choice was identified. The development of biorefinery clusters as a means of lowering risks and investment capital requirement was investigated. The results have been used to propose practical guidelines that can be utilized for hemicelluloses biorefinery development.

CHAPTER 10. CONCLUSIONS, CONTRIBUTIONS AND RECOMMENDATIONS

10.1 Conclusions

The main objective of this thesis was achieved. Novel hemicelluloses biorefinery processes for furfural and ethanol production have been developed and integrated into an existing Kraft dissolving pulp mills.

The use of nanofiltration membranes was experimentally established as a feasible method for prehydrolysate concentration in the novel furfural biorefinery; the results suggest that it can be successfully scaled up. The use of membrane filtration resulted in a reduction of the energy requirement and the size of subsequent process equipments. The furfural process has a thermal energy requirement that is 69 % lower than that of existing furfural production processes. The energy, material and chemical requirements of the biorefinery can be supplied by the receptor mill. The process is also economically feasible at a low furfural selling price.

In the case of the ethanol biorefinery, membrane concentration has been tested for concentration and partial detoxification. It was successfully used to remove most of the fermentation inhibitors, except the phenolic compounds. To eliminate the phenolic compounds, the use of flocculation with ferric sulfate as a coagulant was shown to be a suitable secondary detoxification method. A detoxification strategy was developed by combining nanofiltration with flocculation. The method can be applied to biorefineries involving a biochemical conversion of sugars. The integration of the ethanol process with the receptor mill is feasible.

Guideline for the implementation of hemicelluloses biorefineries into Kraft pulp mills have been proposed based on the results.

10.2 Original contributions

The main findings of this thesis are summarized as follows:

- A stepwise approach was developed to identify the flux decline mechanisms caused by the main compounds present in a prehydrolysate solution. The presence of furfural leads to membrane fouling while the presence of syringaldehyde leads to concentration

polarization. The approach can be used to determine the causes of deteriorating performance for other solutions or membrane systems.

- A response surface model correlating the membrane operating condition and flux decline during prehydrolysate concentration was developed and successfully applied to minimize the decline.
- A novel prehydrolysate detoxification strategy that combines nanofiltration membranes and flocculation with ferric sulfate was developed. It can be successfully applied to biochemical conversion pathways such as ethanol fermentation.
- A novel furfural process that achieves high thermal energy efficiency by means of an optimized heat exchanger network design and the implementation of absorption heat pumps was developed.
- Practical guidelines that would lead to technologically and economically feasible hemicelluloses biorefineries have been developed.

10.3 Recommendations

This thesis left many topics open, it is recommended that future research covers:

- 1 Development of prehydrolysis methods that would be compatible with the receptor mill and not lead to the formation of inhibitors
- 2 Identification of the main mechanisms that govern the retention of each prehydrolysate component during concentration
- 3 The identification and development of solid catalysts for furfural formation
- 4 Fermentation tests to validate the limits of the developed detoxification strategy with different microorganisms
- 5 The use of biological methods (enzymes) for the removal of inhibitors present in the prehydrolysate
- 6 Development of a product selection methodology that takes the demands of the chemical industry into consideration

REFERENCES

- [1] L. Christopher, *Integrated forest biorefineries*: Royal Society of Chemistry, 2012.
- [2] E. Mateos-Espejel, T. Radiotis, and N. Jemaa, "Implications of converting a kraft pulp mill to a dissolving pulp operation with a hemicellulose extraction stage," *Tappi Journal*, vol. 12, pp. 29-38, 2013.
- [3] H. Sixta, "Chemical Pulping Processes," in *Handbook of Pulp*, ed: Wiley-VCH Verlag GmbH, 2008, pp. 229-365.
- [4] G. A. Smook, *Handbook for Pulp & Paper Technologists*, Third Edition ed. Vancouver: Angus Wilde Publications, 2002.
- [5] M. Marinova, E. Mateos-Espejel, N. Jemaa, and J. Paris, "Addressing the increased energy demand of a Kraft mill biorefinery: The hemicellulose extraction case," *Chemical Engineering Research and Design*, vol. 87, pp. 1269-1275, 2009.
- [6] L. Kang, Y. Y. Lee, S.-H. Yoon, A. J. Smith, and G. A. Krishnagopalan, "Ethanol production from the mixture of hemicellulose prehydrolysate and paper sludge," *BioResources*, vol. 7, pp. 3607-3626, 2012.
- [7] M. F. Demirbas, M. Balat, and H. Balat, "Potential contribution of biomass to the sustainable energy development," *Energy Conversion and Management*, vol. 50, pp. 1746-1760, 2009.
- [8] B. E. Dale and S. Kim, *Biomass Refining Global Impact—The Biobased Economy of the 21st Century*: Wiley-VCH Verlag GmbH, 2008.
- [9] C. J. Biermann and C. Biermann, *Handbook of pulping and papermaking* vol. 2: Academic press, 1996.
- [10] M. Ek, G. Gellerstedt, and G. Henriksson, *Wood Chemistry and Wood Biotechnology*: De Gruyter, 2009.
- [11] R. B. Santos, P. Hart, H. Jameel, and H.-m. Chang, "Wood based lignin reactions important to the biorefinery and pulp and paper industries," *BioResources*, vol. 8, pp. 1456-1477, 2013.
- [12] G. Gellerstedt, A. Majtnerova, and L. Zhang, "Towards a new concept of lignin condensation in kraft pulping. Initial results," *Comptes Rendus Biologies*, vol. 327, pp. 817-826, 2004.
- [13] H. Mao, J. M. Genco, S. H. Yoon, A. van Heiningen, and H. Pendse, "Technical Economic Evaluation of a Hardwood Biorefinery Using the "Near-Neutral" Hemicellulose Pre-Extraction Process," *Journal of Biobased Materials and Bioenergy*, vol. 2, pp. 177-185, // 2008.
- [14] M. Iakovlev and A. van Heiningen, "Efficient Fractionation of Spruce by SO₂-Ethanol-Water Treatment: Closed Mass Balances for Carbohydrates and Sulfur," *ChemSusChem*, vol. 5, pp. 1625-1637, 2012.

- [15] M. S. Tunc, J. Chheda, E. van der Heide, J. Morris, and A. van Heiningen, "Pretreatment of hardwood chips via autohydrolysis supported by acetic and formic acid," *Holzforschung*, vol. 68, pp. 401-409, 2014.
- [16] D. Ibarra, V. Köpcke, and M. Ek, "Behavior of different monocomponent endoglucanases on the accessibility and reactivity of dissolving-grade pulps for viscose process," *Enzyme and Microbial Technology*, vol. 47, pp. 355-362, 2010.
- [17] Sateri International. (2014, 31.07.2014). *Dissolving wood pulp and end-use applications*. Available: <http://www.sateri.com/module/13/4/en/end-uses>
- [18] B. Lonnberg, "Industrial Cellulose," in *Regenerated cellulose fibres*, ed: Woodhead Publishing, 2001.
- [19] AGRA Simons, NLK Consultants, and Sandwell Inc, *Water use reduction in the pulp and paper industry*: Paprican, 2001.
- [20] J. Gullichsen and C. J. Fogelholm, *Chemical pulping*: Fapet Oy, 1999.
- [21] U. Wising, T. Berntsson, and P. Stuart, "The potential for energy savings when reducing the water consumption in a Kraft Pulp Mill," *Applied Thermal Engineering*, vol. 25, pp. 1057-1066, 2005.
- [22] AGRA Simons Limited, "A guide to energy savings opportunities in the Kraft pulp industry," Vancouver2005.
- [23] E. Mateos-Espejel, L. Savulescu, F. Maréchal, and J. Paris, "Base case process development for energy efficiency improvement, application to a Kraft pulping mill. Part II: Benchmarking analysis," *Chemical Engineering Research and Design*, vol. In Press, Corrected Proof.
- [24] I. C. Kemp, "Pinch analysis and process integration," *A user guide on process integration for the efficient use of energy*, 2007.
- [25] D. Koufos and T. Retsina, "Practical energy and water management through pinch analysis for the pulp and paper industry," 2001, pp. 327-332.
- [26] C. Bengtsson, R. Nordman, and T. Berntsson, "Utilization of excess heat in the pulp and paper industry--a case study of technical and economic opportunities," *Applied Thermal Engineering*, vol. 22, pp. 1069-1081, 2002.
- [27] J. I. Manassaldi, S. F. Mussati, and N. J. Scenna, "Optimal synthesis and design of Heat Recovery Steam Generation (HRSG) via mathematical programming," *Energy*, vol. 36, pp. 475-485, 2011.
- [28] T. Rafione, M. Marinova, L. Montastruc, S. Domenech, B. Srinivasan, and J. Paris, "Optimization of Water and Energy Consumption in an Integrated Forest Biorefinery," *Journal of science and technology for forest products and processes*, vol. 2, pp. 54-59, 2012.
- [29] D. C. Y. Foo, "State-of-the-Art Review of Pinch Analysis Techniques for Water Network Synthesis," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 5125-5159, 2009.

- [30] L. Savulescu, J. K. Kim, and R. Smith, "Studies on simultaneous energy and water minimisation--Part I: Systems with no water re-use," *Chemical Engineering Science*, vol. 60, pp. 3279-3290, 2005.
- [31] E. Mateos-Espejel, M. Marinova, S. Bararpour, and J. Paris, "Energy Implications of Water Reduction Strategies in Kraft Process. Part II: Results," *PAPTAC 94th Ann. Mtg., Montreal, Canada*, 2008.
- [32] US DOE (Department of Energy), "Industrial heat pumps for steam and fuel savings," 2009.
- [33] A. Costa, B. Bakhtiari, S. Schuster, and J. Paris, "Integration of absorption heat pumps in a Kraft pulp process for enhanced energy efficiency," *Energy*, vol. 34, pp. 254-260, 2009.
- [34] B. Bakhtiari, L. Fradette, R. Legros, and J. Paris, "Retrofit of absorption heat pumps into manufacturing processes: Implementation guidelines," *The Canadian Journal of Chemical Engineering*, vol. 88, pp. 839-848, 2010.
- [35] C. J. Biermann, "Pulping Fundamentals," in *Handbook of Pulping and Papermaking (Second Edition)*, ed San Diego: Academic Press, 1996, pp. 55-100.
- [36] RISI. (2013, 01.08.2014). *2013 Outlook for the global dissolving pulp market*. Available: <http://www.risiinfo.com/risi-store/do/product/detail/2013-outlook-for-global-dissolving-pulp-market.html?source=PA1305SFRH>
- [37] Y. Jin, H. Jameel, H. Chang, and R. Phillips, "Green Liquor Pretreatment of Mixed Hardwood for Ethanol Production in a Repurposed Kraft Pulp Mill," *Journal of Wood Chemistry and Technology*, vol. 30, pp. 86-104, 2010.
- [38] R. Fornell and T. Berntsson, "Process integration study of a kraft pulp mill converted to an ethanol production plant – Part A: Potential for heat integration of thermal separation units," *Applied Thermal Engineering*, vol. 35, pp. 81-90, 2012.
- [39] R. Fornell, T. Berntsson, and A. Åsblad, "Process integration study of a kraft pulp mill converted to an ethanol production plant – part B: Techno-economic analysis," *Applied Thermal Engineering*, vol. 42, pp. 179-190, 2012.
- [40] E. Connor, "The integrated forest biorefinery: The pathway to our bio-future and the range of product possibilities," in *Engineering, Pulping and Environmental Conference 2007, TAPPI, October 21, 2007 - October 24, 2007*, Jacksonville, FL, United states, 2007, pp. 993-1019.
- [41] V. Chambost, J. McNutt, and P. R. Stuart, "Guided tour: Implementing the forest biorefinery (fbr) at existing pulp and paper mills," in *Engineering, Pulping and Environmental Conference 2008, TAPPI, August 24, 2008 - August 27, 2008*, Portland, OR, United states, 2008, pp. 2710-2721.
- [42] G. Closset, D. Raymond, and B. Thorp, "The Integrated Forest Products Biorefinery," IEA Bioenergy2005.
- [43] P. Söderholm and R. Lundmark, "Forest-based Biorefineries," *Forest Products Journal*, vol. 59, p. 7, 2009.

- [44] B. A. Thorp, B. A. Thorp Iv, and L. D. Murdock-Thorp, "Compelling case for integrated biorefineries," in *Paper Conference and Trade Show, PaperCon '08, May 4, 2008 - May 7, 2008*, Dallas, TX, United states, 2008, pp. 884-898.
- [45] E. Hytönen and P. Stuart, "Integrating Bioethanol Production into an Integrated Kraft Pulp and Paper Mill: Techno-Economic Assessment," *Pulp & Paper Canada*, vol. 110, p. 25, 2009.
- [46] M. Moshkelani, M. Marinova, M. Perrier, and J. Paris, "The forest biorefinery and its implementation in the pulp and paper industry: Energy overview," *Applied Thermal Engineering*, vol. 50, pp. 1427-1436, 2013.
- [47] S. Consonni, R. E. Katofsky, and E. D. Larson, "A gasification-based biorefinery for the pulp and paper industry," *Chemical Engineering Research and Design*, vol. 87, pp. 1293-1317, 2009.
- [48] M. Naqvi, J. Yan, and E. Dahlquist, "Black liquor gasification integrated in pulp and paper mills: A critical review," *Bioresource Technology*, vol. 101, pp. 8001-8015, 2010.
- [49] K. Pettersson and S. Harvey, "Comparison of black liquor gasification with other pulping biorefinery concepts – Systems analysis of economic performance and CO₂ emissions," *Energy*, vol. 37, pp. 136-153, 1// 2012.
- [50] L. Lin and M. Strand, "Investigation of the intrinsic CO₂ gasification kinetics of biomass char at medium to high temperatures," *Applied Energy*, vol. 109, pp. 220-228, 9// 2013.
- [51] C. Laaksometsä, E. Axelsson, T. Berntsson, and A. Lundström, "Energy savings combined with lignin extraction for production increase: case study at a eucalyptus mill in Portugal," *Clean Technologies and Environmental Policy*, vol. 11, pp. 77-82, 2009.
- [52] L. Kouisni, P. Holt-Hindle, K. Maki, and M. Paleologou, "The LignoForce system™: a new process for the production of high quality lignin from black liquor," *Journal of science and technology for forest products and processes*, vol. 2, pp. 6-10, 2012.
- [53] M. Kannangara, M. Marinova, L. Fradette, and J. Paris, "Lignin recovery by acid precipitation in a Kraft mill: an energy perspective," *Journal of science and technology for forest products and processes*, vol. 2, pp. 28-32, 2012.
- [54] R. Sun, X. F. Sun, and J. Tomkinson, "Hemicelluloses and Their Derivatives," in *Hemicelluloses: Science and Technology*, ed Washington, DC: American Chemical Society, 2003, pp. 2-22.
- [55] A. K. Chandel, F. A. Antunes, P. V. de Arruda, T. S. Milessi, S. S. da Silva, and M. d. G. de Almeida Felipe, "Dilute Acid Hydrolysis of Agro-Residues for the Depolymerization of Hemicellulose: State-of-the-Art," in *D-Xylitol*, ed: Springer, 2012, pp. 39-61.
- [56] D. Klemm, B. Heublein, H.-P. Fink, and A. Bohn, "Cellulose: Fascinating Biopolymer and Sustainable Raw Material," *Angewandte Chemie International Edition*, vol. 44, pp. 3358-3393, 2005.
- [57] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, and D. B. Levin, "Biomass pretreatment: Fundamentals toward application," *Biotechnology Advances*, vol. 29, pp. 675-685, 11// 2011.

- [58] M. Stöcker, "Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials," *Angewandte Chemie International Edition*, vol. 47, pp. 9200-9211, 2008.
- [59] B. Kamm, M. Kamm, M. Schmidt, T. Hirth, and M. Schulze, "Lignocellulose-based Chemical Products and Product Family Trees," in *Biorefineries-Industrial Processes and Products*, ed: Wiley-VCH Verlag GmbH, 2008, pp. 97-149.
- [60] A. Conner and L. Lorenz, "Kinetic modelling of hardwood prehydrolysis. Part III: Water and dilute acetic acid of southern red oak prehydrolysis," *Wood Fiber Sci*, vol. 18, pp. 248-263, 1986.
- [61] N. Sun, H. Rodriguez, M. Rahman, and R. D. Rogers, "Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass?," *Chemical Communications*, vol. 47, pp. 1405-1421, 2011.
- [62] A. Hiden, A. Kawashima, T. Endo, K. Honda, and M. Morita, "Ethanol-based organosolv treatment with trace hydrochloric acid improves the enzymatic digestibility of Japanese cypress (*Chamaecyparis obtusa*) by exposing nanofibers on the surface," *Bioresource Technology*, vol. 132, pp. 64-70, 3// 2013.
- [63] P. Pienkos and M. Zhang, "Role of pretreatment and conditioning processes on toxicity of lignocellulosic biomass hydrolysates," *Cellulose*, vol. 16, pp. 743-762, 2009.
- [64] P. Kumar, D. M. Barrett, M. J. Delwiche, and P. Stroeve, "Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 3713-3729, 2009.
- [65] P. Alvira, E. Tomás-Pejó, M. Ballesteros, and M. J. Negro, "Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review," *Bioresource Technology*, vol. 101, pp. 4851-4861, 2010.
- [66] E. Springer and J. Harris, "Prehydrolysis of aspenwood with water and with dilute aqueous sulfuric acid," *Svensk. Papperstidn*, vol. 85, pp. 152-154, 1982.
- [67] R. Kenealy William, J. Houtman Carl, J. Laplaza, W. Jeffries Thomas, and G. Horn Eric, "Pretreatments for Converting Wood into Paper and Chemicals," in *Materials, Chemicals, and Energy from Forest Biomass*, ed Washington, DC: American Chemical Society, 2007, pp. 392-408.
- [68] W. W. Al-Dajani and U. W. Tschirner, "Pre-extraction of hemicelluloses and subsequent kraft pulping Part I: Alkaline extraction," *Tappi Journal*, vol. 7, pp. 3-8, 2008.
- [69] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple, *et al.*, "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology*, vol. 96, pp. 673-686, 2005.
- [70] T. Radiotis, X. Zhang, M. Paice, and V. Byrne, "Optimizing Hardwood Prehydrolysis for Simultaneous Production of Bioproducts and Biomaterials," *Journal of Bioprocess Engineering and Biorefinery*, vol. 1, pp. 69-76, // 2012.
- [71] B.-H. Um and G. P. van Walsum, "Mass balance on green liquor pre-pulping extraction of northeast mixed hardwood," *Bioresource Technology*, vol. 101, pp. 5978-5987, 2010.

- [72] X. Pan and J. N. Saddler, "Effect of replacing polyol by organosolv and kraft lignin on the property and structure of rigid polyurethane foam," *Biotechnology for biofuels*, vol. 6, p. 12, 2013.
- [73] J. J. Bozell, S. K. Black, M. Myers, D. Cahill, W. P. Miller, and S. Park, "Solvent fractionation of renewable woody feedstocks: Organosolv generation of biorefinery process streams for the production of biobased chemicals," *Biomass and Bioenergy*, vol. 35, pp. 4197-4208, 10/15/ 2011.
- [74] X. Pan, J. F. Kadla, K. Ehara, N. Gilkes, and J. N. Saddler, "Organosolv ethanol lignin from hybrid poplar as a radical scavenger: relationship between lignin structure, extraction conditions, and antioxidant activity," *Journal of agricultural and food chemistry*, vol. 54, pp. 5806-5813, 2006.
- [75] A. Van Heiningen, "Converting a kraft pulp mill into an integrated forest biorefinery," *Pulp and Paper Canada*, vol. 107, pp. 38-43, 2006.
- [76] W. W. Al-Dajani and U. W. Tschirner, "Pre-extraction of hemicelluloses and subsequent kraft pulping Part I: Alkaline extraction," *Tappi Journal*, vol. 7, pp. 3-8, 2008.
- [77] J. Helmerius, J. V. von Walter, U. Rova, K. A. Berglund, and D. B. Hodge, "Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties," *Bioresource Technology*, vol. 101, pp. 5996-6005, 2010.
- [78] G. V. Duarte, B. V. Ramarao, T. E. Amidon, and P. T. Ferreira, "Effect of hot water extraction on hardwood kraft pulp fibers (Acer saccharum, sugar maple)," *Industrial & Engineering Chemistry Research*, vol. 50, pp. 9949-9959, 2011.
- [79] J. Johakimu and J. Andrew, "Hemicellulose Extraction from South African Eucalyptus grandis using Green Liquor and its Impact on Kraft Pulping Efficiency and Paper Making Properties," *BioResources*, vol. 8, pp. 3490-3504, 2013.
- [80] O. Ajao, M. Rahni, M. Marinova, H. Chadjaa, and O. Savadogo, "Hemicelluloses prehydrolysate concentration by nanomembrane filtration: Feasibility and effect of operating conditions," presented at the 5th Nordic Wood Biorefinery Conference, Stockholm, Sweden, 2014.
- [81] S. Gul and M. Harasek, "Energy saving in sugar manufacturing through the integration of environmental friendly new membrane processes for thin juice pre-concentration," *Applied Thermal Engineering*, vol. 43, pp. 128-133, 2012.
- [82] I. Egüés, C. Sanchez, I. Mondragon, and J. Labidi, "Separation and Purification of Hemicellulose by Ultrafiltration," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 523-530, 2011.
- [83] Y.-L. Lin and C.-H. Lee, "Elucidating the Rejection Mechanisms of PPCPs by Nanofiltration and Reverse Osmosis Membranes," *Industrial & Engineering Chemistry Research*, vol. 53, pp. 6798-6806, 2014/04/23 2014.
- [84] Y. Li, Y. Su, X. Zhao, R. Zhang, J. Zhao, X. Fan, *et al.*, "Surface fluorination of polyamide nanofiltration membrane for enhanced antifouling property," *Journal of Membrane Science*, vol. 455, pp. 15-23, 4/1/ 2014.

- [85] A. De Munari, A. J. C. Semiao, and B. Antizar-Ladislao, "Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter–pesticide complexation and solute–membrane interactions," *Water Research*, vol. 47, pp. 3484-3496, 6/15/ 2013.
- [86] C. Bellona, J. E. Drewes, P. Xu, and G. Amy, "Factors affecting the rejection of organic solutes during NF/RO treatment—a literature review," *Water Research*, vol. 38, pp. 2795-2809, 7// 2004.
- [87] J. Cho, G. Amy, and J. Pellegrino, "Membrane filtration of natural organic matter: factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane," *Journal of Membrane Science*, vol. 164, pp. 89-110, 1/4/ 2000.
- [88] M. K. Purkait, P. K. Bhattacharya, and S. De, "Membrane filtration of leather plant effluent: Flux decline mechanism," *Journal of Membrane Science*, vol. 258, pp. 85-96, 8/1/ 2005.
- [89] S. Stade, M. Kallioinen, A. Mikkola, T. Tuuva, and M. Mänttari, "Reversible and irreversible compaction of ultrafiltration membranes," *Separation and Purification Technology*, vol. 118, pp. 127-134, 10/30/ 2013.
- [90] Y. A. Hussain, M. H. Al-Saleh, and S. S. Ar-Ratrout, "The effect of active layer non-uniformity on the flux and compaction of TFC membranes," *Desalination*, vol. 328, pp. 17-23, 11/1/ 2013.
- [91] K. D. Cobry, V. M. Bright, and A. R. Greenberg, "Integrated electrolytic sensors for monitoring of concentration polarization during nanofiltration," *Sensors and Actuators B: Chemical*, vol. 160, pp. 730-739, 12/15/ 2011.
- [92] B. Mareth, "A reverse osmosis treatment process for produced water: optimization, process control, and renewable energy application," Master's thesis, Texas A&M University, 2006.
- [93] W. Fang, R. Wang, S. Chou, L. Setiawan, and A. G. Fane, "Composite forward osmosis hollow fiber membranes: Integration of RO- and NF-like selective layers to enhance membrane properties of anti-scaling and anti-internal concentration polarization," *Journal of Membrane Science*, vol. 394–395, pp. 140-150, 3/15/ 2012.
- [94] A. Alhadidi, B. Blankert, A. J. B. Kemperman, J. C. Schippers, M. Wessling, and W. G. J. van der Meer, "Effect of testing conditions and filtration mechanisms on SDI," *Journal of Membrane Science*, vol. 381, pp. 142-151, 2011.
- [95] W. Guo, H.-H. Ngo, and J. Li, "A mini-review on membrane fouling," *Bioresource Technology*, vol. 122, pp. 27-34, 10// 2012.
- [96] A. Al-Amoudi and R. W. Lovitt, "Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency," *Journal of Membrane Science*, vol. 303, pp. 4-28, 10/15/ 2007.
- [97] W. S. Ang, S. Lee, and M. Elimelech, "Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes," *Journal of Membrane Science*, vol. 272, pp. 198-210, 3/15/ 2006.
- [98] G.-d. Kang and Y.-m. Cao, "Development of antifouling reverse osmosis membranes for water treatment: A review," *Water Research*, vol. 46, pp. 584-600, 3/1/ 2012.

- [99] J. Q. J. C. Verberk and J. C. van Dijk, "Air sparging in capillary nanofiltration," *Journal of Membrane Science*, vol. 284, pp. 339-351, 11/1/ 2006.
- [100] E. R. Cornelissen, J. S. Vrouwenvelder, S. G. J. Heijman, X. D. Viallefont, D. van der Kooij, and L. P. Wessels, "Air/water cleaning for biofouling control in spiral wound membrane elements," *Desalination*, vol. 204, pp. 145-147, 2/5/ 2007.
- [101] B. Van der Bruggen, M. Mänttari, and M. Nyström, "Drawbacks of applying nanofiltration and how to avoid them: A review," *Separation and Purification Technology*, vol. 63, pp. 251-263, 10/22/ 2008.
- [102] Y. Xiong and Y. Liu, "Biological control of microbial attachment: a promising alternative for mitigating membrane biofouling," *Applied microbiology and biotechnology*, vol. 86, pp. 825-837, 2010.
- [103] E. Palmqvist and B. Hahn-Hägerdal, "Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification," *Bioresource Technology*, vol. 74, pp. 17-24, 8// 2000.
- [104] C. Luo, D. L. Brink, and H. W. Blanch, "Identification of potential fermentation inhibitors in conversion of hybrid poplar hydrolyzate to ethanol," *Biomass and Bioenergy*, vol. 22, pp. 125-138, 2// 2002.
- [105] S. Larsson, E. Palmqvist, B. Hahn-Hägerdal, C. Tengborg, K. Stenberg, G. Zacchi, *et al.*, "The generation of fermentation inhibitors during dilute acid hydrolysis of softwood," *Enzyme and Microbial Technology*, vol. 24, pp. 151-159, 2// 1999.
- [106] W. Parawira and M. Tekere, "Biotechnological strategies to overcome inhibitors in lignocellulose hydrolysates for ethanol production: review," *Critical reviews in biotechnology*, vol. 31, pp. 20-31, 2011.
- [107] L. J. Jonsson, B. Alriksson, and N.-O. Nilvebrant, "Bioconversion of lignocellulose: inhibitors and detoxification," *Biotechnology for Biofuels*, vol. 6, p. 16, 2013.
- [108] T. Hasunuma and A. Kondo, "Development of yeast cell factories for consolidated bioprocessing of lignocellulose to bioethanol through cell surface engineering," *Biotechnology Advances*, vol. 30, pp. 1207-1218, 11// 2012.
- [109] M. Cantarella, L. Cantarella, A. Gallifuoco, A. Spera, and F. Alfani, "Effect of Inhibitors Released during Steam-Explosion Treatment of Poplar Wood on Subsequent Enzymatic Hydrolysis and SSF," *Biotechnology progress*, vol. 20, pp. 200-206, 2004.
- [110] F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques, and R. Bogel-Lukasik, "Hemicelluloses for fuel ethanol: A review," *Bioresource Technology*, vol. 101, pp. 4775-4800, 2010.
- [111] H. B. Klinke, A. B. Thomsen, and B. K. Ahring, "Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass," *Applied Microbiology and Biotechnology*, vol. 66, pp. 10-26, 2004/11/01 2004.
- [112] K. Rumbold, H. J. van Buijsen, K. M. Overkamp, J. W. van Groenestijn, P. J. Punt, and M. J. van der Werf, "Microbial production host selection for converting second-generation feedstocks into bioproducts," *Microb Cell Fact*, vol. 8, p. 64, 2009.
- [113] T. C. Ezeji, N. Qureshi, and H. P. Blaschek, "Acetone butanol ethanol (ABE) production from concentrated substrate: reduction in substrate inhibition by fed-batch technique and

- product inhibition by gas stripping," *Applied Microbiology and Biotechnology*, vol. 63, pp. 653-658, 2004/02/01 2004.
- [114] D. H. Cho, Y. J. Lee, Y. Um, B.-I. Sang, and Y. H. Kim, "Detoxification of model phenolic compounds in lignocellulosic hydrolysates with peroxidase for butanol production from *Clostridium beijerinckii*," *Applied Microbiology and Biotechnology*, vol. 83, pp. 1035-1043, 2009.
- [115] J. Sun, L. Fu, and S. Zhang, "A review of working fluids of absorption cycles," *Renewable and Sustainable Energy Reviews*, vol. 16, pp. 1899-1906, 2012.
- [116] D. Cho, S.-J. Shin, and Y. Kim, "Effects of acetic and formic acid on ABE production by *Clostridium acetobutylicum* and *Clostridium beijerinckii*," *Biotechnology and Bioprocess Engineering*, vol. 17, pp. 270-275, 2012/04/01 2012.
- [117] I. Boukari, M. O'Donohue, C. Rémond, and B. Chabbert, "Probing a family GH11 endo- β -1,4-xylanase inhibition mechanism by phenolic compounds: Role of functional phenolic groups," *Journal of Molecular Catalysis B: Enzymatic*, vol. 72, pp. 130-138, 11// 2011.
- [118] D. Morrison, J. S. van Dyk, and B. I. Pletschke, "The effect of alcohols, lignin and phenolic compounds on the enzyme activity of *Clostridium cellulovorans* XynA," *BioResources*, vol. 6, pp. 3132-3141, 2011.
- [119] F. Kaya, J. A. Heitmann, and T. W. Joyce, "Influence of lignin and its degradation products on enzymatic hydrolysis of xylan," *Journal of Biotechnology*, vol. 80, pp. 241-247, 7/14/ 2000.
- [120] T. P. Mpabanga, A. K. Chandel, S. S. da Silva, and O. V. Singh, "Detoxification Strategies Applied to Lignocellulosic Hydrolysates for Improved Xylitol Production," in *D-Xylitol*, ed: Springer, 2012, pp. 63-82.
- [121] L. Canilha, A. K. Chandel, T. Suzane dos Santos Milessi, F. A. F. Antunes, W. Luiz da Costa Freitas, M. das Graças Almeida Felipe, *et al.*, "Bioconversion of sugarcane biomass into ethanol: an overview about composition, pretreatment methods, detoxification of hydrolysates, enzymatic saccharification, and ethanol fermentation," *BioMed Research International*, vol. 2012, 2012.
- [122] S. I. Mussatto and I. C. Roberto, "Alternatives for detoxification of diluted-acid lignocellulosic hydrolyzates for use in fermentative processes: A review," *Bioresource Technology*, vol. 93, pp. 1-10, 2004.
- [123] W. Pan, J. A. Perrotta, A. J. Stipanovic, C. T. Nomura, and J. P. Nakas, "Production of polyhydroxyalkanoates by *Burkholderia cepacia* ATCC 17759 using a detoxified sugar maple hemicellulosic hydrolysate," *Journal of industrial microbiology & biotechnology*, vol. 39, pp. 459-469, 2012.
- [124] J. M. Lee, R. A. Venditti, H. Jameel, and W. R. Kenealy, "Detoxification of woody hydrolyzates with activated carbon for bioconversion to ethanol by the thermophilic anaerobic bacterium *Thermoanaerobacterium saccharolyticum*," *Biomass and Bioenergy*, vol. 35, pp. 626-636, 1// 2011.

- [125] A. K. Chandel, S. S. da Silva, and O. V. Singh, "Detoxification of lignocellulosic hydrolysates for improved bioethanol production," *Biofuel production-Recent developments and prospects*, pp. 225-246, 2011.
- [126] L. Canilha, J. B. de Almeida e Silva, and A. I. N. Solenzal, "Eucalyptus hydrolysate detoxification with activated charcoal adsorption or ion-exchange resins for xylitol production," *Process biochemistry*, vol. 39, pp. 1909-1912, 2004.
- [127] N.-O. Nilvebrant, A. Reimann, S. Larsson, and L. J. Jönsson, "Detoxification of lignocellulose hydrolysates with ion-exchange resins," *Applied biochemistry and biotechnology*, vol. 91, pp. 35-49, 2001.
- [128] I. S. Horváth, A. Sjöde, N.-O. Nilvebrant, A. Zagorodni, and L. J. Jönsson, "Selection of anion exchangers for detoxification of dilute-acid hydrolysates from spruce," *Applied biochemistry and biotechnology*, vol. 114, pp. 525-538, 2004.
- [129] J. P. A. Silva, L. M. Carneiro, and I. C. Roberto, "Treatment of rice straw hemicellulosic hydrolysates with advanced oxidative processes: a new and promising detoxification method to improve the bioconversion process," *Biotechnology for biofuels*, vol. 6, p. 23, 2013.
- [130] Z. Hou-Rui, Q. Xiang-Xiang, S. Silva, B. Sarrouh, C. Ai-Hua, Z. Yu-Heng, *et al.*, "Novel Isolates for Biological Detoxification of Lignocellulosic Hydrolysate," *Applied Biochemistry and Biotechnology*, vol. 152, pp. 199-212, 2009/02/01 2009.
- [131] L. J. Jönsson, E. Palmqvist, N. O. Nilvebrant, and B. Hahn-Hägerdal, "Detoxification of wood hydrolysates with laccase and peroxidase from the white-rot fungus *Trametes versicolor*," *Applied Microbiology and Biotechnology*, vol. 49, pp. 691-697, 1998/06/01 1998.
- [132] M. Marinova, E. Mateos-Espejel, and J. Paris, "From Kraft mill to forest biorefinery: An energy and water perspective. II. Case study," *Cellulose Chemistry and Technology*, vol. 44, pp. 21-26, 2010.
- [133] C. Wyman, *Handbook on bioethanol: production and utilization*: CRC press, 1996.
- [134] S. K. Picataggio and M. Zhang, "Biocatalyst development for bioethanol production from hydrolysates," in *Handbook on Bioethanol: Production and Utilization*, C. E. Wyman, Ed., ed Washington, DC: Taylor & Francis, 1996, pp. 163-178.
- [135] N. Bawa, "Improvement of Bioethanol Production using *Saccharomyces cerevisiae*," M.Sc, University of Saskatchewan, 2008.
- [136] T. Jeffries and N. Q. Shi, "Genetic engineering for improved xylose fermentation by yeasts," *Recent Progress in Bioconversion of Lignocellulosics*, pp. 117-161, 1999.
- [137] S.-J. Ha, J. M. Galazka, S. R. Kim, J.-H. Choi, X. Yang, J.-H. Seo, *et al.*, "Engineered *Saccharomyces cerevisiae* capable of simultaneous cellobiose and xylose fermentation," *Proceedings of the National Academy of Sciences*, vol. 108, pp. 504-509, 2011.
- [138] G. Marcotullio, "The chemistry and technology of furfural production in modern Lignocellulose-Feedstock biorefineries," Ph.D Thesis, Process and Energy Department, TU Delft, Delft, 2011.

- [139] W. De Jong and G. Marcotullio, "Overview of biorefineries based on co-production of furfural, existing concepts and novel developments," *International Journal of Chemical Reactor Engineering*, vol. 8, pp. 1–25, 2010.
- [140] M. Dashtban, A. Gilbert, and P. Fatehi, "Production of furfural: overview and challenges," *Journal of science and technology for forest products and processes*, vol. 2, pp. 44-53, 2012.
- [141] K. J. Zeitsch, *The Chemistry and Technology of Furfural and its Many By-Products*: Elsevier, 2000.
- [142] L. Montastruc, O. Ajao, M. Marinova, C. B. d. Carmo, and S. Domenech, "Hemicelluloses biorefinery for furfural production, energy requirement analysis and minimization," *Journal of Science and Technology for Forest Products and Processes*, vol. 1, pp. 48-52, 2012.
- [143] N. E. Sammons Jr, W. Yuan, M. R. Eden, B. Aksoy, and H. T. Cullinan, "Optimal biorefinery product allocation by combining process and economic modeling," *Chemical Engineering Research and Design*, vol. 86, pp. 800-808, 2008.
- [144] J. Moncada, L. G. Matallana, and C. A. Cardona, "Selection of process pathways for biorefinery design using optimization tools: A colombian case for conversion of sugarcane bagasse to ethanol, poly-3-hydroxybutyrate (PHB), and energy," *Industrial & Engineering Chemistry Research*, vol. 52, pp. 4132-4145, 2013.
- [145] H. Mao, "Technical evaluation of a hardwood biorefinery using the" near-neutral" hemicellulose extraction " M.Sc, The University of Maine, 2007.
- [146] M. Hamaguchi, J. Kautto, and E. Vakkilainen, "Effects of hemicellulose extraction on the kraft pulp mill operation and energy use: Review and case study with lignin removal," *Chemical Engineering Research and Design*, vol. 91, pp. 1284-1291, 2013.
- [147] C. Chirat, D. Lachenal, and M. Sanglard, "Extraction of xylans from hardwood chips prior to kraft cooking," *Process Biochemistry*, vol. 47, pp. 381-385, 2012.
- [148] C. V. T. Mendes, J. M. S. Rocha, G. D. A. Sousa, and M. G. V. S. Carvalho, "Extraction of Hemicelluloses Prior to Kraft Cooking: A Step for an Integrated Biorefinery in the Pulp Mill," *O PAPEL*, vol. 72, pp. 79-83, 2011.
- [149] J. Cohen, M. Janssen, V. Chambost, and P. Stuart, "Critical Analysis of Emerging Forest Biorefinery (FBR) Technologies for Ethanol Production," *Pulp and Paper Canada*, vol. 111, 2010.
- [150] C. M. Cai, T. Zhang, R. Kumar, and C. E. Wyman, "Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass," *Journal of Chemical Technology & Biotechnology*, pp. n/a-n/a, 2013.
- [151] S. Kürüm and Z. Fonyo, "Comparative study of recovering acetic acid with energy integrated schemes," *Applied Thermal Engineering*, vol. 16, pp. 487-495, 1996.
- [152] G. Yang, M. S. Jahan, L. Ahsan, L. Zheng, and Y. Ni, "Recovery of acetic acid from pre-hydrolysis liquor of hardwood kraft-based dissolving pulp production process by reactive extraction with triisooctylamine," *Bioresource Technology*, vol. 138, pp. 253-258, 2013.

- [153] DalinYebo Trading and Development (Pty) Ltd. (2014, 06.08.2014). *Furfural Market Prices (2014)*. Available: <http://www.dalinyebo.com/item/770-furfural-market-prices-2014>
- [154] USDA Market News. (2014, 06.08.2014). *Weekly Ethanol Summary*. Available: <http://www.ams.usda.gov/mnreports/lsdethanol.pdf>
- [155] G. Marcotullio, "Furfural production in modern lignocellulose-feedstock biorefineries Gianluca Marcotullio,," presented at the UN Economic Commission for Europe (UNECE) and the Food and Agriculture Organization (FAO) Workshop, St. Petersburg, Russia, 2013.
- [156] Renewable Fuels Association (RFA). (2014, 06.08.2014). *Ethanol industry statistics*. Available: <http://www.ethanolrfa.org/pages/statistics>
- [157] T. Browne, R. Gilsenan, D. Singbeil, and M. Paleologou, "Bio-energy and Bio-chemicals Synthesis Report," FPInnovations, Pointe-Claire 2011.
- [158] G. Schild, H. Sixta, and L. Testova, "Multifunctional alkaline pulping. Delignification and hemicellulose extraction," *Cellulose Chemistry & Technology*, vol. 44, p. 35, 2010.
- [159] T. Radiotis, X. Zhang, M. Paice, and V. Byrne, "Optimizing production of xylose and xylooligomers from wood chips," presented at the 3rd Nordic Wood Biorefinery Conference, Stockholm, 2011.
- [160] M. J. Keshtkar, "Steam and Water Combined Analysis, Integration, and Efficiency Enhancement in Kraft Pulping Mills," École Polytechnique de Montréal, 2013.
- [161] O. Ajao, M. Rahni, M. Marinova, H. Chadja, and O. Savadogo, "Membrane based detoxification of prehydrolysate for biofuels production," presented at the MEMPRO 5 – Intégration des membranes dans les procédés Toulouse, France, 2014.
- [162] M. J. Taherzadeh and K. Karimi, "Enzymatic-based hydrolysis processes for ethanol," *BioResources*, vol. 2, pp. 707-738, 2007.
- [163] Y. Lee, P. Iyer, and R. W. Torget, "Dilute-acid hydrolysis of lignocellulosic biomass," in *Recent Progress in Bioconversion of Lignocellulosics*, ed: Springer, 1999, pp. 93-115.
- [164] A. M. Shupe and S. Liu, "Ethanol fermentation from hydrolysed hot-water wood extracts by pentose fermenting yeasts," *Biomass and Bioenergy*, vol. 39, pp. 31-38, 4// 2012.
- [165] J. R. M. Almeida, D. Runquist, V. Sánchez Nogué, G. Lidén, and M. F. Gorwa-Grauslund, "Stress-related challenges in pentose fermentation to ethanol by the yeast *Saccharomyces cerevisiae*," *Biotechnology Journal*, vol. 6, pp. 286-299, 2011.
- [166] A. K. Chandel, G. Chandrasekhar, K. Radhika, R. Ravinder, and P. Ravindra, "Bioconversion of pentose sugars into ethanol: a review and future directions," *Biotechnol Mol Biol Rev*, vol. 6, pp. 008-020, 2011.
- [167] R. J. Wooley, V. Putsche, and N. R. E. Laboratory, *Development of an ASPEN PLUS physical property database for biofuels components*: National Renewable Energy Laboratory Golden, CO, 1996.
- [168] P. Oleskowicz-Popiel, D. Klein-Marcuschamer, B. A. Simmons, and H. W. Blanch, "Lignocellulosic ethanol production without enzymes – Technoeconomic analysis of ionic

- liquid pretreatment followed by acidolysis," *Bioresource Technology*, vol. 158, pp. 294-299, 4// 2014.
- [169] P. C. Pinto, D. V. Evtuguin, and C. P. Neto, "Structure of hardwood glucuronoxylans: modifications and impact on pulp retention during wood kraft pulping," *Carbohydrate Polymers*, vol. 60, pp. 489-497, 2005.
- [170] H. Sixta, "Pulp Properties and Applications," in *Handbook of Pulp*, ed: Wiley-VCH Verlag GmbH, 2008, pp. 1009-1067.
- [171] H. Sixta, M. Iakovlev, L. Testova, A. Roselli, M. Hummel, M. Borrega, *et al.*, "Novel concepts of dissolving pulp production," *Cellulose*, vol. 20, pp. 1547-1561, 2013.
- [172] H. Sixta and G. Schild, "A new generation kraft process," *Lenzinger Berichte*, vol. 87, pp. 26-37, 2009.
- [173] O. Ajao, M. Marinova, O. Savadogo, and J. Paris, "Furfural production in an integrated forest biorefinery: process development and techno-economic assessment," *Chemical Engineering Research and Design*, vol. Submitted, 30 July 2014 2014.
- [174] T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, *et al.*, "Top value added chemicals from biomass. Volume 1-Results of screening for potential candidates from sugars and synthesis gas," DTIC Document 2004.
- [175] S. Jenkins. (2013) Bio-based chemicals gain market acceptance. *Chemical Engineering*. 14-17.
- [176] P. C. A. Bruijninx and B. M. Weckhuysen, "Shale Gas Revolution: An Opportunity for the Production of Biobased Chemicals?," *Angewandte Chemie International Edition*, vol. 52, pp. 11980-11987, 2013.
- [177] J. Lane. (2013, 22.07.2014). *Top Molecules: The DOE's 12 Top Biobased List – what's worked out?* Available: <http://www.biofuelsdigest.com/biobased/2013/01/08/top-molecules-the-does-12-top-biobased-list-whats-worked-out/>
- [178] J. Allen, "Cultivating Capacity for Biobased Materials and Chemicals Through 2017," *Industrial Biotechnology*, vol. 10, pp. 89-90, 2014.
- [179] R. V. Smith, "Industry Cluster Analysis: Inspiring a common strategy for community development," Central Pennsylvania Workforce Development Corporation 2003.
- [180] A. Näyhä, S. Hämäläinen, and H. Pesonen, "Biorefineries-future business opportunity for forest cluster: diffusion of forest biorefineries in Scandinavia, North America and South America," 2009.
- [181] O. Ajao, S. Senay, T. Radiotis, N. Jemaa, and M. Marinova, "The biorefinery cluster: strategy for increased profitability of integrated forest biorefineries," presented at the PAPTAC 98th Ann. Mtg., Montreal, Quebec, 2012.
- [182] M. J. Blair, "Development of forest biorefining in Canada: Overcoming the feedstock barrier," MS25516 M.S., Queen's University (Canada), Ann Arbor, 2014.
- [183] W. Mabee, "Policy options to support biorefining," in *Integrated biorefineries: design, analysis, and optimization*, P. R. Stuart and M. M. El-Halwagi, Eds., ed: CRC Press, 2012, pp. 729-748.

- [184] Industry Canada. (2014, 25.07.2014). *Petrochemicals Industrial Profile*. Available: <http://www.ic.gc.ca/eic/site/chemicals-chimiques.nsf/eng/bt01135.html>
- [185] Canadian Energy Pipeline Association (CEPA). (2014, 26.07.2014). *Pipeline fact book*. Available: <http://www.cepa.com/library/publications>
- [186] A. J. D. Lambert and F. A. Boons, "Eco-industrial parks: stimulating sustainable development in mixed industrial parks," *Technovation*, vol. 22, pp. 471-484, 8// 2002.
- [187] D. L. Van Dyne, M. G. Blase, and L. D. Clements, "A strategy for returning agriculture and rural America to long-term full employment using biomass refineries," *Perspectives on new crops and new uses*. ASHS Press, Alexandria, Va, pp. 114-123, 1999.