UNIVERSITÉ DE MONTRÉAL

DEVELOPMENT AND INTEGRATION OF ACID PRECIPITATION BASED LIGNIN BIOREFINERIES IN KRAFT PULPING MILLS

MIYURU SARANGA KANNANGARA

DÉPARTEMENT DE GÉNIE CHIMIQUE

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

THÉSE PRÉSENTÉE EN VUE DE L'OBTENTION

DU DIPLÔME DE PHILOSOPHIAE DOCTOR

(GÉNIE CHIMIQUE)

AOÛT 2015

© Miyuru Saranga Kannangara, 2015.

UNIVERSITÉ DE MONTRÉAL

ÉCOLE POLYTECHNIQUE DE MONTRÉAL

Cette thèse intitulée:

DEVELOPMENT AND INTEGRATION OF ACID PRECIPITATION BASED LIGNIN BIOREFINERIES IN KRAFT PULPING MILLS

présentée par : KANNANGARA Miyuru Saranga

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

a été dûment acceptée par le jury d'examen constitué de :

M. PERRIER Michel, Ph. D., président

M. PARIS Jean, Ph. D., membre et directeur de recherche

M. FRADETTE Louis, Ph. D., membre et codirecteur de recherche

M. HENRY Olivier, Ph. D., membre

M. VAKKILAINEN Esa Kari, Ph. D., membre

DEDICATION

To my family

ACKNOWLEDGEMENTS

I would like to express my acknowledgements to my supervisors, Prof. Jean Paris, who gave me this opportunity. Your advice and guidance has always helped me to learn and grow as a person and excel in what I do. Your dedication and hard work is always an inspiration for me. Special thanks to Prof. Louis Fradette, who always provided valuable insights to the project. Your suggestions, support and constructive critic made me a better researcher. It was a privilege to learn from such competent and sincere supervisors.

I would like to thank Dr. Mariya Marinova for her support, advice and encouragement during my stay. My thanks also go to Dr. Lamfeddal Kouisni and Dr. Naceur Jemma for their assistance, advice and comments on my laboratory work and the industrial aspects of the project. Thanks to Dr. Zoe Perin-Levasseur for providing a great start to the project. I would also like to thank Mr. Jean-Noel Cloutier, Mr. Raynald Labreque and Dr. Tolnai Balazs for their inputs, advice and comments.

I would like to thank the staff and in particular the technicians of Chemical Engineering Department of Ecole Polytechnique.

I thank the interns, Jalil, Carmen and Ines, who participated in this project and made this thesis a reality. Jalil, thank you for making my life easier during the experimental program.

I would not have made this without constant support and encouragement of my dear friends and colleages Moye, Anna, Sanjeewa, Maryam, Salomeh, Hilda, Ju, Hana, Radia, Sourour, Emir, Inci, Selim, Walid, Mohammad and all other that I might have forgotten to mention here. Thanks for Francois and Meriyem for translating the abstract and support.

I would like to thank my Uncle, Aunty and cousin for their support and encouragement since the day I left home to study abroad.

I would like to thank my parents and brother for their love, support and guidance. You are the constant driving force behind my success.

Finally to my dear wife Indeewari, last 6 years, we have been together were the happiest of my life and thanks for all the love and being patient all this time.

RÉSUMÉ

L'utilisation des ressources fossiles pour la production de biens et de services a des conséquences désastreuses sur l'environnement. Pour réduire leur impact, l'utilisation de matières premières ainsi que d'énergie renouvelables a été proposée en vue du développement d'une bioéconomie durable. L'industrie des pâtes et papiers en Amérique du Nord est actuellement confrontée à de rudes conditions économiques en raison de la diminution de la demande en produits papetiers traditionnels, la concurrence internationale et l'augmentation des prix de l'énergie. Les technologies de bioraffinage, qui transforment les constituants du bois en produits chimiques d'origine biologique à haute valeur ajoutée, représente, pour l'industrie des pâtes et papier, un moyen d'augmenter ses revenus, de diversifier son portefeuille de produits et de devenir plus durable sur le long terme. Elle est particulièrement bien placée pour répondre à cette tâche en raison de l'accès à la biomasse, de la manutention du bois et de l'infrastructure de transport, et de l'expertise existante dans les produits traditionnels obtenus à partir du bois.

L'extraction et la transformation de la lignine aux produits à haute valeur ajoutée a été identifiée comme l'une des voies de bioraffinage les plus rentables dans les usines de fabrication de pâte Kraft. L'extraction de la lignine, qui est une étape cruciale de la bioraffinerie intégrée, interagit à un degré élevé avec l'usine de pâte Kraft. L'importance de cette interaction est renforcée par la possibilité d'augmenter la production de pâte à papier grâce l'extraction de la lignine. Afin de réussir l'intégration de l'unité de bioraffinerie de la lignine dans les usines de fabrication de pâte Kraft, il est nécessaire de comprendre et de traiter les interactions entre les processus d'extraction de la lignine et l'usine de pâte Kraft réceptrice. De plus, il est nécessaire d'améliorer la rentabilité et la performance environnementale des procédés d'extraction de la lignine par l'amélioration de ses opérations unitaires et de répondre aux demandes énergétiques et chimiques internes au procédé. Dans cette thèse, le développement et l'intégration des processus de précipitations acides dans les usines de fabrication de pâte Kraft en vue d'améliorer leur performance économique et environnementale ont été étudiés.

Dans la première partie de cette recherche, les effets de l'énergie de la mise en œuvre du processus de précipitations acides sur la fabrication de la pâte kraft ont été évalués. Une usine de pâte Kraft canadienne représentative a été utilisée comme référence. Bien que le processus de précipitations acides n'ait pas une demande en énergie considérable, l'élimination de la lignine réduit la

production d'énergie de la chaudière de récupération et augmente la demande en vapeur de l'évaporateur. La production d'électricité a également diminué en raison de la diminution de la production d'énergie de la part de la chaudière. Un taux d'extraction de la lignine de 15% a permis une réduction de la récupération de la production d'énergie de la chaudière de 13,5% et une augmentation de 15% de la production de pâte à papier en raison du desembouteillage de la chaudière de récupération. Les déficits en énergie dans le processus Kraft ont été résolus par des mesures combinant des projets d'économie d'énergie identifiés à l'aide de l'analyse Pinch, d'une augmentation de la production d'énergie de la chaudière et de gazéification de la biomasse à cycle combiné. Il a été montré que la lutte contre les déficits d'énergie interne était possible, mais nécessite un haut degré d'intégration d'énergie.

Dans la deuxième partie de l'ouvrage, les effets sur l'équilibre chimique ont été étudiés. Une approche de modélisation basée sur l'équilibre électrolytique, qui a été proposée pour estimer les variations du pH et de la composition chimique de la liqueur noire, ont été utilisés pour simuler le processus de précipitations acides. Un algorithme basé sur le ratio Na / S a été utilisé pour calculer les équilibres chimiques du cycle de liqueur de l'usine de pâte Kraft. L'équilibrage entre Na et S a été réalisé suivant plusieurs stratégies basées sur les contraintes de l'usine et sur le recyclage du filtrat nettoyé. L'élimination complète ou le recyclage excessif de filtrats de lavage ont été trouvés pour augmenter l'exigence de récupération caustique. La demande caustique pourrait être minimisée en recyclant une partie des filtrats de lavage les plus concentrés, de sorte que la perturbation de l'équilibre Na / S soit minimale. L'efficacité de l'installation de lavage a également été trouvée pour affecter la demande de récupération caustique. La stratégie d'équilibrage entre Na et S a également affecté les charges de récupération des cycles opératoires, notamment ceux du train de l'évaporateur, de la caustification et du four à chaux. Par conséquent, les goulets d'étranglement dans les autres opérations de valorisation doivent être pris en compte lors du choix d'une stratégie de sorte que les demandes en produits chimiques soient réduits au minimum et qu'une augmentation maximale de la production de pâte à papier soit obtenue.

Dans les troisième et quatrième parties de cette recherche, les possibilités de réduction des coûts des processus de précipitations acides ont été étudiées. Comme la filtration et l'équipement de lavage représentent une partie importante des coûts en capital dans une usine de précipitation de la lignine, la possibilité d'améliorer la filtration de la lignine par optimisation hydrodynamique a été évaluée. Les conditions hydrodynamiques au cours de coagulation et de la floculation de la

lignine ont été variées et les particules de lignine précipitées ont été caractérisées en termes de propriétés de particules et de filtration. Il a été trouvé que le taux de cisaillement turbulent est le paramètre hydrodynamique déterminant qui contrôle la taille et la forme des particules de la lignine précipitée. Les particules les plus compactes et les plus grandes, qui peuvent être obtenus par contrôle hydrodynamique, ont présenté des propriétés de filtration et de lavage supérieures.

L'optimisation systématique des paramètres a été utilisée comme moyen d'améliorer le rendement et la performance de filtration du procédé de précipitation acide. Les expériences ont été effectuées en utilisant l'approche Taguchi et les résultats ont été analysés en utilisant le rapport S / N et les méthodes statistiques d'analyse de variance. La teneur de la liqueur noire en contenu solide a été identifiée comme le paramètre le plus critique, ce qui a eu la plus grande influence à la fois sur le rendement de la lignine et sur la résistance à la filtration. Les paramètres optimaux définis pour la performance de filtration, qui ont produit une lignine avec la plus basse teneur en cendres de 0,09%, n'a pas fourni le rendement le plus élevé en lignine. Par conséquent, il est prendre en compte qu’un compromis entre la pureté de la lignine et de processus économiques lors de l'élaboration des procédés de précipitation de la lignine pour des applications spécifiques serait nécessaire.

Enfin, la faisabilité technico-économique de l'utilisation de four à chaux gaz de combustion pour l’acidifaction de la liqueur noire a été étudiée. Les résultats expérimentaux ont montré qu'il est possible d'obtenir de la lignine filtrable, bien que la cinétique de l'acidification soit beaucoup plus lente. Une simulation et une analyse économique ont révélé que malgré la réduction du coût en CO_2, le four à chaux approvisionné en gaz de combustion était économiquement moins attrayant que l'achat de CO_2 externe en raison des exigences de nettoyage des gaz et de la taille accrue des réservoirs d'acidification. L'analyse de sensibilité a montré que les prix et la demande de CO2 du procédé doivent être considérablement plus élevés pour qu’il soit économiquement attrayant.

ABSTRACT

The use of fossil fuel resources for manufacture of goods and services has dire consequences on the environment. To reduce the impact, the use of renewable raw materials and energy has been suggested, leading to a sustainable bioeconomy. The pulp and paper industry in North America is currently facing stiff economic conditions due to declining demand for traditional paper commodities, international competition and rising energy prices. The biorefinery technologies, which convert wood components to value added bio-based chemicals and products, can be a means for the pulp and paper industry to increase its revenue, diversify the product portfolio and become more sustainable in the long run. The industry is uniquely positioned to accommodate this task due to access to biomass, existing wood handling and transportation infrastructures and expertise in traditional wood products.

The extraction and conversion of lignin to value added products has been identified as one of the most profitable biorefining pathways in Kraft pulping mills. Extraction of lignin, a crucial step of the integrated lignin biorefinery, has a high degree of interaction with the receptor Kraft pulping mill. The importance of the interaction is further enhanced by the possibility of incremental pulp production with lignin extraction. For successful implementation of the lignin biorefinery in Kraft pulping mills, we should understand and address the interactions between lignin extraction process and receptor Kraft pulping mill. Furthermore, it is necessary to enhance the profitability and environmental performance of the lignin extraction processes by improving its operations and meeting the internal energy and chemical demands. In this thesis, the development and integration of acid precipitation process in Kraft pulping mills to improve its economic and environmental performance have been investigated.

In the first part of this research, the energy impacts of implementing the acid precipitation process on the Kraft pulping mill was evaluated. A representative Canadian softwood Kraft pulping mill have been used as the reference. Although, the acid precipitation process did not have considerable energy demands, the lignin removal reduced the recovery boiler energy production and increased the evaporator steam demand. The electricity production was also decreased due to reduced recovery boiler steam production. A total of 15% lignin extraction reduced the recovery boiler energy production by 13.5% and allowed an increase of pulp production capacity by 15% through recovery boiler debottlenecking. The energy deficits in the Kraft process was addressed by

measures combining energy savings projects identified using Pinch analysis, biomass boiler energy production increase and biomass gasification combined cycle. It was shown that addressing the energy deficits internally was feasible, but requires high degree of energy integration.

In the second part of the work, the impact of integrating a lignin biorefinery on the chemical balance of Kraft pulping mill have been investigated. A modeling approach based on electrolyte equilibrium, which was proposed to estimate pH and chemical composition variations of the black liquor, have been used to simulate the acid precipitation process. A calculation sequence based on Na/S balances was utilized to calculate the chemical balances of the liquor cycle of the Kraft pulping mill. Balancing Na and S have been performed according to several strategies based on mill constraints and wash filtrate recycle. Complete disposal or excessive recycle of wash filtrates have been found to increase the make-up caustic requirement. The caustic demand could be minimized by recycling a part of most concentrated wash filtrates so that disruption of the Na/S balance was minimum. The efficiency of the washing setup was also found to affect the make-up caustic demand. The Na and S balancing strategy also affected the loads to the recovery cycle operations including evaporator train, recausticizing and lime kiln. Therefore, the bottlenecks in the other recovery operations have to be taken into account in selecting a strategy so that chemical demands are minimized and maximum pulp production increase is obtained.

In the third and fourth parts of this research, possibilities of reducing the costs of acid precipitation process have been investigated. As filtration and washing equipment represent a significant portion of capital costs in a lignin precipitation plant, the feasibility of improving lignin filtration by hydrodynamic optimization has been evaluated. The hydrodynamic conditions during lignin coagulation and flocculation were varied and the precipitated lignin particles were characterized in terms of particle and filtration properties. The turbulent shear rate was found to be the determining hydrodynamic parameter that controlled the size and shape of the precipitated lignin particles. More compact and larger particles, which could be obtained by hydrodynamic control, provided superior filtration and washing properties.

The systematic parameter optimization was used as means of improving the yield and filtration performance of the acid precipitation process. The experiments were performed using the Taguchi statistical design of experiments approach and the results were analyzed using signal-to-noise ratio and analysis of variance statistical methods. The black liquor solid content have been identified as

the most critical parameter, which had the largest influence on both lignin yield and filtration resistance. The optimal parameters set for filtration performance, which produced lignin with lowest ash content of 0.09%, did not provide the highest lignin yield. Therefore, considering trade-offs between lignin purity and process economics would be required, when developing lignin precipitation processes for specific applications.

Lastly, the economic and technical feasibility of using lime kiln flue gases for black liquor acidification was investigated. The experimental results showed that it is feasible to obtain filterable lignin, however, the kinetics of the acidification was considerably slower. A simulation and economic analysis revealed that despite the elimination of CO_2 cost, the lime kiln flue gas supply was less attractive economically than external CO_2 purchase due to the gas cleaning requirements and increased size of acidification vessels. The sensitivity analysis showed that CO_2 price and CO_2 demand of the process has to be considerably higher that current values for the use of flue gases to be economically attractive.

TABLE OF CONTENTS

DEDICATION III

ACKNOWLEDGEMENTS IV

RÉSUMÉ V

ABSTRACT VIII

TABLE OF CONTENTS XI

LIST OF TABLES XVIII

NO TABLE OF FIGURES ENTRIES FOUND.LIST OF FIGURES XX

LIST OF SYMBOLS AND ABBREVIATIONS XXIII

INTRODUCTION 1

CHAPTER 1 LITERATURE REVIEW 1

1.1 Context and motivation 4

1.2 Canadian Forestry Sector 5

1.3 Kraft pulping 5

1.4 Kraft Pulping Mill as an Integrated Biorefinery 8

1.4.1 Hemicellulose Extraction and Utilization 8

1.4.2 Cellulose and Fiber based Products 8

1.4.3 Energy and Water for Kraft mill Forest Biorefineries 9

1.4.4 Lignin Extraction from Black Liquor 10

1.4.5 Recovery Boiler Debottlenecking and Pulp Production Increase 11

1.4.6 Lignin Applications 11

1.4.7 The Properties of Lignin 13

1.5 Aggregation of Lignin in Aqueous Solutions 13

1.5.1 Aggregate Kinetics and Structure 14

1.5.2 Effect of pH, Ionic Strength and Temperature 15

1.6 Acid Precipitation Process 16

1.6.1 Effects of Operating Parameters 17

1.6.2 Filtration and Washing 19

1.6.3 Commercially Available Versions of the Process 21

1.7 Implementation of Acid Precipitation Process in Kraft Pulping Mills 21

1.7.1 Impact on the Recovery boiler and Production Increase 22

1.7.2 Impacts on the Evaporator Train 23

1.7.3 Impacts on Mill Total Energy Balance 23

1.7.4 Impacts on Chemical Balance 23

1.8 Process integration opportunities within Kraft process 24

1.8.1 Energy Integration 24

1.8.2 Water and Chemical Integration 25

1.9 Critical Review 27

CHAPTER 2 OBJECTIVES, METHODOLOGY AND THESIS ORGANISATION 29

2.1 Specific objectives 29

2.2 Methodology 29

2.3 Organisation of the Thesis 31

CHAPTER 3 ARTICLE 1: LIGNIN RECOVERY BY ACID PRECIPITATION IN A KRAFT MILL: AN ENERGY PERSPECTIVE 33

3.1 Introduction 33

3.2 Lignin extraction process integrated into a Kraft mill 34

3.3 Extraction and recycle of black liquor 36

3.4 Impacts on mill energy balance 37

3.4.1 Impacts on the Evaporator Train 37

3.4.2 Impacts on the Recovery boiler 38

3.5 Addressing the energy deficits 39

3.5.1 Strategy 1: Steam Saving Projects and Condensing Power 41

3.5.2 Strategy 2: Additional Biomass Use 41

3.5.3 Strategy 3: IGCC Cycle and Steam Saving Projects 42

3.6 Conclusion 43

3.7 Acknowledgements 43

3.8 References 43

CHAPTER 4 ARTICLE 2: PROCESS MODELLING AND NA/S BALANCES OF LIGNIN BIOREFINERIES IMPLEMENTED IN KRAFT PULPING MILLS: APPLICATION TO A CANADIAN SOFTWOOD MILL 45

4.1 Introduction 46

4.2 Process description 47

4.2.1 Kraft process liquor cycle 47

4.2.2 Acid precipitation process 48

4.3 Simulation approach 49

4.3.1 Liquor cycle balances 50

4.3.2 Recovery boiler energy production and lignin extraction ratio 54

4.3.3 Modeling the BL acidification 56

4.3.4 Acid precipitation and liquor cycle mass and energy balances 58

4.4 Results and discussion 60

4.4.1 Implementation strategies 60

4.4.2 Impact on Na/S balances 61

4.4.3 Increase in steam and water demand and effluent production 66

4.4.4 Pulp production increase and implementation constraints 67

4.5 Conclusions 68

4.6 Acknowledgements 69

4.7 References 69

CHAPTER 5 ARTICLE 3: EFFECT OF MIXING HYDRODYNAMICS ON THE PARTICLE AND FILTRATION PROPERTIES OF PRECIPITATED LIGNIN 72

5.1 Introduction 73

5.2 Materials and methods 76

5.2.1 Experimental setup 76

5.2.2 Black liquor samples 77

5.2.3 Characterization of the black liquors, filtrates, and lignin samples 78

5.2.4 Experimental Procedure 78

5.2.5 Characterization of the hydrodynamic conditions in the stirred tank 79

5.2.6 Characterization of specific filtration resistance and lignin yield 80

5.2.7 Characterization of particle size distributions and structures 81

5.3 Results and Discussion 82

5.3.1 Effect of hydrodynamic conditions on particle properties 82

5.3.2 Size distribution 85

5.3.3 Aggregate structure 86

5.4 Effect hydrodynamic conditions on filtration, washing and yield 90

5.4.1 Filtration resistance 90

5.4.2 Lignin yield 91

5.4.3 Washing time and ash content 91

5.4.4 Lignin filtration rate 92

5.5 Verification of the reproducibility of the results using black liquors from other Kraft pulping mills 93

5.6 Conclusions 96

5.7 Acknowledgements 97

5.8 References 97

CHAPTER 6 ACID PRECIPITATION OF LIGNIN FROM BLACK LIQUOR: OPTIMIZATION OF FILTRATION PERFORMANCE AND YIELD USING TAGUCHI METHOD.....100

6.1 Introduction 100

6.2 Methodology 102

6.2.1 Experimental work 102

6.2.2 Black liquor, filtrate and lignin characterization.....104

6.2.3 Calculation of lignin yield and filtration resistance 105

6.2.4 Mixing tank characterization.....106

6.3 Statistical analysis 107

6.3.1 $\boldsymbol{S/N}$ ratio computation 107

6.3.2 Analysis of variance (ANOVA) computation.....107

6.3.3 Prediction of optimum performance 108

6.4 Results and discussion.....109

6.4.1 Preliminary selection of operating parameters.....109

6.4.2 Design of experiments.....112

6.4.3 Lignin Yield Optimization 113

6.4.4 Filtration Performance Optimization 115

6.4.5 ANOVA Results.....117

6.4.6 Selection of Overall Optimum Operating Conditions.....120

6.4.7 Result Validation.....121

6.4.8 The Acid Precipitation Process and Pulp Mill Interaction.....122

6.5 Conclusion 122

6.6 Acknowledgements 124

CHAPTER 7 FEASIBILITY AND ECONOMICS OF USING LIME KILN FLUE GASES FOR PRECIPITATION OF LIGNIN FROM BLACK LIQUOR 125

7.1 Introduction 125

7.2 Experimental Section 126

7.2.1 Experimental setup 126

7.2.2 Analytical Procedures 127

7.2.3 Black Liquor Properties 127

7.2.4 Experimental Results 128

7.3 Economic Evaluation 129

7.3.1 Process Flowsheets and Simulation 129

7.3.2 Economic Analysis 131

7.4 Conclusion 133

CHAPTER 8 GENERAL DISCUSSION 134

8.1 Process Implementation and Integration 134

8.1.1 Energy Impacts and Mitigation 134

8.1.2 Lignin Extraction Ratio and Pulp Production Increase 135

8.1.3 Process Modelling and Liquor Cycle Chemical Balance 136

8.1.4 Internal Supply of Chemicals 138

8.2 Process Development 139

8.2.1 Effects of Mixing Hydrodynamics 139

8.2.2 Systematic Parameter Optimization 141

CHAPTER 9 CONCLUSION AND RECOMMENDATIONS 143

9.1 Conclusion 143

9.2 Original Contributions 144

9.3 Recommendations 145

9.3.1 Integrated Forest Biorefineries (IFBR) 145

9.3.2 Process Modelling of the Lignin Biorefinery 146

9.3.3 Lignin Floc Strength Measurement and Improvement 146

9.3.4 Novel Precipitation Reactor Proposals 147

9.3.5 Control and Stabilization of the Acid Precipitation Process 147

9.3.6 Control of Lignin Properties 148

BIBLIOGRAPHY 149

LIST OF TABLES

Table 1-1: Typical softwood and hardwood composition (Biermann, 1996) 6

Table 1-2: A summary of lignin extraction methods from black liquor. 10

Table 1-3: The specifications of lignin feedstock for carbon fiber production as defined by Oak Ridge National Laboratory (ORNL) (Baker, 2011; Luo, Genco, Cole, & Fort, 2011).....13

Table 1-4 : The ranges of pH, temperature and solid content reported in the literature. 19

Table 3-1: Main parameters of the Kraft mill 35

Table 3-2: Key parameters of the lignin biorefinery.....36

Table 3-3: Increase of evaporator steam demand with rate of filtrate recycle for given configurations.....37

Table 3-4: List of proposed steam saving projects.....40

Table 3-5: Comparison of strategies proposed to address mill power and steam deficits. 42

Table 4-1: The components included in the liquor cycle balance.....52

Table 4-2: The BL composition of the studied mill.....53

Table 4-3: Specifications of the lignin extraction process 59

Table 4-4: Pulp mill parameters for mill balances 60

Table 4-5: Implementation strategies of lignin biorefinery in Kraft pulping mill 61

Table 4-6: Chemical additions, purges and Na_2CO_3 flow for each strategy 64

Table 4-7: Steam, water demand and effluent production increase based on the implementation strategy of the biorefinery process 66

Table 4-8: Feasible pulp production increase, lignin extraction and capacities utilized in the liquor cycle for the studied mill.....67

Table 5-1: Properties of the black liquor samples.....77

Table 5-2: The power levels and corresponding to the Reynolds numbers and RPMs for the PBT and MB impeller assemblies. 80

Table 5-3: Average rates of lignin filtration for the power levels used. 93

Table 5-4: Particle sizes at the end of the ageing operation for black liquors A, B, C, and D for three acidification and ageing power level combinations. 94

Table 5-5: Process performance parameters for selected specific power levels for liquors A, B, C, and D. 95

Table 6-1: Properties of oxidized black liquor used in this work. 105

Table 6-2: The specific power levels, RPMs and Re numbers of operation. 106

Table 6-3: The parameters (factors) and their levels.....113

Table 6-4: Experimental results for lignin yield 114

Table 6-5: Experimental results for filtration resistance and ash content of lignin cake 116

Table 6-6: Results of ANOVA for lignin yield.....118

Table 6-7: Results of ANOVA for filtration resistance of lignin cake 119

Table 6-8: Results of ANOVA for ash content of washed lignin cake 120

Table 7-1: The properties of the investigated black liquor. 127

Table 7-2: The results of the experiments using different black liquors.....128

Table 7-3 : Parameters of lignin precipitation process.....130

Table 7-4 : Economic analysis for two processes. 131

LIST OF FIGURES

Figure 1-1: Number of people directly employed by the forest sector in the provinces of Quebec, British Columbia and Ontario (Statistics-Canada, 2013). 4

Figure 1-2: Overview of Kraft process 6

Figure 1-3: Chemical recovery cycle of the Kraft process (Smook, 1992a) 7

Figure 1-4 Cryo-TEM image of a DLCA fractal lignin aggregate (Norgren & Edlund, 2014). Reprinted with permission from Norgren, M., Edlund, H., Lignin: Recent advances and emerging applications. Current Opinion in Colloid & Interface Science 2014; 19 (5); 409-416. Copyright 2015 by Elsevier. 15

Figure 1-5: The main operations in the acid precipitation process 17

Figure 2-1 : Overall methodological approach 30

Figure 3-1: Implementation of lignin extraction in the evaporator train of the Kraft mill according to configuration 1 and 2. 36

Figure 3-2: Reduction of HHV of black liquor with the extraction of lignin 38

Figure 3-3: Impacts of lignin extraction on the energy balance of the mill 39

Figure 3-4: Composite curves generated by pinch analysis for the reference mill. 40

Figure 4-1: A basic flow diagram of the liquor cycle in a Kraft pulp mill 48

Figure 4-2: A flowsheet of the lignin extraction process 49

Figure 4-3: Simulation framework used for the analysis 50

Figure 4-4: The calculation sequence utilized for estimating the Na/S balances of the liquor cycle 51

Figure 4-5: Comparison of the results for Model 1 where phenol hydroxyl groups of lignin is included and Model 2 where only inorganic compounds of BL is used for equilibrium and compared with experimental data by Wallmo et al. (2007). 58

Figure 4-6: Overall Na/S balances of the liquor cycle of studied mill (without lignin biorefinery integration) (Units: t/d) 62

Figure 4-7: Na/S balances of the liquor cycle with integrated lignin biorefinery plant for proposed strategies (units: t/d) 63

Figure 4-8: Sensitivity of the caustic demand on the chemical recovery efficiency and wash liquor consumption of first washing step (Wash liquor strength 0.4 M H_2SO_4) 65

Figure 5-1: Flow diagram of the acid precipitation process. 73

Figure 5-2: Two-stage pitched-blade turbine (PBT) and Maxblend (MB) impeller assemblies and their dimensions. 76

Figure 5-3: Changes in particle size during the ageing operation using the 0.003, 0.011, and 0.107 kW/m^3 ageing power levels for flocs acidified at 1.029 kW/m^3 acidification power level with the MB and PBT impeller assemblies. (a) Median diameter (DV_{50}) (b) Sauter mean diameter ($D_{3,2}$). 83

Figure 5-4: Changes in particle size during the ageing operation using the 0.011, and 0.107 kW/m^3 ageing power levels for flocs acidified at 0.107 kW/m^3 acidification power level with the MB and PBT impeller assemblies. (a) Median diameter (DV_{50}) (b) Sauter mean diameter ($D_{3,2}$). 84

Figure 5-5 : Volume weighted and number weighted distributions for PBT and MB mixing assemblies at the start (t = 0) and end (t = 60 min) of the ageing operation for the 1.029 kW/m^3 and 0.107 kW/m^3 acidification power levels and the 0.011 kW/m^3 ageing power level. (a) Volume weighted distribution (t = 0). (b) Volume weighted distribution (t = 60 min). (c) Number weighted distribution (t = 0). (d) Number weighted distribution (t = 60 min). 85

Figure 5-6: Fractal dimension (D_f) of the lignin flocs at the start and end of the acidification step. 87

Figure 5-7: SEM images showing the size, distribution, and structure of precipitated lignin at 6000x magnification at the start of the ageing operation (t = 0). (a) 1.029 kW/m^3 acidification power level, (b) 0.107 kW/m^3 acidification power level. 87

Figure 5-8: SEM images showing the size, distribution, and structure of precipitated lignin at 3000x magnification. (a) 1.029 kW/m^3 acidification power level (at the start of the ageing operation), (b) 0.107 kW/m^3 acidification power level (at the start of the ageing operation), (c) 1.029

kW/m^3 acidification power level (at the end of the ageing operation), (d) 0.107 kW/m^3 acidification power (at the end of the ageing operation).....89

Figure 5-9: Filtration resistances of precipitated lignin cakes for the two impeller assemblies at different acidification and ageing power levels. 90

Figure 5-10: Lignin yields (%) for the two impeller systems and five different acidification and ageing power level combinations. 91

Figure 5-11: Washing times (min/100 g of lignin (dry basis)) for the MB and PBT assemblies for different acidification and ageing power level combinations. 92

Figure 6-1: The stirred tank setup used for the experiments. 103

Figure 6-2: Variation of filtration resistance and lignin yield with precipitation pH 110

Figure 6-3: Variation of the filtration resistance and lignin yield with precipitation temperature 110

Figure 6-4: Variation of filtration resistance and yield with black liquor solids content (%).....112

Figure 6-5: Main effect plots for S/N ratios of lignin yield: (a) Black liquor solids content (%), (b) Precipitation pH, (c) Ageing residence time (min), (d) Agitation rate (RPM) 115

Figure 6-6: Main effect plots for S/N ratios of (A) lignin cake filtration resistance and (B) ash content of washed cake for (a) Black liquor solids content (%), (b) Precipitation pH, (c) Ageing residence time (min), (d) Agitation rate (RPM) 117

Figure 7-1 : Acid precipitation process flowsheet with lime kiln flue gas CO_2 supply.....130

Figure 7-2 : The sensitivity of the payback period of the process 1 to the (a) CO_2 price (b) CO_2 demand 132

LIST OF SYMBOLS AND ABBREVIATIONS

A	Filtration Area
ADt	Air Dried Ton
$\overline{A}_i$	Mean Effect of Factor A
ANOVA	Analysis of Variance
BL	Black Liquor
c	Concentration
CPPA	Canadian Pulp and Paper Association
Cryo-TEM	Cryogenic Transmission Electron Microscopy
D	Impeller Diameter
$D_{3,2}$	Sauter mean diameter
D_f	Mass Fractal Dimension
DLCA	Diffusion Limited Cluster-Cluster Aggregation
DLVO	Derjaguin-Landau-Verwey-Overbeek theory
DOE	Design of Experiments
DOF	Degrees of Freedom
DV_{50}	Median diameter
E	Energy Flow Rate
EDL	Electrical Double Layer
ESP	Electrostatic Precipitator
F	Wood Feed Rate
GL	Green Liquor
GWA	Generator Waste Acid
HHRR	Hearth Heat Release Rate

HHV	Higher Heating Value
I	Scattered Light Intensity
IFBR	Integrated forest Biorefinery
IGCC	The Integrated Gasification Combined Cycle
LP	Low Pressure
$\dot{m}$	Component Mass Flow Rate
$\dot{M}$	Total Mass Flow Rate
MB	Maxblend™
MEA	Monoethanolamine
MP	Medium Pressure
MS	Mean Sum of Squares
n	Refractive Index of the Dispersant
N	Agitation Rate
NCC	Nanocrystalline Cellulose
N_P	Power Number
NRTL	Non Random Two Liquid Model
O.D.	Oven Dried
OA	Orthogonal arrays
ODt	Oven Dried Ton
P	Total Power Input
P (%)	Percentage Contribution
PAN	Polyacrylonitrile
PBT	Pitched blade turbine
pKa	Acid Dissociation Contant

Q	Scattering Vector
Re	Reynolds Number
RB	Recovery Boiler
ref	Reference Value
RLCA	Reaction Limited Cluster-Cluster Aggregation
R_M	Filter Medium Resistance
RPM	Revolutions Per Minute
S/N	Signal-to-Noise Ratio
SEM	Scanning Electron Microscopy
SLRP	Sequential Liquid-Lignin Recovery and Purification
SS	Sum of Squares
T	Sum of Total Observations
Tad	Adiabatic Temperature
UV	Ultraviolet
V	Volume
WL	White Liquor
Y_i	Response Value
$\boldsymbol{\alpha}$	Specific Filtration Resistance
Δp	Pressure Differential
ε	Turbulent Kinetic Energy Dissipation
$\eta_{Causticizing}$	Causticizing Efficiency
η_{RB}	Recovery Boiler Energy Efficiency
$\eta_{Reduction}$	Reduction Efficiency

θ	Scattering Angle
λ	Wave Length of Radiation in Vacuum
μ	Dynamic Viscosity
ρ	Density

INTRODUCTION

The North American pulp and paper industry has been facing difficult economic conditions since last decade due to declining demand for traditional paper commodities, higher production costs and competition from low cost overseas producers. The integrated forest biorefinery (IFBR), which convert lignocellulosic biomass into novel bioproducts and chemicals, has been proposed as a means of improving the product portfolio and profitability of pulping mills, making them competitive and sustainable in the long run. This has led widespread research and development in the area of biorefining.

An IFBR located in a pulping mill usually convert a wood component such as hemicellulose or lignin, which is currently utilized for low value combustion, into a value added product. The idea of IFBR is promising as it allows the use of existing infrastructure, wood supply network, and utilities in the pulping mill. Numerous biorefining technologies that valorize wood components into value added products are currently being evaluated for the implementation in the pulping mill. Lignin extraction and conversion is amongst the most promising of such applications.

Among the available pulping methods, Kraft pulping is the dominant method in the world. In Kraft pulping, the lignin and hemicellulose components of wood are selectively removed using chemicals. Removed lignin, hemicellulose and spent chemicals are entrained in the spent liquor, called black liquor, which is concentrated and combusted in the recovery boiler to regenerate the spent chemicals and to generate steam and power for the mill. The produced pulp has higher quality than the pulp produced from the other methods due to higher strength and low lignin content.

Lignin can be extracted from the black liquor stream by the acid precipitation process and then converted into wide array of bioproducts and biochemicals, in the context of IFBR. In the acid precipitation process, lignin is precipitated with CO_2 treatment; precipitated lignin is filtered and then washed. Lignin extraction reduces the thermal load to the recovery boiler of Kraft pulping mill. This is advantageous as many North American Kraft pulping mills have gradually increased their pulp production over the years, thus reaching the thermal limits of the recovery boiler. In such cases, removing lignin from black liquor permits the increase of the pulp production capacity (Loutfi, Blackwell, & Uloth, 1991).

Kraft lignin is currently being investigated as a feedstock for manufacture of novel bioproducts such as carbon fibers, phenol formaldehyde resins, carbon blacks and polyurethanes. Most of the technologies that convert lignin into value added products still require significant scientific and technical breakthroughs. Many lignin products can be alternatively produced using petroleum feedstock. The volatile petroleum prices demand the lignin extraction and conversion processes to be highly cost efficient for lignin products to be economically competitive. The current cost of lignin extraction and conditioning has been reported to be higher than the desired cost (Chien-Wei Chen, 2014; Farag & Chaouki, 2015).

The IFBR should also facilitate the sustainable production of energy and products, thus reducing environmental impacts. The successful implementation lignin biorefineries to achieve cost efficiency and sustainability depends on the development of cost effective biorefinery designs, implementation with minimum disruptions in the pulping mill, maximizing lignin extraction and pulp production increase and, minimization of energy and chemical demands through process integration. This thesis deals with acid precipitation based lignin biorefinery development and its integration in Kraft pulping mills. To achieve cost effective design, process optimization potentials were investigated. The process economics and environmental performance has been improved with optimal implementation and integration of the lignin biorefinery in a Kraft pulping mill. The scope of the biorefinery was limited to extraction and primary treatment of lignin.

Optimization of lignin filtration and yield is necessary to reduce the capital and operating costs of the acid precipitation process. It was shown that lignin particle size and structure can be controlled by the manipulation of hydrodynamic conditions during lignin aggregation and growth. The lignin filtration and washing operations could be optimized by precipitating lignin particles with desirable particle properties. The yield and lignin filtration were optimized using Taguchi experimental approach. Potentials for process improvement have been identified.

Feasibility of supplying energy and chemicals for lignin biorefinery from the Kraft pulping mill has been determined. The steam savings identified with Pinch analysis could be used to compensate the energy demands. The feasibility of using CO_2 from lime kiln flue gases in the precipitation process was validated and the profitability of the proposals were evaluated. The chemical balances of the Kraft mill liquor cycle was analyzed for the optimal implementation of lignin biorefinery

with minimum disruptions. Guidelines and strategies for the optimal implementation in terms of caustic demand and pulp production increase have been proposed.

Chapter 1 LITERATURE REVIEW

1.1 Context and motivation

Canada has vast sustainably managed forest resources, mainly located in the lands unsuitable for food crops. The forest resources has been traditionally used by a wide array of industries ranging from pulp, paper and wood products to heat and power. The forest industry is an important sector of the Canadian economy, contributing significantly to the Gross Domestic Product (GDP) with a revenue of $53 billion and employing 321,000 Canadians. However, the industry has faced a period of decline. The demand for products such as newsprint is gradually decreasing and the wood pulp products are facing severe competition from low cost overseas producers. The wood products such as lumber were hard hit by the recent recession in United States. This has resulted in capacity reductions and closure of several pulp and paper mills. The local communities, which were dependent on the industry, have been affected. (Brown, Gilsenan, Singbeil, & Paleologou, 2011; Marinova, Mateos-Espejel, Jemaa, & Paris, 2009). Figure 1-1 shows the decline of employment in the forest sector in Canadian provinces with largest forest industry activity.

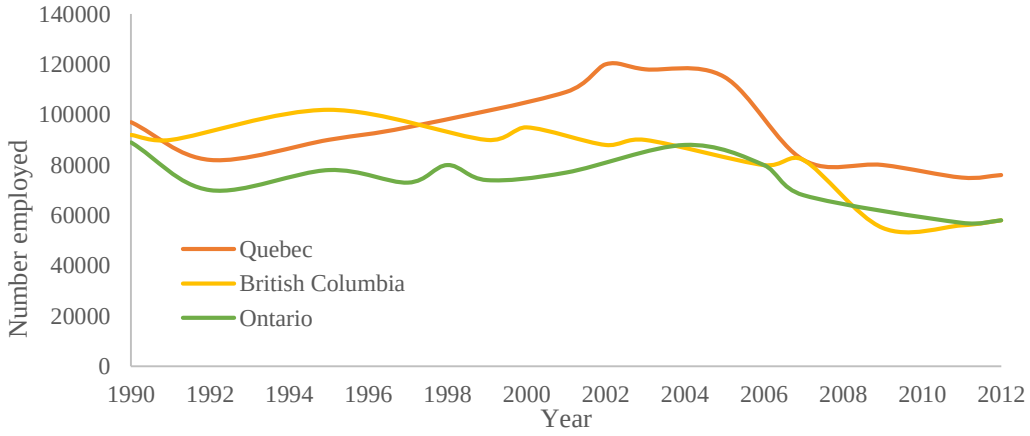

Figure 1-1: Number of people directly employed by the forest sector in the provinces of Quebec, British Columbia and Ontario (Statistics-Canada, 2013).

Under the given circumstances, it is imperative to transform the forest industry to produce novel and sustainable products, thereby improving its competitiveness and profitability and ensuring the operation of current pulp mills and creating new job opportunities.

1.2 Canadian Forestry Sector

Canada has 347 million hectares of sustainably managed forest land, which has been traditionally used for the manufacture of solid wood and pulp and paper products. Solid wood products include lumber, structured panels and wood composites while the pulp and paper products include newsprint, market pulp, tissue and towel grade pulp, and packaging materials. The wood residue is combusted to generate on site heat and power and in some cases excess power is sold to the grid. The industry is highly integrated with saw mills, which manufacture lumber and wood chips to the mills. The local communities are concentrated around the industrial sites and are heavily dependent on it. The demand for newsprint has been gradually declining and market pulp products also face fierce competition from overseas low cost manufactures. This has resulted in large declines in pulp and paper production, costing large number of job losses (Brown et al., 2011; Natural-Resources-Canada, 2015)

1.3 Kraft pulping

Around 50% of export revenue generated from the Canadian forestry sector comes from pulp and paper products (Natural-Resources-Canada, 2015). The available pulping methods can be categorized into mechanical pulping and chemical pulping. In mechanical pulping, the wood fibers are mechanically disintegrated to create pulp, while they are chemical liberated during chemical pulping processes. Chemical pulping can be subdivided into sulfite pulping and Kraft pulping. Kraft pulping is the dominant pulping method for manufacturing pulp and paper in the world today. Chemical pulping accounts for 70% of north American pulp production, 95% of which is Kraft pulping (Smook, 1992d).

Wood consists mainly of cellulose, hemicellulose and lignin in different proportions depending on the wood species. Table 1-1 shows the composition of two main wood types: hardwood and softwood. During Kraft pulping, the lignin component of wood is selectively removed to liberate cellulose fibers. The Kraft pulps can be basically categorized as hardwood and softwood pulps.

Table 1-1: Typical softwood and hardwood composition (Biermann, 1996)

Component	**Percentage**	
	Hardwood	**Softwood**
Cellulose	40-50	45-50
Hemicellulose	15-35	10-25
Lignin	18-25	25-35
Extractives	1-5	3-8
Ash	0.4-0.8	0.2-0.5

An overview of the Kraft process is shown in Figure 1-2. In this process, wood undergoes the delignification operation, where lignin is selectively removed from wood by high temperature chemical treatment so that cellulose fibers can be disintegrated. Delignification is common to all the chemical pulping methods. However, the chemicals used and process conditions differ according to the type of chemical pulping method. Na_2S and NaOH are used in the Kraft process. After the delignification, the pulp is washed, generating a wash liquor called black liquor. It predominantly contains lignin and spent chemicals used for delignification. The washed pulp is bleached to increase the brightness of the pulp and then dried. The dried pulp can be marketed or sent to paper making processes. The Kraft pulp usually has higher strength and whiteness than the other pulps. The spent chemicals in the black liquor are regenerated in the chemical recovery cycle of the Kraft process and reused for the delignification.

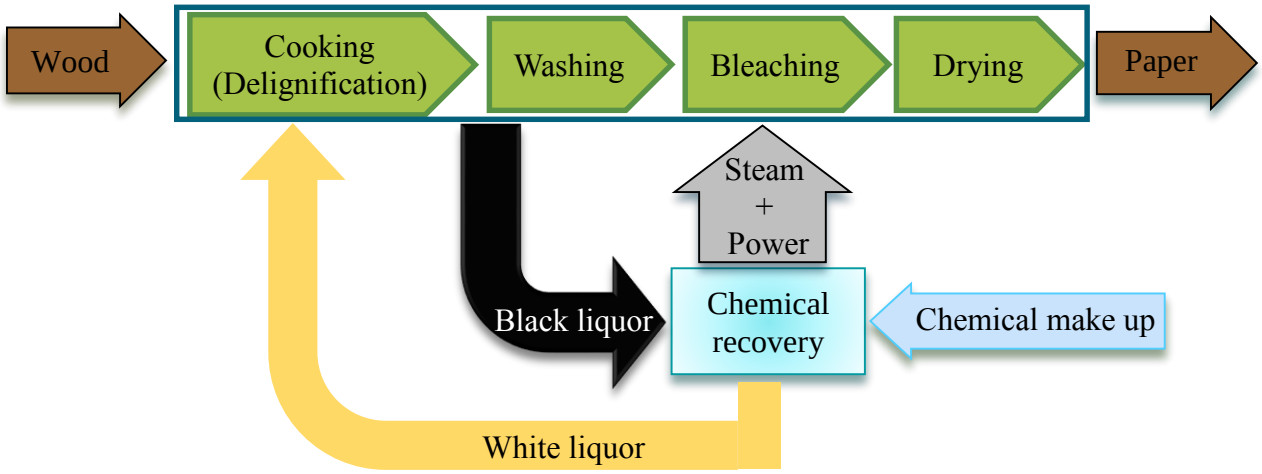

Figure 1-2: Overview of Kraft process

An overview of the chemical recovery is shown in Figure 1-3. During the regeneration process, heat and power are generated, addressing most of the steam and power demands of the Kraft process. The chemical recovery cycle of the Kraft pulping process significantly improves its economic attractiveness (Biermann, 1996; Smook, 1992c).

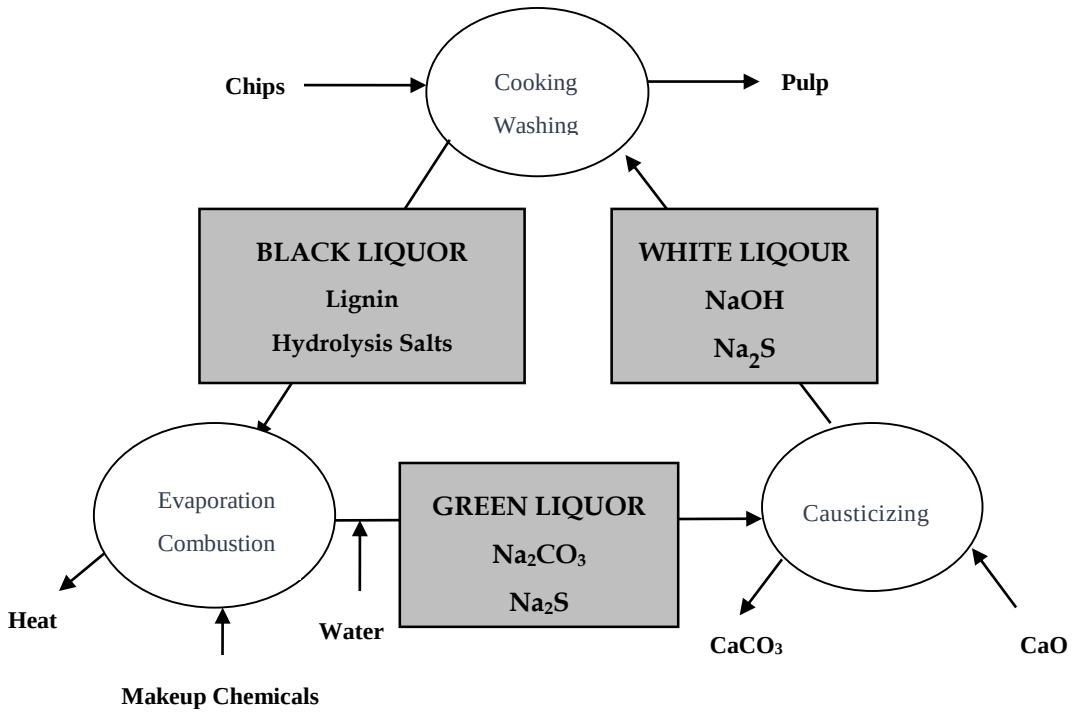

Figure 1-3: Chemical recovery cycle of the Kraft process (Smook, 1992a)

During chemical recovery, black liquor is concentrated in evaporators and combusted in the recovery boiler. The smelt stream from the recovery boiler is dissolved in water to form green liquor, a mixture of predominantly Na_2CO_3 and Na_2S. Na_2CO_3 in the green liquor is converted to NaOH by addition of the CaO in the causticizing section, converting CaO to $CaCO_3$. The $CaCO_3$ is regenerated in the lime kiln and re-used in the causticizing. The re-generated mixture of chemicals, which is called white liquor, is recycled back to the delignification operation. Makeup chemicals are added to compensate the losses (Biermann, 1996; Smook, 1992a).

1.4 Kraft Pulping Mill as an Integrated Biorefinery

Van Heiningen (2006) proposed the conversion of Kraft pulping mills to integrated forest biorefineries (IFBR), which produce novel biomaterials and chemicals in addition to traditional pulp and paper products. Kraft pulping mills have yields of about 50% or slightly lower, because more than half of the wood input is dissolved in spent liquor. The dissolved fraction is mainly hemicellulose and lignin and they are utilized for low value combustion in the recovery boiler. The conversion of hemicellulose and lignin to higher value components can improve the competiveness and profitability of Kraft pulping mills operating with traditional pulp and paper commodities as the key products.

1.4.1 Hemicellulose Extraction and Utilization

The hemicellulose in wood can be extracted prior to pulping using a number of methods including acid, alkaline and hot water treatment. Each method has its advantages and disadvantages such as chemical usage, cellulose degradation, impact on pulp yield and sticky lignin deposits and inhibitor formation. The hemicellulose extraction should not excessively degrade the pulp quality and the prehydrolysate generated should meet the composition requirements for further processing (Duarte, Ramarao, Amidon, & Ferreira, 2011; Helmerius, von Walter, Rova, Berglund, & Hodge, 2010; Mao, Genco, Yoon, van Heiningen, & Pendse, 2008). The extracted hemicelluloses can be converted using chemical or biological methods into a large array of chemicals and products including biofuels, organic acids, sugar alcohols and furans (Ajao, 2014).

1.4.2 Cellulose and Fiber based Products

Although, initial integrated biorefinery proposals focused on recovery and increased value of the components that end up in spent liquors, recent developments have been increasingly concentrated on the use of cellulose in producing novel products and chemicals. Dissolving pulp, the most common type of speciality cellulose, can be used in the textile manufacturing. Kraft pulp can be converted into dissolving pulp by implementing a hemicellulose extraction operation (Mateos-Espejel, Radiotis, & Jemaa, 2013). The Canadian softwood fibers have been reported to have wide array of useful properties that are advantageous in fiber applications such as fiber glass, composite materials and replacement material in plastic making (Brown et al., 2011). The acid hydrolysis of

Kraft pulp can liberate nanocrystalline cellulose (NCC), which can be used in enhancing the properties of mixtures and composite materials (Xu, Q. et al., 2013).

1.4.3 Energy and Water for Kraft mill Forest Biorefineries

Most of the Canadian pulp mills are old and therefore have higher water and energy consumption than modern mills. The median energy consumption of Canadian bleached Kraft pulp mill is 16.27 GJ/ODt while it is 8.6 GJ/ODt for a modern mill (Natural-Resources-Canada, 2006). Therefore, most of the Canadian mills have considerable energy savings potential facilitated by internal energy and water recovery and, upgrading older equipment. The water consumption is related to the energy consumption of the plant. Reducing steam consumption will eventually reduce the water consumption. Therefore, apart from the standard steam and water saving methods such as internal heat recovery, water systems closure, equipment performance analysis and energy upgrading, studies also focused on combined methods of water and energy saving, which led to significant steam and water savings (Keshthkar, 2013; Savulescu, Kim, & Smith, 2005).

Due to high potential energy and water savings in Kraft pulping mills, there have been many efforts to internally supply the energy and water requirements of biorefinery plants. Marinova et al. (2009) suggested combined energy efficiency improvement strategies to provide the energy requirement for a biorefinery based on hemicellulose extraction. They used internal heat recovery, water systems closure, condensate recovery and absorption heat pump integration as energy saving strategies and managed to save 5.04 GJ/ADT energy. It has been shown that net steam demand increase can be reduced from 48 to 3 MW using process integration when near-neutral hemicellulose extraction is implemented in Scandinavian Kraft pulping mill (Lundberg, Axelsson, Mahmoudkhani, & Berntsson, 2012).

Similarly, energy optimization techniques have been suggested to save energy when lignin extracted from black liquor (Olsson, Axelsson, & Berntsson, 2006). Process integrated evaporation, which is to use available heat in the Kraft process to heat up the evaporated, have been used to create steam surplus in the process. There have been studies based on the improvements in condensers and in evaporator section to create an energy surplus (Wising, Algehed, Berntsson, & Delin, 2006). More efficient condensing turbines were used for electricity production. All these studies have a common element (resolving pinch violations) to optimize the heat exchanger network and to save energy.

1.4.4 Lignin Extraction from Black Liquor

Lignin extraction is an interesting option for an IFBR. Lignin extraction from black liquor has been practiced since decades and Kraft lignin is commercially available. Processes to extract lignin vary depending on the method of acidification, the principles of separation and the maturity of the technology. They are summarized in Table 1-2.

Table 1-2: A summary of lignin extraction methods from black liquor.

Method	Description
Lignin extraction by acid precipitation.	This method involves the pH reduction of black liquor using an acid such as CO_2 or H_2SO_4 to precipitate lignin. Different process schemes exists to increase the efficiency of the purification of lignin, demonstrated at pilot, demonstration and industrial scale (Gooding, 2012; Kouisni, Holt-Hindle, Maki, & Paleologou, 2012; Loutfi et al., 1991; Tomani, 2010).
Lignin extraction by membrane separation.	The process has been demonstrated at a pilot scale membrane module, however with limited lignin retention. The alteration of pH or temperature of black liquor was not necessary (Bhattacharjee, Datta, & Bhattacharjee, 2006; Joensson, Nordin, & Wallberg, 2008; Joensson & Wallberg, 2009; Wallberg & Joensson, 2006).
Lignin separation using electrochemical treatment.	The process also produces NaOH, H_2 and O_2 other than lignin. The process is investigated at laboratory scale. Work is required to determine the type of the electrolyte equipment and process conditions (Cloutier, Azarniouch, & Callender, 1993, 1994, 1995; Jin, Tolba, Wen, Li, & Chen, 2013).
Other methods.	Several other methods are available, including cellulosic enzymatic hydrolysis and organic acid precipitation to separate lignin. These methods are only demonstrated at laboratory scale (Argyropoulos, Sun, & Palu, 2002; Zhao & Luo, 2010).

Among the methods of lignin separation, acid precipitation is the most technically mature and it also has commercial applications. Uloth, and Wearing (1989a) reported that acid precipitation had

higher lignin yield and lower capital and operating costs in comparison to ultrafiltration. The impurities were also lower in the lignin extracted by acid precipitation. Lignin extraction by electrolysis is also an attractive process which has several benefits such as production of NaOH, H_2 and O_2 (Cloutier et al., 1993). Apart from direct lignin extraction, black liquor upgrading into different components such as gasification to syngas and pyrolysis to aromatics have also been reported in the literature (Maciel, Job, Mussel, & Pasa, 2012; Preto, Zhang, & Wang, 2008; St. Pierre, Duran, & van Heiningen, 2015).

1.4.5 Recovery Boiler Debottlenecking and Pulp Production Increase

Many relatively old Kraft pulping mills have been increasing their pulp production, but this is limited because they reach the maximum thermal capacity of the recovery boiler. By removing a fraction of organic load to the recovery boiler, the heat load can be reduced thereby debottlenecking the recovery boiler for additional pulp production capacity. Removal of heat load is more effective with lignin extraction due to its high calorific value, however, debottlenecking with hemicellulose extraction is also a possibility (Mao, Genco, Heiningen, et al., 2008). The early lignin extraction projects, therefore, were focused on incremental pulp production by recovery debottlenecking and combusting the recovered lignin in biomass boiler or lime kiln (Uloth & Wearing, 1989b)

1.4.6 Lignin Applications

Lignin has been used in industrial applications since decades. The first commercial lignins were the lignosulfonates from sulfite pulping industry. It was mainly used as additive to animal feed and road dust suppressant. After sulfite pulps were mostly replaced by Kraft mills, the use of Kraft lignin increased. Kraft lignin is the dominant portion of commercial lignin today, making up 89% of the total production. The current applications of Kraft lignin are as rubber reinforcers, activated carbon, carbon black substitute and phenolic resin component. The main producer of Kraft lignin in world market is the MeadWestvaco Corporation. Lignin is also obtained as a byproduct of organosolv pulping, called organosolv lignin (Kamm, Gruber, & Kamm, 2006).

Lignin has the potential to be used as carbon black substitute in rubber products, particularly in tire manufacturing. Lignin, after carbonization, has similar properties to carbon black in terms of structure and thermal conductance (Gindl-Altmutter et al., 2015; Snowdon, Mohanty, & Misra, 2014). The industrial carbon black prices vary between 1200 and 2200 US$/t, depending on the

application. Assuming lignin can be provided at 750 – 1000 US$/t price range, the north American tire manufacturing industry has the capacity to absorb 1 million tons of lignin per year (Brown et al., 2011).

Lignin can be used to partly replace the phenol in phenol-formaldehyde resins, which is used as an adhesive in wood composite applications. For plywood, lignin can replace up to 50% of phenol component. Kraft lignin can be converted to phenol-formaldehyde resins by copolymerization with phenol and formaldehyde in the presence of sodium hydroxide (Abdelwahab & Nassar, 2011; Danielson & Simonson, 1998). The use of lignin for phenol also reduces the formaldehyde consumption, providing added cost benefit. The phenol prices are in the range of 1,000-2,000 US$/t, with a North American demand of about 350,000 t/a for resin applications, this corresponds to lignin phenol-formaldehyde resin demand of 105,000 t/a at 30% substitution (Brown et al., 2011).

The use of lignin as a pre-curser for carbon fiber is, perhaps, the most investigated topic of the lignin applications in recent years. The carbon fibers are currently manufactured using petroleum derived polyacrylonitrile (PAN). The high cost of PAN has prohibited the wide spread use of carbon fibers, limiting their applications to most specialized uses that include aerospace, wind turbines, high end vehicles and sporting goods. Lignin can be used to produce carbon fibers by utilizing the melt spinning process and it has advantages over PAN in terms of structure, stabilization, carbon content and yield (Chien-Wei Chen, 2014; Norgren & Edlund, 2014). Moreover, supplying lignin as low cost PAN substitute will increase the demand, promoting the use of carbon fibers in low cost applications such as automobiles. Use of carbon fiber in automotive parts is highly desirable as it significantly increases the fuel economy due to light weight (Brown et al., 2011; Frank, Steudle, Ingildeev, Sporl, & Buchmeiser, 2014). The industry goal for producing lignin as carbon fiber precursor have been estimated at 1100 US$/t for PAN substitution, although current costs of lignin production is higher (Chien-Wei Chen, 2014).

The applications described above are considered as most promising, however, lignin has a wider variety of applications, for which the development is currently at preliminary level. Several researchers (Saito et al., 2013; Yang & Ragauskas, 2012) showed the feasibility of producing polyurethane thermoplastics and foams using lignin. Further applications from lignin include carbon nanotubes, waste water purification, bioplastics, nanocomposites, absorbents,

emulsification agents (He, He, Yang, & Lu, 2013; Norgren & Edlund, 2014; Stewart, 2008; Zhou, Qiu, Yang, Lou, & Ouyang, 2007).

1.4.7 The Properties of Lignin

The properties of lignin have been reported in terms of composition, structure including functional groups, thermal properties such as glass transition temperature, molecular weight, polydispersity and surface properties (Norgren & Edlund, 2014; Saake & Lehnen, 2000; Stewart, 2008). The required properties greatly depend on the application. Extensive research on the production of lignin carbon fibers have resulted in a preliminary set of required specifications for lignin feedstock and it is considered the most stringent conditions among the lignin applications. These specifications are shown in Table 1-3.

Table 1-3: The specifications of lignin feedstock for carbon fiber production as defined by Oak Ridge National Laboratory (ORNL) (Baker, 2011; Luo, Genco, Cole, & Fort, 2011)

Specification	**Value**
Ash content	< 0.1%
Lignin content	> 99%
Volatile material	< 5 wt% measured at 250°C
Particulate matter (none melting)	< 500 ppm (greater than 1 μm diameter)

Apart from these specifications, higher molecular weight with lower polydispersity is preferable for carbon fiber manufacture. The commercial Kraft lignin manufacturing processes have focused on reducing the lignin ash content, which mainly depends on the efficiency of the lignin washing step. They were able to reduce ash contents to below 0.1% by using improved washing techniques (Kouisni et al., 2012; Tomani, 2013).

1.5 Aggregation of Lignin in Aqueous Solutions

During the delignification step of the Kraft process, the aryl ether bond cleavages between lignin structures are attacked by hydrogen sulfide ions at high alkalinities, releasing Kraft lignin fragments. These lignin structures are soluble at high pH values due to dissociation of the phenolic

groups. The molecular weight of Kraft lignin can be in the range of ~150 - 200,000 (Gellerstedt & Henriksson, 2008; Norgren, Edlund, & Wågberg, 2002). The pK_a values of lignin phenol groups are in the range of 6.2 – 11.3, depending on the type and pattern of the phenolic structures (Ragnar, Lindgren, & Nilvebrant, 2000). Moreover, the apparent pK_a value of Kraft lignin molecules have been reported to be dependent on their molecular weight.(Norgren & Lindstrom, 2000b)

The colloidal stability of lignin in black liquor is maintained by the surface charges of lignin molecules, which exist due to dissociated phenolic and carboxyl groups at highly alkaline conditions. As the pH decreases, some of the phenolic groups get protonated, reducing the surface charge, destabilizing the colloidal system, leading to lignin aggregation. This phenomena is governed by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which describe the colloidal stability as a balance between electrical double layer (EDL) force and van der Waals attraction force.(Norgren et al., 2002; Norgren, Edlund, Wågberg, Lindström, & Annergren, 2001)

1.5.1 Aggregate Kinetics and Structure

High molecular Kraft lignin fragments, which form lignin macromolecules, are reported to be compact and spherical due to their cross linked structures. When the solution conditions worsen (increase of ionic strength or reduction of pH), they aggregate to form colloids particles or nuclei. The nuclei grow in size and number with time, forming final fractal lignin structures (Norgren et al., 2002). The aggregate structure of numerous materials have been found to be dependent on kinetics of aggregation based on two well defined regimes, diffusion limited cluster-cluster aggregation (DLCA) and reaction limited cluster-cluster aggregation (RLCA) (Lin et al., 1989). During DLCA, the repulsion forces between colloids are negligible, leading to rapid aggregation upon contact, forming loose and highly disordered structures. In RLCA regime, substantial repulsions between colloidal particles are present, making particles to collide several times before aggregating. More denser and compact aggregates are formed in RLCA regime. However, it should be noted that these regimes are defined for perikinetic aggregation, in which the particle collisions occur due to Brownian motion, and they are not strictly valid for orthokinetic aggregation, where particle collisions occur due to turbulence.

Norgren et al observed that lignin aggregation occur in both RLCA and DLCA regimes, depending on the solution conditions (Norgren et al., 2002). Figure 1-4 shows a Cryo-TEM image of a DLCA lignin aggregate with fractal dimension (d_f) of ~1.9 (Norgren & Edlund, 2014). These aggregates

have sizes ranging in the order of 100 nm up to 1-2 μm. They had fractal dimension values varying from d_f =1.9 to 2.45 (Norgren et al., 2002). Usually, the denser aggregates formed in the RLCA regime have fractal dimensions around d_f ~2.1 (Lin et al., 1989).

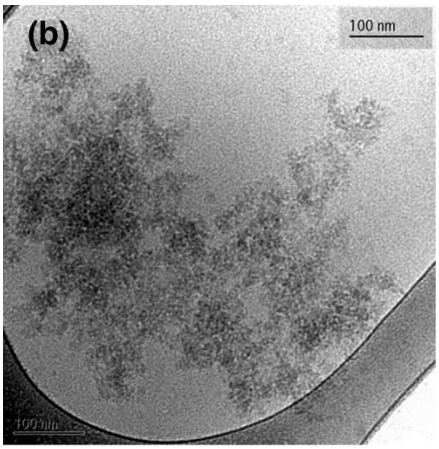

Figure 1-4 Cryo-TEM image of a DLCA fractal lignin aggregate (Norgren & Edlund, 2014). Reprinted with permission from Norgren, M., Edlund, H., Lignin: Recent advances and emerging applications. Current Opinion in Colloid & Interface Science 2014; 19 (5); 409-416. Copyright 2015 by Elsevier.

1.5.2 Effect of pH, Ionic Strength and Temperature

The main solution conditions that affect the colloidal stability are the solution pH, temperature and ionic strength, according to the DLVO theory. With decreasing pH, the phenolic and carboxylic groups of lignin get protonated, reducing surface charge and promoting the aggregation. The lignin phenol (coniferyl alcohol) groups have average pK_a values of about 10.2, but the apparent pK_a values of lignin molecules can be higher, depending on their molecular weight (Norgren et al., 2001; Norgren & Lindstrom, 2000a; Sri, Yasar, & Douglas, 1989). Hence, the high molecular weight lignin fractions start aggregating at higher pH values. This was confirmed by Zhu, and Theliander (2015), who reported that the average molecular weight decreases with increasing yield, i.e. decreasing pH and temperature or increasing ionic strength. As pH decreases further, the lignin fractions with relatively low pK_a values aggregate and precipitate out from the solution. By reducing the pH to very low values, most of the lignin can be precipitated out from the solution except acid soluble lignin, which are the lower molecular weight fractions of lignin (Rose, 2013).

The isoelectric point of Kraft lignin have been reported to be around pH 1.0 (Dong, Fricke, Moudgil, & Johnson, 1996).

Norgren et al. (2002) observed that Kraft lignin (Indulin AT) solutions reached the critical coagulation concentration at 1.3 M ionic strength (in terms of NaCl) for a pH of 10.5 and temperature of 70°C. The solubility of lignin decreases with increasing ionic strength and this promotes aggregation by increasing the quantity of precipitated lignin (Evstigneev, 2011; Theliander, 2010). Better aggregation of colloids in higher ionic strength solutions is due to the compression of the electrical double layer (EDL), which results in reduced electrostatic repulsion force. The thickness of the EDL is defined by the Debye length, which is inversely proportional to ion concentration and the valence of the electrolytes (Norgren et al., 2001).

The dissociation of a solute usually increases with increasing temperature. However, temperature also increases the dissociation of water increasing hydrogen ion concentration. This enhances the protonation of weakly dissociating lignin phenol groups, thus reducing the net dissociation and the surface charges. As a result, the pK_a values of lignin molecules increases with increasing temperature (Norgren et al., 2001) Although, higher pK_a values promotes aggregation, higher thermal energy content in EDL can increase the electrostatic repulsion forces, improving colloidal stability and lignin solubility (Lee, Stack, Richardson, Lewis, & Garnier, 2012). Increase in lignin solubility with increasing temperature has been reported (Evstigneev, 2011; Theliander, 2010; Zhu, Westman, & Theliander, 2014).

1.6 Acid Precipitation Process

Lignin recovery using acid precipitation has been practised for a long time. First patents for a process for acidification of black liquor and separation of lignin were proposed in 1940s (Tomlinson & Tomlinson, 1948). Numerous aspects of the process have since been investigated including, the yield, filtration and purification (Alen, Patja, & Sjöström, 1979; Kim, Hill, & Fricke, 1987; Uloth & Wearing, 1989b). The first detailed preliminary process designs, that can be found in the literature, were proposed by Loutfi et al. (1991). Their design included black liquor oxidation to minimize H_2S emissions, acidification with CO_2 to pH 8.5 to precipitate lignin particles, slurry ageing, slurry cooling and filtration and washing of the filter cake with H_2SO_4 and water. The lignin yield was 70% and the produced lignin had 1.5 % by wt. Na content. The motives of early lignin

precipitation projects were incremental pulp production by recovery boiler debottlenecking and use of the separated lignin as a fuel (Davy, Uloth, & Cloutier, 1998; Loutfi et al., 1991). Therefore, higher ash content was acceptable in the lignin product. Figure 1-5 shows a basic flow diagram of the acid precipitation process.

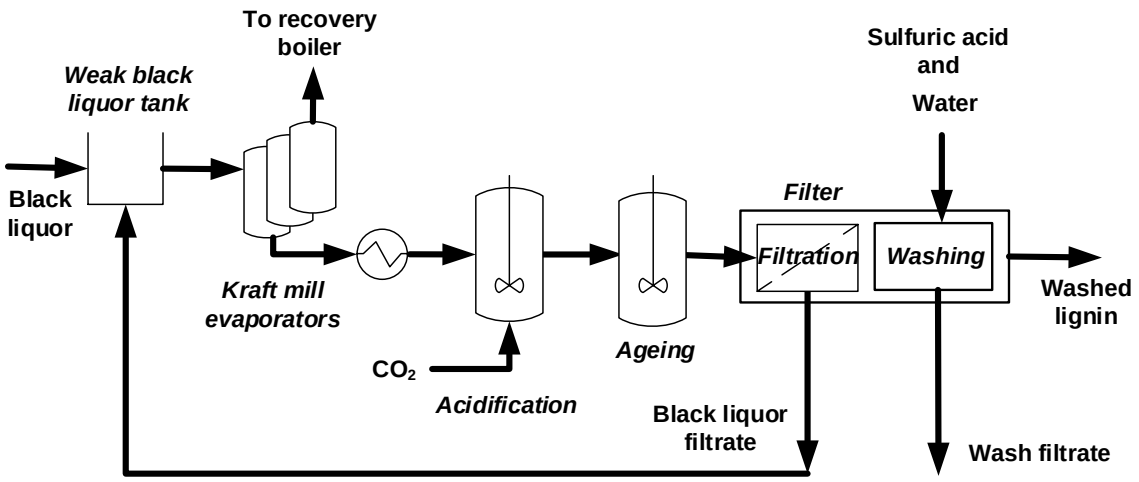

Figure 1-5: The main operations in the acid precipitation process

To use lignin as a feedstock for manufacture of value added chemicals and products, the purity has to be high, a low ash content in the separated lignin product is required. As a result, the recent developments in acid precipitation process have been focused on reducing the ash content of lignin. After lignin filtration, a re-slurry washing operation, has been proposed, to improve the efficiency of lignin washing, producing high purity lignin (Ohman, Wallmo, & Theliander, 2007a). Kouisni et al. (2012) proposed black liquor oxidation, before acidification, and reported that it improved the filtration, producing high purity lignin. Also, there have been efforts in precipitating lignin in liquid form at high temperature and pressure, decantation and purification, to produce low ash product (Lake & Blackburn, 2014).

1.6.1 Effects of Operating Parameters

The yield of lignin precipitation and the filterability of precipitated particles are highly dependent on the process operating parameters namely precipitation pH, temperature, ionic strength and mixing conditions. Although, it is possible to obtain higher yields by varying the operating

parameters, the precipitated lignin is readily filterable only in a narrow range of parameters (Loutfi et al., 1991; Ohman & Theliander, 2007; Wallmo, Richards, & Theliander, 2009).

The lignin yield increases with decreasing pH. Lignin starts precipitating when the pH is about10.8 and at pH as low as 3 up to 95% of lignin may be precipitated (Alen et al., 1979; Uloth & Wearing, 1989b). However, when the pH is below 8, the precipitated lignin is reported to be formed as fine particles, which is difficult to filter. Furthermore, formation of gases such as CO_2 and H_2S is observed at such lower pH values (Uloth & Wearing, 1989b). Loutfi et al. (1991) reported that pH 8-9 range results in easily filterable lignin. A more recent investigation by Kouisni et al. (2011) used pH 9.5 for the precipitation. Therefore, it can be concluded that pH 8-10 as the optimum range, which provide sufficient yield and easily filterable lignin.

As discussed in section 1.5.2, the yield has been reported to decrease with increasing temperature due to increased lignin solubility. However, low temperatures affect the filterability of the lignin. It has been reported that the precipitated lignin was difficult to filter if the temperature is below 70°C (Ohman & Theliander, 2007). The filterability of lignin increases with the temperature (Loutfi et al., 1991; Wallmo, Richards, et al., 2009). Optimum temperature of lignin precipitation is in the range of 80 to 85°C to provide good filterability. When the temperature is higher than 85°C lignin is precipitated as a soft and sticky material or large clumps which is difficult to filter (Fredrik & Theliander, 2007; Loutfi et al., 1991; Uloth & Wearing, 1989b). Howell, and Thring (2000) concluded that optimal temperature is around 80°C. This phenomena can be due to the fact that some of the lignin reaches glass transition temperature and is transformed into liquid form. The glass transition temperatures of Kraft lignin has been reported to be in the range of 70-170°C, depending on the molecular weight (Helander et al., 2013). Kouisni et al. (2011) used 70-75°C as the precipitation temperature range.

The black liquor solid content has also been reported to influence the acid precipitation process. The optimum solids concentration for lignin yield was 27% using pine Kraft black liquor (Alen et al., 1979). Higher solids content has been reported to decrease the lignin solubility and increase the yield (Evstigneev, 2011; Theliander, 2010). However, the solids concentration cannot be increased to more than about 42% as the precipitate is then formed as fine particles. The optimal solids concentration for Canadian wood species have been reported to be in the range of 30-40% (Loutfi et al., 1991). Table 1-4 summarizes the discussed ranges of operating parameters.

Table 1-4 : The ranges of pH, temperature and solid content reported in the literature.

Process condition	Range
pH	8 - 10.8
Temperature (°C)	70 - 85
Solid content (%)	27 - 42

Wallmo, Richards, et al. (2009) investigated the effect of ageing operation conditions on the lignin filtration. The filtration resistance decreased with increasing residence time and temperature, and decreasing agitation rate. They also noticed an increasing filtration resistance with increasing agitation rate during acidification step. A Rushton turbine was used in both acidification and ageing steps. Howell, and Thring (2000) performed lignin precipitation from hardwood black liquor using waste acid from ClO_2 generator. They varied the mixing speed during acid addition and concluded that lower mixing speeds (80 RPM) are preferable. None of these studies provided dimensions and characteristics of the mixing systems utilized for hydrodynamic characterization.

1.6.2 Filtration and Washing

As discussed in section 1.6.1, the filtration properties of precipitated lignin is largely influenced by the process operating parameters. The specific filtration resistances of lignin cake have been reported to be generally high, varying between 1E+10 and 1E+12 m/kg. The lowest filtration resistance recorded was about 8E+09 m/kg for softwood black liquors (Ohman & Theliander, 2007; Ohman, Wallmo, & Theliander, 2007b; Wallmo, Richards, et al., 2009; Wallmo, Theliander, Jonsson, Wallberg, & Lindgren, 2009). It is generally known that large particles with uniform size distributions are easily filterable, however, this has not received much attention in the literature. Ohman, and Theliander (2007) observed a decrease in lignin particle size with decreasing temperature.

The unwashed lignin cake has been reported to contain large amounts of chemically bound cations, particularly Na (10.8-16.4 % by wt.), and Sulfur around 2.0 % by wt. (Loutfi et al., 1991; Ohman & Theliander, 2006). This is expected since lignin precipitated at ~pH 9 still has negative surface charges, which attract counter ions such as Na. The procedure to wash lignin included washing of lignin filter cake with water or with a dilute acid (Alen et al., 1979; Kim et al., 1987; Loutfi et al.,

1991; Uloth & Wearing, 1989b). Kim et al. (1987) concluded that the lignin washed with H_2SO_4 contains less Na than lignin washed with HCl and therefore dilute H_2SO_4 is preferred for lignin washing.

Attempts to wash lignin using water only, have not been successful. Alen et al. (1979) washed lignin with water by using different wet lignin to water mass ratios and found that 3.8-5.4 % of sodium from black liquor was present in the lignin after washing. Uloth, and Wearing (1989b) found that the sodium content of lignin was 3.9% before washing and 0.3% after two washing steps using sulfuric acid. Kouisni et al. (2011) managed to reduce Na and ash content to 0.01% and 0.15%, respectively, by washing with 0.4 N sulfuric acid followed by 0.01 N sulfuric acid and water.

Ohman, and Theliander (2006) investigated the washing operation more thoroughly using semi-empirical models and experimental data. They found that, during cake washing, the ionic strength of the lignin filter cake reduces faster than the pH, creating ionic strength gradients in the cake. As discussed in section 1.5.2, lower ionic strength increases the lignin solubility, causing an increase in lignin concentration of the wash filtrate. With re-dissolution, the larger lignin aggregates can break into smaller aggregates, blocking the porous spaces of the cake making washing ineffective. To overcome the lignin loss and to obtain lignin with high purity, Ohman et al. (2007a) proposed a way to even out the gradient in ionic concentration and pH by re-dispersing lignin cake in acidic wash water at pH < 3.75 (re-slurry washing), filtering the new slurry and washing the new filter cake with acidic wash water (displacement washing).

Kouisni et al. (2012) reported that black liquor oxidation, prior to acidification, improved the filtration rate of lignin. They observed filtration rates of lignin obtained from oxidized and un-oxidized black liquor to vary in the ranges of 100-200 $kg/m^2.h$ and 0-100 $kg/m^2.h$, respectively. They employed displacement washing directly after filtration, without re-slurring the cake. The extracted lignin was of high purity, having ash contents in the range 0.1-0.7%. They attributed the improvement in filtration and washing to the desirable size distribution of precipitated lignin from oxidized black liquor. The black liquor oxidation has also been reported to reduce the CO_2 demand and sulfur gas emissions.

Lake, and Blackburn (2014) reported a method of separating lignin by precipitating it in the liquid form. It included the carbonation of black liquor at high temperature and pressure to precipitate

lignin entirely in liquid form and reacting liquid lignin phase with sulfuric acid at pH 2-3 to converting liquid lignin into large solid particles. The solid lignin particles were filtered and washed with acid to reduce ash content. The ash content of the final lignin was around 1%.

1.6.3 Commercially Available Versions of the Process

MeadWestvaco has been producing Kraft lignin under the commercial name Indulin®. The production of Indulin® reported is about 60 000 tons annually, with ash content of about 1.6% (Luo et al., 2011; Smolarski, 2012). The recent efforts in producing high quality lignin have resulted in several other process versions, which are commercially available.

The LignoBoost™ process employs the re-slurry stage (discussed in section 1.6.2) to produce low ash lignin. This process has been reported to generate lignin with 0.01-1% ash content and currently operates at demonstration and industrial scale (Tomani, 2013). The LignoForce™ process employs a black liquor oxidation technology and it has been reported to produce lignin with 0.1-0.7% ash content. It currently operates at demonstration scale (Kouisni et al., 2012; VanCaeseele, 2014). The SLRP™ (Sequential Liquid-Lignin Recovery and Purification) process utilizes a liquid lignin precipitation method. This process has been reported to operate at pilot scale in a continuous mode and produces lignin at 1% ash content. It was reported to require less capital and operating costs than the LignoBoost™ process (Gooding, 2012; Lake & Blackburn, 2014).

1.7 Implementation of Acid Precipitation Process in Kraft Pulping Mills

The acid precipitation process can be implemented within the multiple effect evaporator train of the Kraft mill liquor cycle, as shown in Figure 1-5. It receives black liquor usually at 30-40% solids content. After precipitation, the lignin lean black liquor filtrate and wash filtrates are recycled back. The lignin removal, chemical losses and additions and water addition, have been reported to have impacts on mill balances and operations (Vakkilainen & Valimaki, 2009; Wising et al., 2006). This is discussed in details in the following sections.

1.7.1 Impact on the Recovery boiler and Production Increase

Valimaki, Niemi, and Haaga (2010) found that the hearth heat release rate (HHRR) and adiabatic temperature (T_{ad}) of the recovery boiler are the critical parameters which determine the extent of feasible lignin extraction. They reported estimated reduction of higher heating value (HHV) of black liquor from 14.0 to 12.0 MJ/kg at 70% lignin extraction. To maintain the lowest limits for HHRR (2.5 MW/m^2) and T_{ad} (1450°C), the lignin extraction should not exceed 50%. The steam generation was reduced by 20% due to lower heat load to the recovery boiler. When the heat load was maintained at fixed value with a production increase of 25% to keep the steam production constant, the smelt flow rate from the recovery boiler was the limiting factor for a 50% lignin extraction. Vakkilainen, and Valimaki (2009) found that at 40% lignin removal, the superheating limit of the recovery boiler was reached and the minimum load that recovery boiler can run corresponds to 50% lignin removal. They reported an estimated reduction of HHV of black liquor from 14.1 to 9.9 MJ/kg at 90% lignin extraction. However, the lower furnace of the recovery boiler starts running with difficulties from a level of 30% lignin removal. They also studied the increase of the black liquor flow rate into recovery boiler (production increase) and concluded that 60% of lignin removal can be achieved before the superheating limit of the recovery boiler is reached.

Hamaguchi, and Vakkilainen (2010) reported an estimated reduction of HHV of black liquor from 14.3 to 13.1 MJ/kg at 30% lignin extraction and this reduced the steam production of the recovery boiler by 21%. It has been reported that the minimum HHV of black liquor for efficient recovery boiler operation falls in the range of 12.5 to 12.8 MJ/kg for Canadian Kraft pulping mills, allowing lignin extraction of 46-66 t/d from a softwood Kraft pulping mill with capacity of 400 adt/d (Benali et al., 2014; Perin-Levasseur, Z., Savulescu, & Benali, 2011). Loutfi et al. (1991) reported a maximum 9.5% lignin extraction ratio, which corresponds to 57 t/d lignin removal from a mill running at 770 adt/d capacity.

Vakkilainen, and Valimaki (2009) and Hamaguchi, and Vakkilainen (2010) reported that the air requirement and flue gas production decreases with decreasing HHV, allowing more black liquor to be burned at lower HHV. This eliminates the need of significant retrofits in flue gas side of the recovery boilers burning lignin lean black liquor at higher flow rates.

It has to be emphasized that the above reported lignin extraction ratios and HHV reduction should not be taken as absolute values but rather as trends, since those values are dependent on the black liquor composition.

1.7.2 Impacts on the Evaporator Train

The multiple effect evaporator steam demand has been reported to increase when the wash filtrates from the acid precipitation process are recycled. Hamaguchi, and Vakkilainen (2010) estimated this to be 3% increase at 30% lignin extraction for Lignoboost^{TM} process. The viscosity of black liquor has been reported to reduce with lignin removal, with reductions up to 90% can be achieved at solids contents above 40% (Moosavifar, Sedin, & Theliander, 2009; Moosavifar, Sedin, & Theliander, 2006). A viscosity decrease in the range 10-90% can lead to increase in heat transfer coefficients of about 4-124 %, thus making positive reductions in heat transfer surface areas. A decrease in boiling point elevation has also been observed at low lignin contents. Therefore, reduction in viscosity and boiling point elevation could lead to possible lower heat transfer area in the evaporators, thus increasing the available capacities.

Benali et al. (2014) reported the increase in inorganics components (Na_2CO_3 and Na_2SO_4) in black liquor, which can result in increased fouling. They suggested careful monitoring of carbonate to sulfate ratios and critical solids concentrations in the evaporator train during lignin precipitation.

1.7.3 Impacts on Mill Total Energy Balance

As discussed in sections 1.7.1 and 1.7.2, the lignin extraction decreases recovery boiler steam production and increases the evaporator train steam demand. Hamaguchi, and Vakkilainen (2010) performed an energy balance on a modern Kraft pulping mill with integrated lignin precipitation process. They estimated a 21% reduction in recovery boiler steam generation with 10.2% increase in recovery boiler capacity in terms of total solids flow, for 30% lignin extraction. The electricity production decreased by 54 MW. In a separate study, (Olsson et al., 2006) reported 19-30% decrease in mill power generation, when lignin corresponding to 326-500 GWh/a was removed.

1.7.4 Impacts on Chemical Balance

The implementation of an acid precipitation process in a Kraft pulping mill have been reported to disrupt the sodium and sulfur (Na/S) balance of the liquor cycle (Loutfi et al., 1991; Tomani, 2010;

Wising et al., 2006). The precipitated lignin contains significant amount of Na ranging from 10.2 to 16.4% by wt., removal of Na is achieved by washing with acid (Loutfi et al., 1991; Ohman & Theliander, 2006). The wash filtrates contain large amounts of Na, which needs to be recycled back to the liquor cycle. However, the total sulfur in wash filtrates can exceed the mill sulfur requirement, thus disrupting the sulfur balance.

Wising et al. (2006) reported that the re-alkalization of spent liquor from an acid precipitation process would be necessary before returning it to evaporators as low alkali content, which can result in increased black liquor viscosity. They suggested that re-alkalizing of spent liquor with white liquor, which increases the processing demand in the lime kiln. (Axelsson, Olsson, & Berntsson, 2006) and (Loutfi et al., 1991) discussed the impact of acid precipitation process on a Kraft mill chemical balance and suggested that the sulfur added from the wash filtrates can be best purged from the Kraft mill as recovery boiler electrostatic precipitator (ESP) dust. To make up for the Na loss, NaOH has to be added. Loutfi et al. (1991) suggested adding Na_2CO_3 to compensate for Na loss, however with an increase in causticizing section loading.

Benali et al. (2014) discussed the changes in the black liquor chemical composition resulting from the implementation of the acid precipitation process, predicting impacts on the evaporator train. However, mill wide chemical balances have not been performed. None of the above studies provided detailed Na/S balance estimates to evaluate the chemical additions, purges and changes in the loads to chemical recovery operations.

1.8 Process integration opportunities within Kraft process

The lignin extraction reduces the steam production in the recovery boiler and increase evaporator steam demand, creating net energy deficit in the Kraft process, unless the mill has a surplus of energy. Moreover, the acid precipitation process requires chemicals (CO_2 and H_2SO_4) and water to operate. This section discusses the reported work on mass and energy integration of acid precipitation with the receptor Kraft pulping mill.

1.8.1 Energy Integration

The energy optimization technologies, including pinch analysis, have been utilized to identify the potential energy savings in the Kraft pulping mills to address energy deficits created by lignin

removal. Laaksometsä, Axelsson, Berntsson, and Lundström (2009) showed that energy savings of 4.2 GJ/adt identified by pinch analysis was sufficient to provide increased energy demands created by lignin extraction, in an eucalyptus Kraft pulping mill. Olsson et al. (2006) compared lignin extraction versus increased power generation to export surplus steam from a Kraft pulping mill. They concluded that lignin has to be priced above traditional biofuel use in order to be competitive. Benali et al. (2014) showed that steam demand can increase by 27%, depending of the amount of lignin extracted and the pulp production increase. They proposed 14.1 MW steam savings, based on pinch analysis to address the increased demand, for a Canadian Kraft pulping mill. Hamaguchi, and Vakkilainen (2010) proposed steam production increase in biomass boiler to address the energy deficits created by lignin extraction.

1.8.2 Water and Chemical Integration

The water demand in the acid precipitation process is mainly earned by lignin washing and cooling of the incoming black liquor. Benali et al. (2014) estimated this to be 2.5% increase in total water demand for a 50 t/d lignin plant. They obtained 14.8% savings in water consumption by applying water pinch analysis, demonstrating the feasibility of internal water supply.

1.8.2.1 Internal CO_2 supply

Several studies suggested that the cost of CO_2 is the largest operating cost of the lignin precipitation plant and therefore using flue gas from lime kiln or recovery boiler to supply CO_2 for the precipitation process could improve its economics (Loutfi et al., 1991; Olsson et al., 2006; Tomani, Axegard, Berglin, Lovell, & Nordgren, 2011). Benali et al. (2014) analyzed CO_2 capture from flue gases using monoethanolamine (MEA) for lignin precipitation and concluded that the operating costs were prohibitive ($17 million/a). The annualized capital costs varied from 4,980 – 1,531,000 $/a without considering the flue gas cleaning and supplementary equipment costs. The carbon capture process proposals, found in the literature, have been economically evaluated at the scale of power plants, which emit large quantities of CO_2. The lignin plants have capacities of about 50 t/d with 12-15 t/d CO_2 demand. Therefore, the differences in economies of scale have to be taken into account during the analysis.

Wallmo, Richards, et al. (2009) concluded that the use of pure CO_2 is not essential for precipitation. They conducted studies with CO_2 mixtures at 99.7%, 50%, 15% concentrations and observed

variations in acidification kinetics. When 99.7% CO_2 is used, it took around 25 min to reach pH 9 while it took around 60 min to reach pH 9 when 50% CO_2 is used. They did not observe differences in filtration resistance of lignin cakes precipitated with dilute CO_2. The cake washing or economic analysis have not been performed.

1.8.2.2 Internal H_2SO_4 supply

ClO_2 is required by most bleaching sequences of the mills that produce bleached pulp. Due to highly unstable nature of ClO_2 it is usually produced on site. It is manufactured by reduction of sodium chlorate ($NaClO_3$) with suitable reducing agent in a concentrated acidic medium. Some variations of the process produce Generator Waste Acid (GWA), which consist of H_2SO_4 and Na_2SO_4. Several studies suggest the use GWA for lignin precipitation (Davy et al., 1998; Howell & Thring, 2000). These studies consider the use of GWA for precipitation operation and not for the washing as it contains considerable amounts of Na_2SO_4. The use of GWA for acidification of black liquor is limited by the availability as well as impact on the Na/S balance.

Addition of GWA to black liquor can easily exceed the limit of sulfur in the liquor cycle. This forces a purge of additional sulfur and consequently increases caustic demand. Therefore, the recent studies and commercially available processes use CO_2 for black liquor acidification (Kouisni et al., 2012; Lake & Blackburn, 2014; Ohman & Theliander, 2006; Ohman et al., 2007a; Theliander, Ohman, Axegard, & Tomani, 2005). The use of salt cake or GWA can be an interesting option to provide H_2SO_4 for lignin washing, although, it needs to be purified. Several commercial processes are available for purification of GWA (Cloutier & Beaudoin, 2014; NORAM-Engineering, 2015).

1.9 Critical Review

As discussed in the presented literature review, there is considerable amount of work and knowledge available regarding the development, implementation and process integration of acid precipitation based lignin biorefineries in Kraft pulping mills. The process development efforts have been concentrated on analysis of lignin yield and filtration with varying operating parameters and washing step improvement (Kouisni et al., 2012; Ohman et al., 2007a; Theliander, 2010; Wallmo, Richards, et al., 2009). The implementation studies have focused on recovery boiler and energy balance impacts and pulp production increase (Vakkilainen & Valimaki, 2009; Valimaki et al., 2010 ; Wising et al., 2006) while the process integration has dealt with estimation of energy demands and compensation using steam savings projects (Axelsson et al., 2006; Laaksometsä et al., 2009). There is a lack of studies in the following areas.

- The studies on energy balance impacts of the implementation and energy integration potential between biorefinery and Kraft pulping mill have mostly been performed on actual or model Scandinavian Kraft pulping mills. There is a lack of investigations assessing the impacts lignin precipitation on the steam and power balance of the Kraft mill and addressing the energy deficits in the Canadian context.
- The disruption of the chemical balance of the liquor cycle caused by lignin precipitation have been reported in the literature. There have been qualitative suggestions on re-adjusting the balance. However, there is a lack of studies with detailed Na/S balance of the liquor cycle in a Kraft mill with lignin precipitation. Furthermore, computer modeling of acid precipitation process, which can largely assist chemical balance estimations, has not received much attention. Also, there are no clear guidelines on balancing the Na and S of a liquor cycle with integrated lignin biorefinery.
- While, there are many studies investigating the effect of operating parameters on the filtration and yield of acid precipitation, systematic parameter investigation has received less attention. As a result, studies on the process optimization or parameter identification could not be found in the literature.
- The hydrodynamic conditions during colloidal aggregation and particle growth have been reported to shape the particle size and structure in coagulation and flocculation processes.

However, this important aspect has not received much attention in the literature on lignin precipitation processes. There is clearly a lack of studies investigating the effects of hydrodynamics on lignin precipitation and, filtration and washing performances.

- It has been reported that CO_2 is a major operating cost factor in lignin precipitation plants. However, there is a lack of studies determining the effects of using flue gases for the black liquor acidification and its effect on filtration and washing. The economic attractiveness of such proposals have not been determined.

The treatment of above mentioned points could considerably improve the design and integration of lignin biorefineries. The success of the commercial implementation of biorefineries depends on the cost effectiveness and environmental sustainability. Achieving that requires optimal biorefinery design and implementation. In addition, it is required to determine the opportunities for process integration in terms of energy and chemicals and, their profitability. This was achieved in this thesis. The knowledge gaps identified were treated.

Chapter 2 OBJECTIVES, METHODOLOGY AND THESIS ORGANISATION

The primary objective of this work was to investigate the cost efficient and sustainable development and integration of acid precipitation based lignin biorefineries in Kraft pulping mills. Although there is a considerable amount of previous work on the subject, several knowledge gaps, which deserve investigation, were identified and formulated as specific objectives. At the conclusion of the project, simulation models, strategies for biorefinery implementation and integration, and process improvement guidelines were delivered. The understanding and knowledge gained in this work should lead to development of cost effective and sustainable lignin biorefineries integrated in Kraft pulping mills.

2.1 Specific objectives

The following specific objectives have been defined for this project.

- To assess the impacts of acid precipitation process on the energy balance of a representative Canadian softwood Kraft pulping mill and to propose mitigation measures.
- To develop models and guidelines for performing chemical balances for a Kraft mill with integrated lignin biorefinery.
- To determine the effect of mixing hydrodynamics on properties of precipitated lignin particles and filtration performance.
- To systematically investigate and optimize the operating conditions of acid precipitation process.
- To determine the feasibility and economic attractiveness of using lime kiln flue gases for precipitation of lignin.

2.2 Methodology

In this work, the scope of the lignin biorefinery was limited to the extraction stage consisting of precipitation, filtration and washing. Further conditioning and conversion operations are required to convert lignin as feedstock for value added products. However, these operations are highly

dependent on the final valued added product, which have not been defined in this project. Figure 2-1 shows the overall methodological approach of the project.

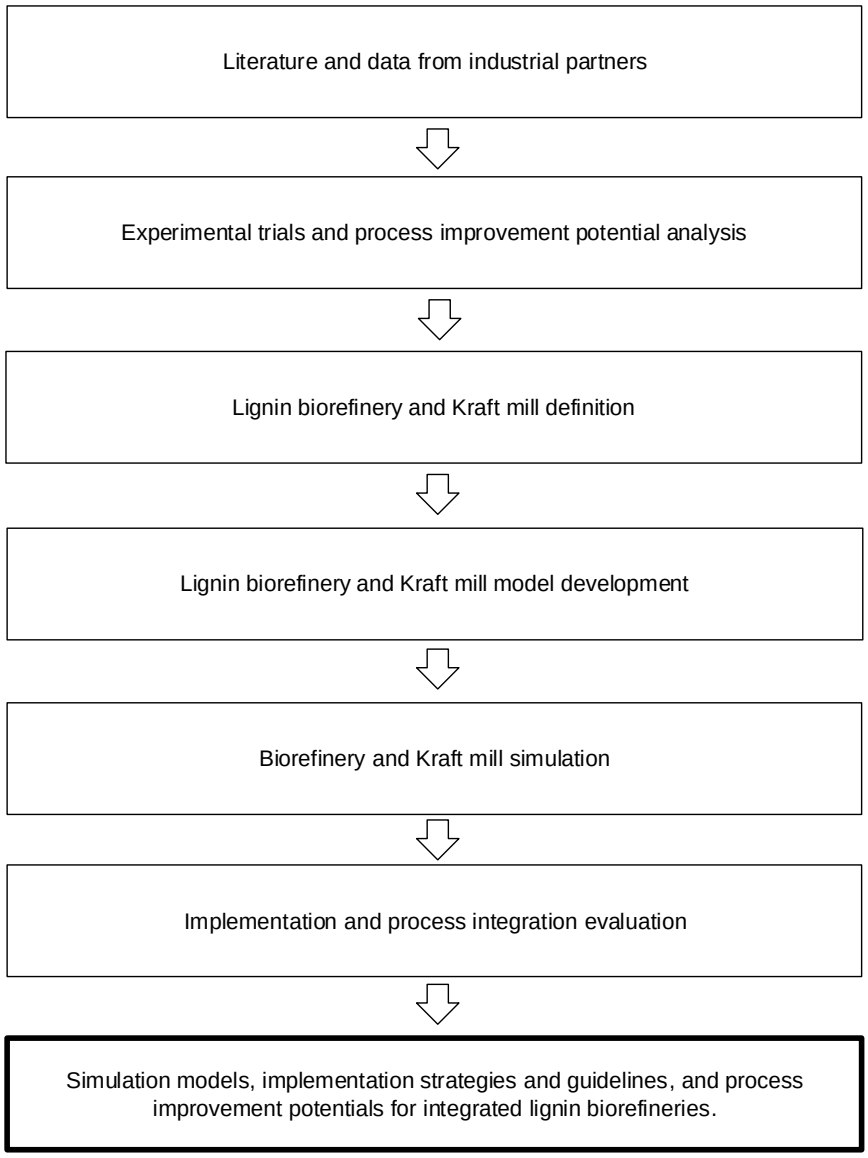

Figure 2-1 : Overall methodological approach

The data for the definition of a lignin biorefinery were obtained mainly from pilot scale lignin precipitation trials, provided by the industrial partners. It was based on the acid precipitation process with a single filtration and washing step. Data from literature and laboratory trials have also been used. Simulation models for the lignin biorefinery and Kraft pulping mill were developed. Aspen Plus®, CadsimPlus® and Excel™ were used as simulation software. Two Kraft pulping mills were used in the study, a representative Canadian softwood bleached Kraft pulping mill with 750

adt/d capacity and a softwood bleached Kraft pulping mill with 285 adt/d capacity, which is located in eastern Canada. The biorefinery implementation has been performed according to proposed guidelines and strategies. Process integration measures in terms of energy and chemicals were proposed.

During the process development phase, the improvement and optimization of the process, which leads to cost effective process designs, were experimentally investigated. All the experimental trials were conducted at laboratory scale using up to 1.8 L black liquor quantities. The possibility of improving lignin filtration and washing by manipulating mixing hydrodynamics has been studied. Systematic optimization of process operating parameters to obtain higher yield and filtration performance have been conducted. Black liquor samples from three different Canadian softwood Kraft pulping mills were used in the experimental investigations. Fundamental understanding of lignin aggregation and growth as well as process performance behavior were gained.

2.3 Organisation of the Thesis

The following five chapters present the results of this thesis. In chapter 3 (Article 1), the energy impacts of implementing lignin biorefinery in Kraft pulping mill is presented. The energy deficits and demands were quantified and mitigation measures using process integration have been performed. This article has been published in J-FOR, The Journal of Science and Technology for Forest Products and Processes in 2012.

Chapter 4 (Article 2) presents the process modelling and chemical balances of implementing lignin biorefinery in a Kraft pulping mill. Process modelling of a lignin biorefinery and liquor cycle of the Kraft mill incorporating chemical balances have been conducted. The simulation models have been utilized in analysing the Na/S balances of the liquor cycle. Strategies and guidelines for lignin biorefinery implementation have been proposed. This article has been submitted to Industrial Chemistry and Engineering Research journal in July, 2015.

Chapter 5 (Article 3) treats the feasibility of improving lignin filtration by manipulation of mixing hydrodynamics. In this article, the effects of hydrodynamic conditions during lignin precipitation on the aggregation and growth of the lignin flocs has been investigated. Differences in size and shape of lignin flocs, that produced considerable improvements in lignin filtration, were observed.

The optimal hydrodynamic conditions for aggregation and growth of lignin particles have been defined. This article will be submitted to Chemical Engineering Research and Design journal.

Chapter 6 presents an optimization study of process operating parameters of the acid precipitation to obtain higher filtration performance and yield. The critical operating parameters have been identified and behavior of process performance with varying operating parameters have been discussed. Also, the optimal ranges of operating parameters and the effect on process economics are discussed. This chapter will be formulated as an original research paper.

Chapter 7 treats the technical feasibility and economics of using lime kiln flue gases for precipitation step of lignin biorefinery. The feasibility have been determined for several types of black liquor and process simulation and economic analysis have been conducted.

Chapter 8 summarizes the results of the work in general. In this chapter, connections between different results have been made. Limitations and improvements of the current work has been discussed.

In chapter 9, general conclusions and recommendations for future work are presented. The original contributions have been listed.

Chapter 3 ARTICLE 1: LIGNIN RECOVERY BY ACID PRECIPITATION IN A KRAFT MILL: AN ENERGY PERSPECTIVE

Miyuru Kannangara, Mariya Marinova, Louis Fradette, Jean Paris
Research Unit on Energy Efficiency and Sustainable Development of the Forest Biorefinery, Chemical Engineering Department, Polytechnique Montreal, C.P. 6079 succ. Centre-Ville, Montréal (QC) Canada H3C 3A7

ABSTRACT

Lignin, which is currently burned in the Kraft mill recovery boiler, can be recovered and converted to a broad spectrum of bio-based products using the acid precipitation process. In this process, a part of the black liquor is extracted from the evaporator train and treated with CO_2 to precipitate the lignin. The precipitated lignin is washed with H_2SO_4 and water to remove impurities. Removal of lignin and recycle of dilute liquor back to the mill affect the Kraft mill energy balance. The objective of this study is to quantify the impact of lignin extraction on the energy balance of the Kraft mill. The study mill is a representative Canadian bleached Kraft pulp mill with a pulp production capacity of 750 adt/d. The acid precipitation process is based on the LignoForce System^{TM} process developed by FPInnovations. It has been implemented in the model Kraft mill, and mass and energy balances have been performed on the integrated biorefinery plant and receptor mill. In the case of 15% lignin extraction from the m ill, the recovery boiler steam production was decreased by 13.5%, and evaporator steam demand was increased by 2.4%–14.6%. The steam and power deficits created by lignin extraction were estimated. Strategies including steam reduction measures, energy efficiency improvement, and increased use of biomass fuel have shown that addressing energy deficits internally is possible.

KEYWORDS

Lignin, acid precipitation, Kraft mill, integration, energy balance

3.1 Introduction

Lignin is considered to be the second most abundant naturally occurring polymer on Earth. In Kraft pulping, it is selectively removed from wood and burned in the recovery boiler to produce steam

and power for the process. Instead of using lignin for energy generation, it can be extracted and converted into a broad spectrum of bio-based products such as phenolic resins and carbon fibres, which provide higher profit margins. Furthermore, removal of lignin can serve to offload a recovery boiler which has reached its thermal design limits, thus removing a major bottleneck to increasing pulp production. Several liquor have been proposed, among which acid precipitation is currently being commercialized. In this process, black liquor is acidified to precipitate lignin. Lignin is separated and then washed with dilute sulphuric acid to remove impurities and to produce purified lignin for further processing. Among the commercial variations of the acid precipitation process are the LignoForceSystem™ process developed by FPInnovations and the Lignoboost™ process developed by Innventia (Kouisni et al., 2011; Tomani, 2010).

The removal of lignin reduces the HHV of black liquor and therefore decreases recovery boiler steam production. This affects the overall steam and power balance of the mill and creates steam and power deficits. Furthermore, recycle of dilute liquors to the mill chemical recovery system increases the energy demand for the evaporator train (Perin-Levasseur, Z. et al., 2011; Tomani et al., 2011; Wising et al., 2006). As measures to address these energy and power deficits, process-integrated evaporation, steam savings based on pinch analysis, evaporator and equipment upgrades, and use of condensing turbines have been proposed (Axelsson et al., 2006; Laaksometsä et al., 2009; Olsson et al., 2006).

The objective of this study is to quantify the impact of lignin extraction on the energy balance of a representative Canadian Kraft mill. Energy production is analyzed in terms of steam and power, and strategies to address steam and power deficits are proposed.

3.2 Lignin extraction process integrated into a Kraft mill

The receptor mill under study is a representative Canadian bleached Kraft mill with a pulp production capacity of 750 adt/d. This mill is used as the reference Kraft process for integration of the lignin biorefinery. The digester processes softwood at a yield of 46%. Pulp is washed, bleached, and dried to produce market pulp. Black liquor produced during washing is concentrated in a six-effect evaporator train and combusted in the recovery boiler. Mill steam and power demands are covered entirely by recovery-boiler and biomass-boiler energy production. High pressure steam produced in the boilers is used to generate power for internal use in the mill. Medium- and low-

pressure steam produced in the turbines is used to cover the steam requirements. CADSIM Plus® is used to simulate the mill. This is a process simulator, specialized for pulp and paper processes, which is widely used in Canada. The main parameters of the Kraft mill can be found in Table 3-1.

Table 3-1: Main parameters of the Kraft mill

Parameter	**Value**
Process yield (%)	42
Digester yield (%)	46
Lignin in black liquor (% of DS)	40
Steam production (GJ/adt)	18.7
Steam consumption (GJ/adt)	17.9
Electricity production (MW_e)	22
Electricity consumption (MW_e)	22
Fresh-water consumption (m^3/adt)	40.1

The acid precipitation process used is based on the LignoForceSystem™ process developed by FPInnovations and currently commercialized by NORAM (Kouisni et al., 2011). In the process, the black liquor is pretreated with O_2, and the pH of the black liquor is reduced by CO_2 injection. Due to this pH reduction, the lignin in the black liquor solution is coagulated and precipitated. The resulting slurry with the precipitated lignin is passed through a filter press to separate the lignin. This filtered lignin contains high levels of ash and sodium and hence is not suitable for further processing. Therefore, the lignin is washed with dilute sulphuric acid and water to remove these impurities. Table 3-2 shows the main parameters of the acid precipitation-based lignin biorefinery.

Table 3-2: Key parameters of the lignin biorefinery

Parameter	Value
Process yield (%)	67
CO_2 demand (t/t lignin)	0.25
H_2SO_4 demand (t/t lignin)	0.35
Water demand (t/t lignin)	12.5
Lignin output (t/d)	73
Lignin purity (%)	98

3.3 Extraction and recycle of black liquor

Approximately 22% of the black liquor was diverted after the 3rd effect of the evaporator train to achieve 15% lignin extraction. The spent liquor and washing filtrates were recycled back to the Kraft recovery cycle to minimize chemical losses. The washing filtrates contain predominantly water, sulphuric acid, and other Kraft pulping chemicals in small amounts. Therefore, recycling the dilute filtrates adds an extra load to the evaporator train. This recycle is performed according to one of two configurations. In the first, the spent liquor and filtrates are recycled to the weak black liquor tank, where they are mixed with the rest of the dilute black liquor. In the second configuration, the spent liquor and filtrates are introduced at the entry of the 2nd effect of the evaporator train (Figure 3-1).

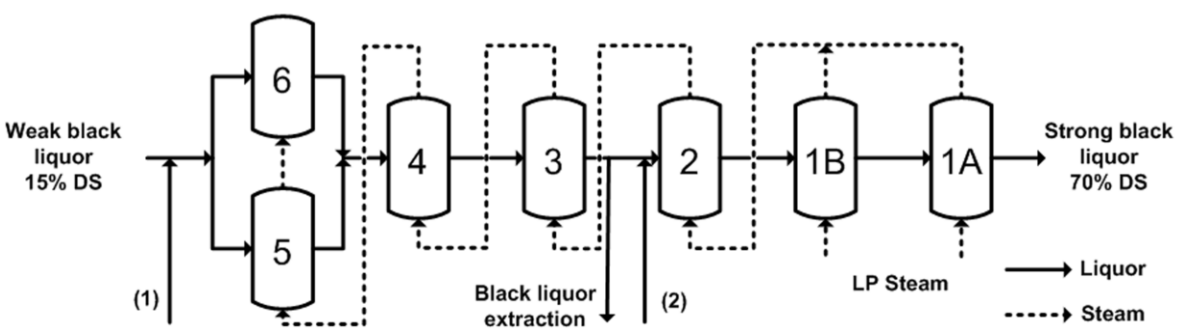

Figure 3-1: Implementation of lignin extraction in the evaporator train of the Kraft mill according to configuration 1 and 2.

The amount of recycled filtrate was varied to observe the impact on evaporator steam demand. Mass and energy balances of the integrated biorefinery and Kraft mill were performed, and the variations in mill energy production and consumption were analyzed. The power and steam deficits within the mill created by lignin removal were determined.

3.4 Impacts on mill energy balance

3.4.1 Impacts on the Evaporator Train

The increase in steam demand for the evaporator train is higher for configuration 1. Without any filtrate recycle, the increase is 7.3% for configuration 1 and 2.4% for configuration 2 (Table 3-3). When spent liquor is recycled back to the weak black liquor tank, it increases the amount of black liquor flowing through effects 3, 4, 5, and 6. Due to this increased flow rate, steam consumption is increased. However, this is avoided in configuration 2 because the spent liquor is recycled to the downstream black liquor flow. Furthermore, steam demand gradually increases with the amount of filtrate recycled. At least some of the filtrates have to be recycled to recover available chemicals and organic material. However, excessive recycle increases the evaporator steam demand significantly and can also disrupt the Na/S balance of the mill due to the addition of extra S with the sulphuric acid. The disruption of the Na/S balance is not discussed in this paper.

Table 3-3: Increase of evaporator steam demand with rate of filtrate recycle for given configurations

Filtrate recycle (t/t of lignin)	**Evaporator steam demand increase (%)**	
	Configuration 1	**Configuration 2**
0	7.3	2.4
2	9.7	4.8
4	12.2	7.3
6	14.6	9.7

Lignin extraction positively affects the heat-transfer coefficient of black liquor due to reduced viscosity (Moosavifar et al., 2009). The increase in the heat-transfer coefficient results in a decrease

in the evaporation area required for a given amount of evaporation. Therefore, moderate increases in evaporation steam demand should be possible without upgrading evaporator capacities.

3.4.2 Impacts on the Recovery boiler

In the case of 15% lignin removal, the black liquor HHV is reduced from 13.9 MJ/kg to 13.1 MJ/kg. When more lignin is removed from black liquor, HHV is further reduced (Figure 3-3). The reduction in HHV is basically due to the change in black liquor composition caused by lignin removal. Black liquor flow to the recovery boiler is also decreased. At 15% lignin extraction, recovery boiler steam production is reduced by 13.5%. In addition, a slight decrease in boiler efficiency from 57% to 55% is also observed. When lignin is extracted, the organic-to-inorganic ratio of black liquor is reduced, which results in reduced efficiency. This further decreases the steam and power production capacity of the mill.

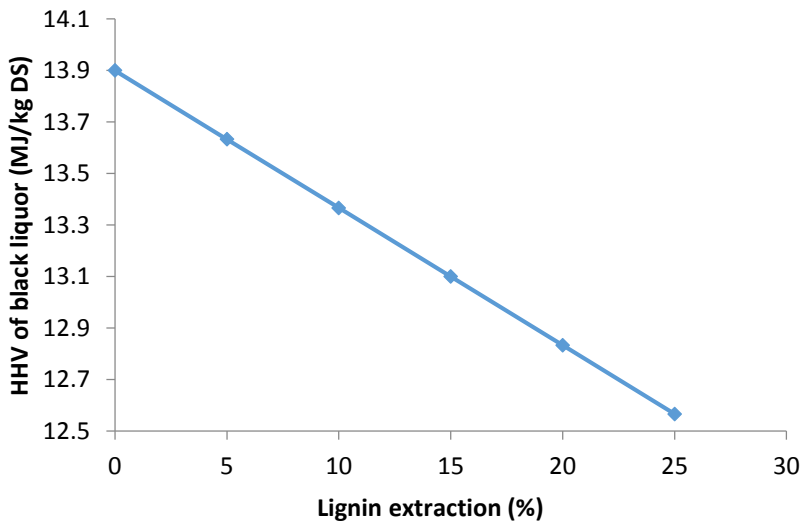

Figure 3-2: Reduction of HHV of black liquor with the extraction of lignin

Mill steam production is reduced by 1.6 GJ/adt after lignin extraction. Mill steam consumption is increased by 0.3 GJ/adt, creating a net steam deficit of 1.9 GJ/adt. Furthermore, power production is reduced by 1.9 MW_e (Figure 3-4). Power consumption of the lignin extraction process is estimated to be approximately 0.2 MW_e. This results in a net power deficit of 2.1 MW_e.

In the case where the recovery boiler is overloaded, production can be increased by approximately 15% when lignin is extracted. The steam and power demands are assumed to increase

proportionally with pulp production. This increases the net steam deficit to 3.0 GJ/adt and the power deficit to 3.3 MW_e. These values have been estimated by assuming that recovery-boiler and biomass-boiler steam production remain the same for the mill with 15% increased production and the reference mill.

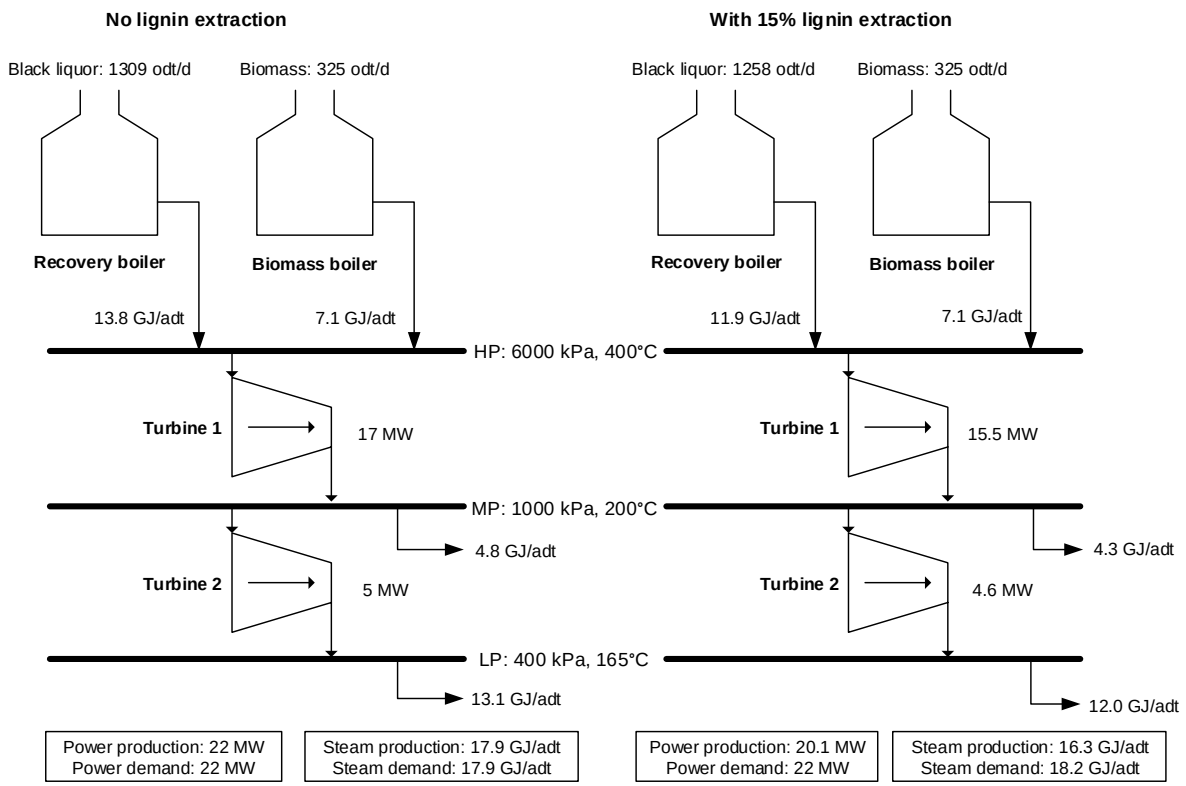

Figure 3-3: Impacts of lignin extraction on the energy balance of the mill

3.5 Addressing the energy deficits

A methodology based on constrained data extraction, in which steam is categorized as replaceable or non-replaceable, has been used to collect data from the mill for pinch analysis (Kamal, 2011). In this method, the non-replaceable steam is accounted for in the cold composite curve so that it is added to the minimum heating requirement. Lignin extraction in the integrated reference mill was used for pinch data extraction. The composite curves have been created to identify steam-saving potentials and projects (Figure 3-4).

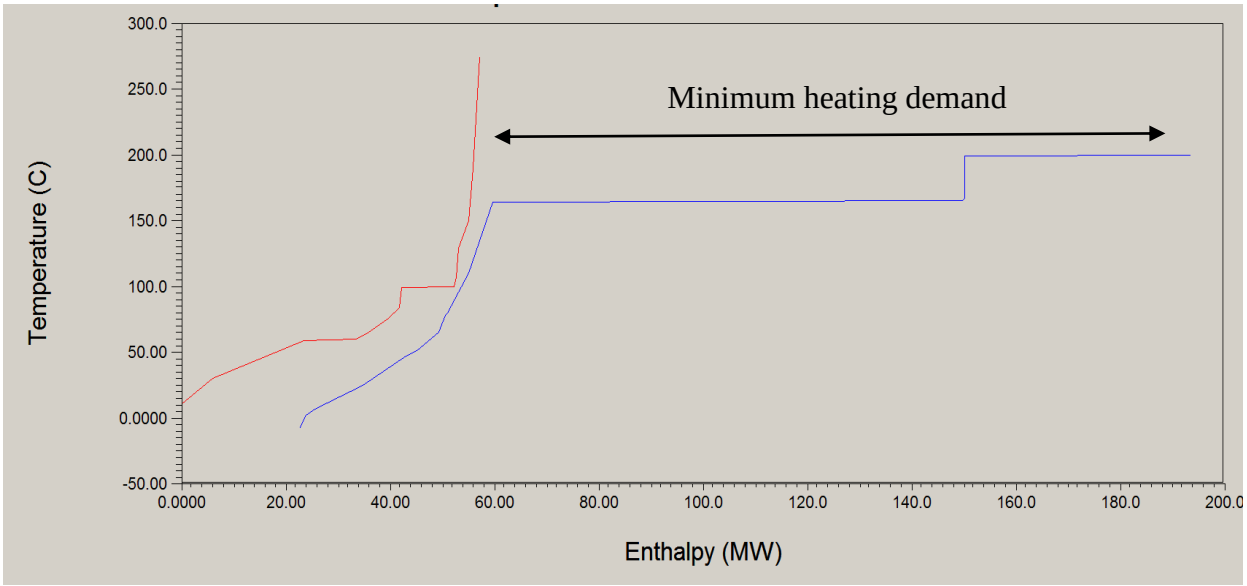

Figure 3-4: Composite curves generated by pinch analysis for the reference mill.

According to pinch analysis, the minimum heating demand is 14.9 GJ/adt, which is provided by LP and MP steam. Several projects have been proposed to solve pinch violations and to avoid non-isothermal mixing (Table 3-4). The LP steam demand can be reduced by a total of 3.1 GJ/adt by implementing these projects. The implementation of the proposed projects decreases the LP steam demand by 3.1 t/d, which represents a 17% reduction in total steam demand.

Table 3-4: List of proposed steam saving projects

Projects	**Savings (MW)**
Recausticizing	1
Boiler air (pre heating)	10
Dearator (make up water)	5
Hot water production (Non isothermal mixing)	6
Washers (Non-isothermal mixing)	5
Total	*27*

Although the implementation of steam saving projects can address the steam deficits, some means of providing for the power deficits must be considered if all the steam and power demands are to be met internally. Three strategies, which include steam-saving measures identified by the pinch analysis, energy conversion efficiency improvements, and increasing fuel inputs, have been proposed to cover the mill energy deficits created by lignin extraction. These strategies have been applied to two cases: lignin extraction only, and lignin extraction with a 15% pulp production increase. Table 3-5 summarizes the proposed strategies.

3.5.1 Strategy 1: Steam Saving Projects and Condensing Power

Mill steam demand is addressed by steam reduction projects identified by the pinch analysis. The LP steam demand can be reduced by 3.1 GJ/adt by implementing these projects. MP steam demand is covered by changing the ratio of MP/LP steam production at the turbines. However, the power demand cannot be satisfied only by implementing steam-reduction projects. To compensate for the power deficit, a condensing turbine with an isentropic efficiency of 86% is installed to use the LP steam saved by the steam-saving projects. In this way, approximately 2 MW of electricity can be produced, thus compensating for the power deficit. In the case of a pulp production increase, however, the current steam savings are not enough to cover the steam and power demands completely. Approximately 4.8 GJ/adt of steam savings are required to address the steam and power demands using this strategy, which will require a higher level of process integration.

3.5.2 Strategy 2: Additional Biomass Use

Additional biomass is combusted in the biomass boiler under the assumption that the mill has the capacity to burn more fuel. Additional wood or part of the extracted lignin can be used as the additional biomass. By burning an extra 85 t/d of biomass, the steam and power deficits of the Kraft mill can be addressed. If the lignin is extracted for the purpose of debottlenecking the recovery boiler, the extracted lignin can be used again in the process as a fuel. In the case of a 15% pulp production increase, by combusting 83 t/d of extracted lignin and an additional 47 t/d of biomass, the energy requirements can be covered. A biomass-to-steam conversion efficiency of 75% is assumed for these estimates.

3.5.3 Strategy 3: IGCC Cycle and Steam Saving Projects

The integrated gasification combined cycle (IGCC) increases the electrical efficiency of the biomass-to-power conversion from 12% to 23% (Rofouieeraghi, 2012). The biomass boiler has been replaced by the IGCC process, which uses biomass as a fuel. The mill can produce 29.5 MW_e of electricity due to the increased electrical efficiency of the IGCC system. The electricity surplus can be sold to generate further revenue. The steam deficit, which is 2.7 GJ/adt, can be addressed by implementing steam saving projects. Furthermore, CO_2 in the syngas can be captured and used for lignin precipitation, thus reducing the operating costs of the lignin plant. Steam and power demands for the case of a 15% pulp production increase can also be addressed using this strategy. The power deficit can be addressed and the 3.1 GJ/adt steam deficit can be covered by the steam-saving projects.

Table 3-5: Comparison of strategies proposed to address mill power and steam deficits.

Strategy	**Lignin combusted (t/d)**	**Extra biomass (t/d)**	**Power surplus (MW_e)**	**Steam savings required (GJ/adt)**
		No pulp production increase		
1	0	0	0	3.1
2	0	85	0	0
3	0	0	7.5	2.7
		With 15% pulp production increase		
1	0	0	0	4.8
2	83	47	0	0
3	0	0	5.4	3.1

It is possible to address the power and steam deficits created by lignin extraction using the strategies described above. In a real mill situation, the choice of strategy depends on several factors, such as the availability of extra biomass, the possibility of producing more energy in utility boilers, the

desire to increase pulp production, and the feasibility of steam-saving projects. As the next step, an economic analysis should be carried out to investigate the profitability of the various options.

3.6 Conclusion

Lignin extraction by acid precipitation alters the energy balance of the Kraft mill. In the case of extraction of 15% lignin from the mill, recovery-boiler steam production was decreased by 13.5% and evaporator steam demand was increased by 2.4%–14.6%, depending on the implemented recycle configuration and the amount of filtrates recycled. Recycling the spent liquor upstream of the evaporator train resulted in a lesser increase in evaporation steam demand. A power deficit of 2.1 MW_e and a steam deficit of 2.7 GJ/adt are created by integrating a 15% lignin extraction unit into the Kraft mill. If lignin is extracted to debottleneck the recovery boiler, pulp production can be increased by approximately 15%. In this case, the mill steam and power deficits are increased to 3.3 GJ/adt and 3.3 MW_e respectively. Steam reduction measures of 3.1 GJ/adt have been identified through pinch analysis. Three strategies based on steam reduction measures, energy-conversion efficiency improvements, and extra fuel inputs are proposed to address power and steam deficits. The possibility of addressing steam and power deficits internally has been demonstrated.

3.7 Acknowledgements

The authors acknowledge the financial support provided by NSERC and industrial partners.

3.8 References

Axelsson, E., Olsson, M. R., & Berntsson, T. (2006). Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade. *Nordic Pulp and Paper Research Journal, 21*(4), 485-492.

Kamal, W. (2011). *Analysis of Energy Systems and Performance Improvement of a Kraft Pulping Mill.* École Polytechnique de Montréal.

Kouisni, L., Fang, Y., Paleologou, M., Ahvazi, B., Hawari, J., Zhang, Y., & Wang, X. M. (2011). Kraft lignin recovery and its use in the preparation of lignin-based formaldehyde resins for plywood. *Cellulose Chemistry and Technology, 45*(7-8), 515-520.

Laaksometsä, C., Axelsson, E., Berntsson, T., & Lundström, A. (2009). Energy savings combined with lignin extraction for production increase: case study at a eucalyptus mill in Portugal. *Clean Technologies and Environmental Policy, 11*(1), 77-82.

Loutfi, H., Blackwell, B., & Uloth, V. (1991). Lignin recovery from kraft black liquor: preliminary process design. *Tappi Journal, 74*(1), 203-210.

Moosavifar, A., Sedin, M., & Theliander, H. (2009). Changes in viscosity and boiling point elevation of black liquor when a fraction of lignin is removed - Consequences in the evaporation stage. *Appita Journal, 62*(5), 383-390.

Olsson, M. R., Axelsson, E., & Berntsson, T. (2006). Exporting lignin or power from heat-integrated kraft pulp mills: A techno-economic comparison using model mills. *Nordic Pulp and Paper Research Journal*.

Perin-Levasseur, Z., Savulescu, L., & Benali, M. (2011). Lignin production path assessment: Energy, water, and chemical integration perspective. *J-FOR, 1*(3), 25-30.

Rofouieeraghi, P. (2012). *Biomass gasification integrated into a reference Canadian Kraft mill.* École Polytechnique de Montréal.

Tomani, P. (2010). The lignoboost process. *Cellulose Chemistry and Technology, 44*(1-3), 53-58.

Tomani, P., Axegard, P., Berglin, N., Lovell, A., & Nordgren, D. (2011, May 9-12, 2011). *Integration of lignin removal into kraft pulp mill and use of lignin as biofuel.* Paper presented at the 5th International colloquium on Eucalyptus Pulp, Porte Seguro, Bahia, Brazil.

Wising, U., Algehed, J., Berntsson, T., & Delin, L. (2006). Consequences of lignin precipitation in the pulp and paper industry.

Chapter 4 ARTICLE 2: PROCESS MODELLING AND NA/S BALANCES OF LIGNIN BIOREFINERIES IMPLEMENTED IN KRAFT PULPING MILLS: APPLICATION TO A CANADIAN SOFTWOOD MILL

Miyuru Kannangara, Mariya Marinova, Louis Fradette, and Jean Paris

Research Unit on Energy Efficiency and Sustainable Development of the Forest Biorefinery,

Department of Chemical Engineering, Polytechnique Montreal, C.P. 6079, succ. Centre-Ville,

Montréal, QC, Canada H3C 3A7

Abstract

The implementation of lignin biorefineries in Kraft pulping mills has been studied with an emphasis on minimization of the disruption of Na/S balances. A simulation approach based on Aspen Plus® electrolytes and MS Excel™ is proposed to accurately model the changes in liquor cycle balances brought forth by the biorefinery integration. The biorefinery implementation was investigated using four strategies for balancing Na and S based on wash filtrate recycle, black liquor pH re-adjustment, make-up chemical additions and purges. For the studied Canadian softwood Kraft pulping mill, a lignin extraction ratio of 15% was feasible according to the calorific value constraints. The NaOH make-up demand was minimized at 146 kg/t of lignin by minimization of the disruption of Na/S balances. The sensitivity analysis revealed that NaOH demand is a function of the chemical recovery efficiency of the lignin washing step and it is feasible to reduce it below 100 kg/t of lignin when the washing operation is conducted with efficiency higher than 85% and wash water demand lower than 5 t/t lignin. The analysis of the liquor cycle balances showed that the Na/S balancing strategy also affects the loads of evaporator, causticizing loop and lime kiln operations, thus becoming potential bottlenecks for the pulp production increase. The guidelines for implementing the lignin biorefinery in the studied Kraft mill under given constraints were provided. General recommendations on implementation of lignin biorefineries in Kraft pulping mills were formulated.

Keywords

Lignin biorefinery, Kraft process, Process integration, chemical balances

4.1 Introduction

The pulp and paper industry in North America and Europe has been facing difficult economic conditions since last two decade due to the falling demand for commodity papers including newsprint and international competition. The industry has been actively seeking to use existing infrastructure and equipment to separate wood components and convert them into novel bio-products and chemicals. In this context, the integrated recovery of lignin from black liquor (BL) has gained interest of the Kraft pulping industry as a way to separate a wood component and to increase pulp production. Many Kraft pulping mills have been increasing their pulp production over the years and have reached the thermal limit of the recovery boiler. The heat load to recovery boiler is reduced by removing lignin, thus allowing mills to increase pulp production without expensive recovery boiler upgrade.

The acid precipitation process has been identified as the most promising technology to remove lignin in terms of economics (Alen et al., 1979; Loutfi et al., 1991; Uloth & Wearing, 1989a). In this process, lignin is precipitated from BL by acidification with CO_2, separated using filtration and purified using sulfuric acid and water. The process can produce high purity lignin which can be utilized as feedstock for many value added products including phenol formaldehyde resins, carbon fibers and polyurethane foams (Bozell, Holladay, Johnson, & White, 2007; Silva et al., 2009).

Only a fraction of lignin can be recovered from BL to prevent excessive decrease of BL calorific value, which hinders the safe and efficient operation of the recovery boiler. Therefore, lignin is precipitated from a portion of BL that is diverted from the multiple effect evaporator train of the mill. The filtrates resulting from lignin filtration and washing, containing mainly water, lignin, hemicelluloses and spent chemicals are entirely or partly returned to the Kraft mill. The implementation of lignin biorefinery affects the operations of the Kraft liquor cycle, in which the chemicals required for Kraft pulping is recovered and produced, in terms of increased steam demands, chemical requirements and operational loads. Although, lignin biorefinery process is not energy intensive, the lignin removal reduces the steam production in the recovery boiler resulting in a net energy deficit in the Kraft process. The entire or partial recycle of filtrates with additional chemicals disrupts the sodium and sulfur (Na/S) balances of the liquor cycle, which has to be re-adjusted using additional NaOH make-up and chemical purges. Excessive disruption of the Na/S balance can negatively affect the profitability of the process due to the high cost of NaOH.

The published work on the implementation and process integration of lignin biorefineries in Kraft pulping mills concentrate on energy integration, resource integration and impact assessment. The energy integration studies have been focused on estimating net energy deficits in the Kraft process and using the energy optimization techniques including Pinch analysis to propose energy saving projects (Hamaguchi & Vakkilainen, 2010; Kannangara, Marinova, Fradette, & Paris, 2012; Laaksometsä et al., 2009; Olsson et al., 2006). The mass integration of CO_2 and water from receptor Kraft mill to be used in the lignin biorefinery have been investigated using techno-economical studies (Benali et al., 2014). Other studies addressed the general consequences of lignin precipitation, effects of combusting BL with reduced lignin in recovery boilers and effects on the evaporator train (Moosavifar et al., 2009; Vakkilainen & Valimaki, 2009; Wising et al., 2006).

However, none of these studies focus on process modelling of precipitation process or chemical balances of liquor cycle in detail during the implementation of the lignin biorefinery. The absence of such studies, in our opinion, is largely due to unavailability of published simulation frameworks and process specification data to be used as inputs and validations for the precipitation process and Kraft mill balances. In this paper, we have proposed an appropriate simulation approach for the analysis of implementation of the lignin biorefinery in a Kraft pulping mill in terms of chemical balances. The data for the liquor cycle balances and lignin precipitation process have been taken from long term average data of a Canadian softwood Kraft pulping mill and pilot scale lignin precipitation trials performed in the same mill. Although, the main emphasis has been given to the chemical balances, the energy balances have been included since the energy intensive Kraft mill operations are affected by the lignin extraction. Guidelines for the optimal implementation lignin biorefinery in a Kraft pulp mill in terms of resource utilization and profitability were proposed.

4.2 Process description

4.2.1 Kraft process liquor cycle

The main purpose of the liquor cycle is to recover the chemicals that was used in the Kraft pulping process. In the delignification step of the Kraft process, lignin is selectively removed to liberate cellulose fibers at high temperature and strong alkali conditions using NaOH and Na_2S. The removed lignin along with spent chemicals is entrained in the BL stream during pulp washing. BL is concentrated from 13-18% to 65-75% in the multiple effect evaporator train and it is combusted

in a recovery boiler to generate steam and regenerate delignification chemicals. In the recovery boiler, Na_2SO_4 is converted into Na_2S and the efficiency of this conversion is defined by the reduction efficiency. The regenerated smelt coming out from the recovery boiler is dissolved in water to generate GL. Na_2CO_3 rich GL is converted into NaOH rich white liquor (WL) in the causticizing operation. WL, after composition adjustments, can be used in the delignification step. Therefore, the chemicals in the liquor cycle of the Kraft mill is conserved. However, chemical losses can mainly happen in the pulp washers and the recovery boiler, which require addition of makeup chemicals (Smook, 1992b; Stevens, Grace, & Leopold, 1989). A basic flow diagram of the liquor cycle is given in Figure 4-1.

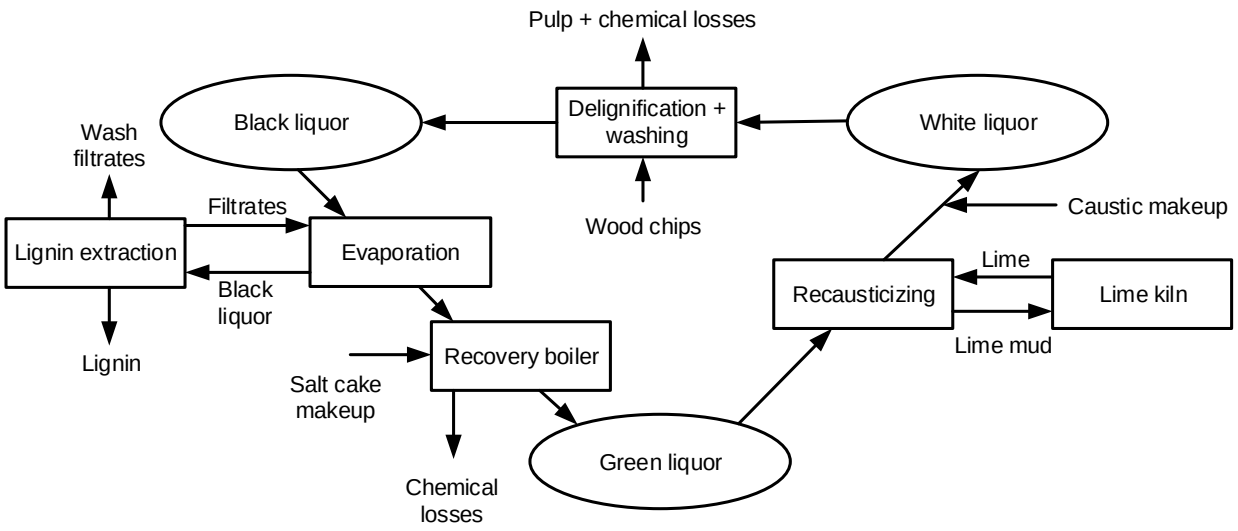

Figure 4-1: A basic flow diagram of the liquor cycle in a Kraft pulp mill

4.2.2 Acid precipitation process

Figure 4-2 shows a flowsheet of the main steps of the acid precipitation process. A portion of BL of 30-40% solids content is diverted from the multiple effect evaporator train, cooled down to 70-80°C temperature, and acidified using CO_2 to a pH of 9-10. The resulting slurry is further agitated in an ageing vessel for 60-90 min residence time and it is filtered. The filtrate, which contains the remaining lignin, organic compounds and spent chemicals with a solids content of 25-30%, is recycled back to the evaporator train.

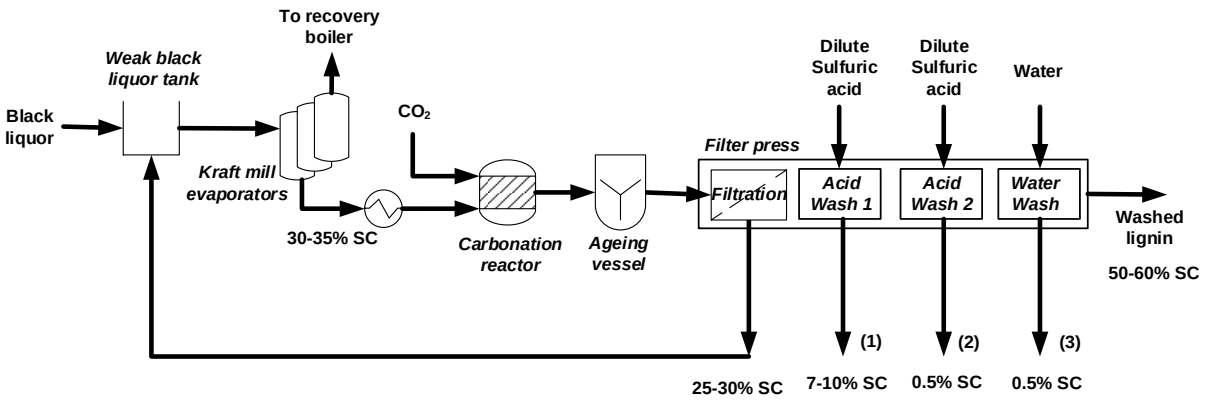

Figure 4-2: A flowsheet of the lignin extraction process

The lignin cake, containing 12-16.3% bound Na, is washed with dilute sulfuric acid (Acid wash 1) to remove Na and residual liquor remaining in the cake. Acid wash 1 can be either re-slurry washing or displacement washing (Kouisni et al., 2012; Tomani, 2010). In case of re-slurry washing, the pH of the slurry is adjusted to the range of 2-3 to remove bound Na. The removal efficiency of bound Na is, hence, mainly depends on the slurry pH.

In a displacement type washing, most of the chemicals in the lignin cake are removed during acid wash 1. The acid demand, removal efficiency of Na and the amount of solids in wash filtrate 1 can vary depending on cake properties and wash liquor penetration. The wash filtrate 1, generated by the displacement acid wash 1, has a solid content of 7-10% solids. In this study, the data used for acid precipitation process was taken from such displacement washing operation.

After acid wash 1, the cake is usually further washed with dilute sulfuric acid and water during acid wash 2 and water wash to remove the remaining Na and increase the purity of the cake. If re-slurry washing is performed re-filtration of the slurry is required. The sulfuric acid and water requirements depend on the desired purity of the cake. The process can produce washed lignin cake at 50-60% solid content of high purity lignin with ash content below 0.1%.

4.3 Simulation approach

The process flowsheet consists of two main sections: the receptor Kraft pulping mill and biorefinery plant. The chemical balances of the Kraft mill liquor cycle and recovery boiler energy balance were modeled using MS Excel™. Aspen Plus® was used to simulate the acid precipitation

plant, which require the estimation of the pH variations and BL composition changes. The Kraft mill multiple effect evaporator train was also simulated in Aspen Plus® because of direct exchange of process streams between lignin biorefinery plant and evaporator train. The data was exchanged by linking Aspen Plus® with MS Excel™. The points of data exchange between two simulations were weak BL stream and strong BL stream as shown in Figure 4-3.

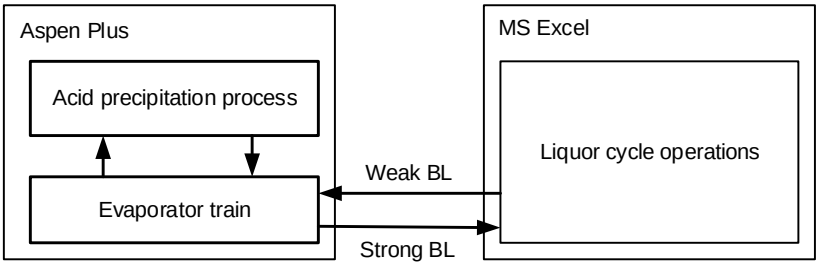

Figure 4-3: Simulation framework used for the analysis

4.3.1 Liquor cycle balances

The chemistry of the chemical recovery process is very complex due to the number of involved components and irreversible consecutive and competitive reactions occurring in the solid and gas phases at high temperature. Na/S balances can be used as a simple approach to model the component mass balances of the liquor cycle (Andersson, 2014; Dahlin, 2015; Saturnino, 2012). In this approach, the balance of total Na and S is maintained while adding/purging the deficit/excess Na and S so that desired composition and flow rates of $NaOH$ and Na_2S in the WL are obtained. The sequential calculation procedure of performing Na/S balances is shown in Figure 4-4. The mass balances of the liquor cycle has been estimated based on this calculation sequence. The main components in liquor cycle streams have been included in the balances as shown in Table 4-1.

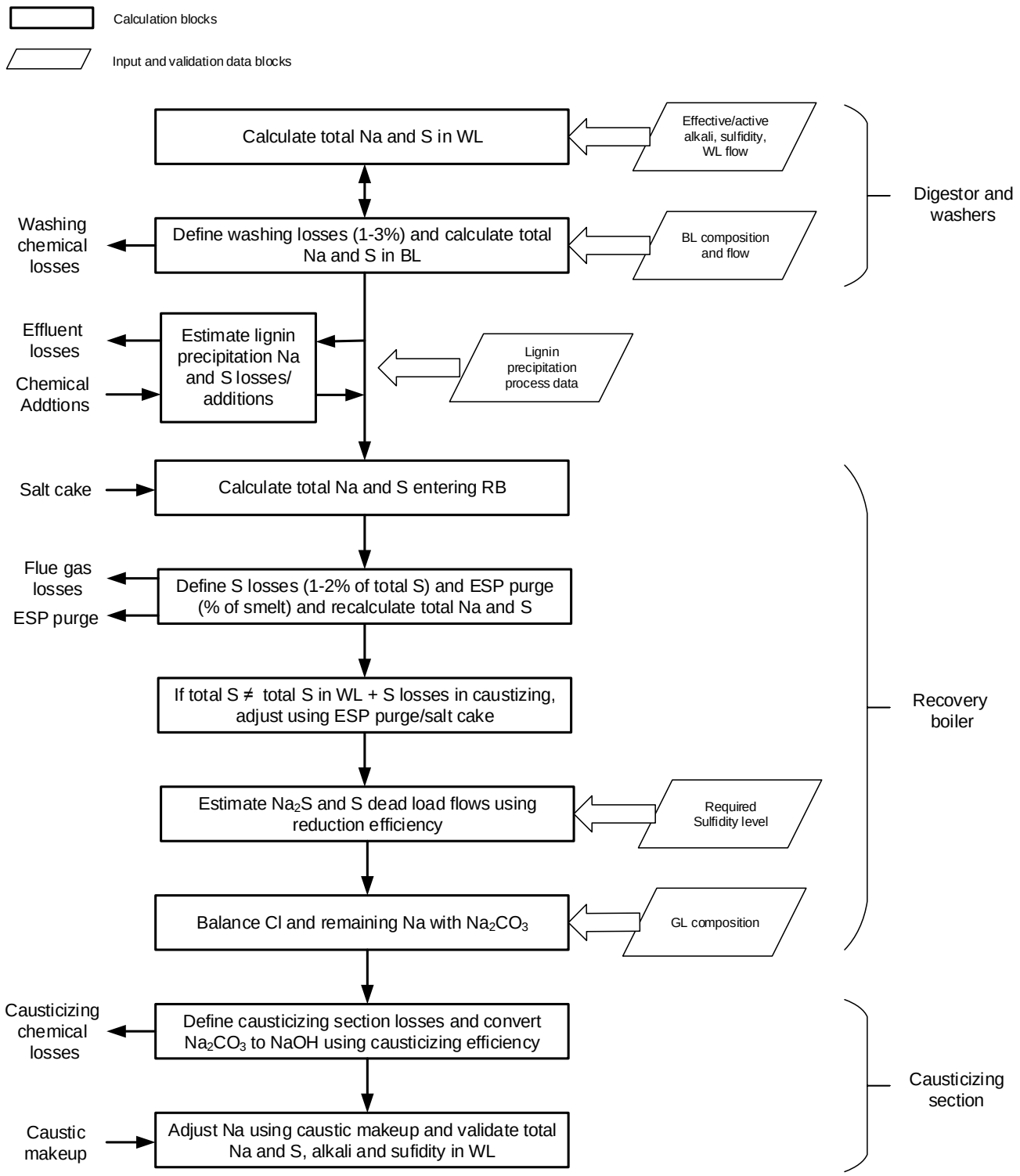

Figure 4-4: The calculation sequence utilized for estimating the Na/S balances of the liquor cycle

Table 4-1: The components included in the liquor cycle balance

Component class	**Components**
Inorganics	$NaOH, Na_2CO_3, Na_2S, Na_2SO_4, Na_2S_2O_3, Na_2SO_3, NaCl,$ organically bound Na and S in BL
Organics	Lignin, hemicellulose and cellulose

The starting point of the balance is the estimation of the flow rate and composition of the WL required by the delignification step. The required $NaOH$ and Na_2S are estimated using Effective alkali (EA) on O.D. (oven dry) wood and Sulfidity as given in Eq. 1 and 2.

$$\text{EA on O.D. wood (\%)} = \frac{\dot{m}_{NaOH} + 0.5 \times \dot{m}_{Na_2S}\ (as\ Na_2O)}{\dot{F}_{O.D.Wood}} \times 100 \quad (1)$$

$$Sulfidity\ (\%) = \frac{\dot{m}_{Na_2S}}{\dot{m}_{NaOH} + \dot{m}_{Na_2S}} \times 100\ (as\ Na_2O) \quad (2)$$

$\dot{m}_{NaOH}$ and $\dot{m}_{Na_2S}$ are the $NaOH$ and Na_2S mass flow rates in the WL and $\dot{F}_{O.D.Wood}$ is the input wood flow rate (oven dry) to the delignification. The deadload components including Na_2CO_3 $Na_2SO_4, Na_2S_2O_3$ and Na_2SO_3, which contribute to Na and S in the liquor cycle, arise due to inefficiencies of the recovery operations (mainly recovery boiler and causticizing). It is important to include the contribution of those component in the Na/S balance as well. The total Na and S in WL can be estimated either from WL composition and flow rate measurements or from the total Na and S flows of BL using the losses during pulp washing (usually around 1-3%). In this particular case, we have used the BL total Na and S to estimate WL Na and S as detailed composition data were available for BL, as shown in Table 4-2. After this step, both compositions and flow rates of WL and BL are known. Table 4-4 shows the pulp mills parameter used for the balances.

Table 4-2: The BL composition of the studied mill

Component	**Composition (% O.D. Solids)**
$NaCl$	1.5
Na_2CO_3	4.9
$Na_2S_2O_3$	5.4
Na_2SO_3	1.0
Na_2SO_4	4.9
Na_2S	0.5
$NaOH$	1.0
Organically bound Na	11.5
Na	18.6
S	4.0
Lignin	34.1
Total organics	62.0
Total inorganics	37.9

Salt cake, which is added to the BL, is usually used as the S make-up of the liquor cycle. In the next step of the Na/S balance calculation, the total Na and S input to the recovery boiler is estimated using the BL flow and salt cake make-up. In the recovery boiler, there are minor Na losses and ~1-2% S losses with flue gases. Any additional S can be removed using an electrostatic precipitator (ESP) dust purge along with Na. A typical precipitator dust composition with Na/S weight ratio of 1.4 have been used in this calculation (Lockhart, 2008). The total amount of Na and S, which enters the recovery process, are therefore calculated after anticipated losses and purges. The required total S flow rate is adjusted by changing salt cake input. When lignin biorefinery plant is integrated in the liquor cycle, the Na and S losses/additions due to wash filtrate disposal/recycle have to be

included before this step. During recovery boiler operation, the input of S is converted into Na_2S and S deadload components including $Na_2SO_4, Na_2S_2O_3$ and Na_2SO_3 as defined by the reduction efficiency ($\eta_{Reduction}$).

$$\eta_{Reduction}(\%) = \frac{\dot{M}_{NA_2S}}{\dot{M}_{S,total}} \times 100 \tag{3}$$

$\dot{M}_{NA_2S}$ is the mole flow of Na_2S and $\dot{M}_{S,total}$ is the total mole flow rate of S. After S balance, the Cl is balanced as $NaCl$ and the remaining Na is balanced as Na_2CO_3. This sequence of calculations allows to estimate the smelt flow and composition, which is translated into green liquor (GL) flow and composition. The GL composition measurements, if available, can be used to validate the obtained results.

The conversion of Na_2CO_3 to $NaOH$ is calculated using causticizing efficiency ($\eta_{Causticizing}$) to obtain the WL composition. $\dot{m}_{NaOH}$ and $\dot{m}_{Na_2CO_3}$ are the mass flow rate of $NaOH$ and Na_2CO_3 after causticizing section, which are given in the form of Na_2O.

$$\eta_{Causticizing}(\%) = \frac{\dot{m}_{NaOH}}{\dot{m}_{NaOH} + \dot{m}_{Na_2CO_3}} \times 100 \ (as\ Na_2O) \tag{4}$$

The WL produced after the causticizing usually requires a make-up of $NaOH$ to adjust the Na and effective alkali levels of the delignification step, which is the final step of the calculation procedure. The data requirements explained in this algorithm were kept minimum for the purpose of analyzing chemical balances of the main operations of the liquor cycle. If more data is available, they can be used to validate and further improve the balances of each operation.

4.3.2 Recovery boiler energy production and lignin extraction ratio

The energy balances of recovery boiler has been included in the liquor cycle simulation. The recovery boiler energy production has been estimated using the total energy conversion efficiency (η_{RB}) equation.

$$\eta_{RB}(\%) = \frac{\dot{E}}{\dot{M}_S \times HHV_{BL}} \tag{5}$$

$\dot{E}$ is the rate of energy production, $\dot{M}_S$ is the total solid flow rate to the recovery boiler and HHV_{BL} is the calorific value of the BL. The extraction of lignin decreases the calorific value of BL, which can hinder the safe and efficient operation of the recovery boiler. Therefore, the ratio of lignin extraction is dependent on the constraints set by the recovery boiler. One way of estimating the lignin extraction ratio is (1): Defining a minimum BL calorific value as allowed by the recovery boiler and (2): Increasing the lignin extraction until the calorific value reaches the defined calorific value (Benali et al., 2014; Perin-Levasseur, Z, Benali, & Paris, 2010). The original BL considered in this study had a calorific value of 13.72 MJ/kg (O.D. basis) at 34.1% lignin content while the filtrate after lignin extraction had a calorific value of 8.62 MJ/kg (O.D. basis) at 17% lignin content. Considering the dilutions with added chemicals (CO_2 and H_2SO_4), this reduction of lignin content accounts to ~ 56% of lignin extraction, which is in accordance with the process lignin yield of 52%.

The recovery boiler in the studied mill had a minimum operating calorific value in the range from 11.86 to 12.32 MJ/kg (O.D. basis) as recommended by the operators. The linear interpolation has shown that ~15% of lignin extraction to obtain 12.32 MJ/kg value. However, it is recommended validating this value with a measured caloric value of a liquor containing appropriate portions of original BL and filtrates. The estimated 15% lignin extraction corresponds to 24 t/d of lignin removal from the mill. The addition and removal of inorganics compounds also affect the HHV of BL.

The HHV of BL has usually been estimated according to the ultimate analysis of black liquor or by means of regression using large number of proximate analysis data sets (Hamaguchi & Vakkilainen, 2010; Vakkilainen, 2000; Vakkilainen & Valimaki, 2009; Valimaki et al., 2010). In the absence of such data, an absolute prediction of HHV depending on the BL composition can be erroneous. Therefore, we have used a differential type equation (Eq. (6)), which is based on total energy content and considers the deviations from a reference calorific value, for preliminary estimation of HHV and to minimize the prediction error. The reference calorific value can be a measured calorific value for BL of a known composition, which has similar composition to the BL after lignin extraction.

$$HHV_{BL} = \frac{HHV_{BL,ref} \times \dot{m}_{BL,Ref} + HHV_L \times (\dot{m}_L - \dot{m}_{L,ref}) + HHV_O \times (\dot{m}_O - \dot{m}_{O,ref})}{\dot{m}_{BL}} \qquad (6)$$

HHV_{BL} is the estimated calorific value of the BL, $HHV_{BL,ref}$ is the reference calorific value at reference composition.z $HHV_L$and HHV_O are the calorific values of lignin and other remaining organics, which were 27.5 MJ/kg and 13.7 MJ/kg respectively for this particular calculation. $\dot{m}_L$ and $\dot{m}_O$ are the current flow rates of lignin and remaining organics and $\dot{m}_{L,ref}$ and $\dot{m}_{O,ref}$ are the reference flow rates of lignin and remaining organics. $\dot{m}_{BL}$ and $\dot{m}_{BL,Ref}$ are the current and reference total solids flow rates. For this particular mill, $HHV_{BL,ref}$ of 12.32 MJ/kg was assumed at BL composition resulted in recycling BL filtrate and 5 t/t of lignin of wash filtrates at lignin extraction rate of 15%.

4.3.3 Modeling the BL acidification

The basic chemistry of the acid precipitation process involves the reduction of the BL pH by means of acid. At high pH, the phenol and carboxyl hydroxide groups of lignin are dissociated providing lignin macromolecules negative surface charges. As the pH is reduced, these charges are neutralized causing lignin to coagulate and precipitate.

The solution pH can be modeled using electrolyte chemical equilibria that describe ionic dissociation and acid-base reactions. Electrolyte capabilities in Aspen Plus® have been used to simulate acid precipitation of BL (Benali et al., 2014; Perin-Levasseur, Z et al., 2010). In this paper, the electrolyte NRTL physical property model has been used to represent the aqueous electrolytes equilibrium behavior of BL.

The components that participate in the reactions in large quantities were included in the simulation. The inorganic components were set to participate in the electrolyte equilibrium and organic solid compounds including lignin, hemicellulose, lignin bound Na and S were treated as inert solid components. The physical properties for lignin, hemicelluloses and cellulose have been retrieved from the literature (Wooley & Putsche, 1996). In addition to the standard electrolyte components generated in Aspen Plus®, the phenol hydroxyl groups in lignin were included in the ionic equilibria to model the acid consumption by the phenolic groups in lignin. The electrolyte equilibria of the inorganic compounds are given in Eq. (7) - (15) and lignin phenolic group ionic equilibria is given in Eq. (16).

$$H_2O \leftrightarrow H_3O^+ + OH^- \quad (7)$$

$$H_2O + HCO_3^- \leftrightarrow CO_3^{2-} + H_3O^+ \quad (8)$$

$$2H_2O + CO_2 \leftrightarrow HCO_3^- + H_3O^+ \quad (9)$$

$$2H_2O + SO_2 \leftrightarrow H_3O^+ + HSO_3^- \quad (10)$$

$$H_2O + H_2SO_4 \leftrightarrow H_3O^+ + HSO_4^- \quad (11)$$

$$H_2O + HSO_4^- \leftrightarrow H_3O^+ + SO_4^- \quad (12)$$

$$H_2O + H_2S \leftrightarrow H_3O^+ + HS^- \quad (13)$$

$$H_2O + HS^- \leftrightarrow H_3O^+ + S^{2-} \quad (14)$$

$$H_2O + HSO_3^- \leftrightarrow H_3O^+ + SO_3^- \quad (15)$$

$$C_6H_5OH + H_2O \leftrightarrow C_6H_5O^- + H_3O^+ \quad (16)$$

Since, the main components that participate in the reactions in large quantities were considered in the model, the model behavior, the predicted pH change with acid addition, has been compared with experimental data (Wallmo, Richards, & Theliander, 2007) as shown in Figure 4-5. A model including lignin phenol groups (Eq. (7) - (16)) and a model including only inorganic components (Eq. (7) - (16)) were tested to verify the significance of the behavior of lignin phenolic groups. The temperature, lignin phenol content and pKa value for Eq. (16) were taken as 25°C, 30% (3.4 mmol/g of lignin) and 10, respectively. The physical and chemical properties for the rest of the simulation is taken from Aspen Plus® databanks.

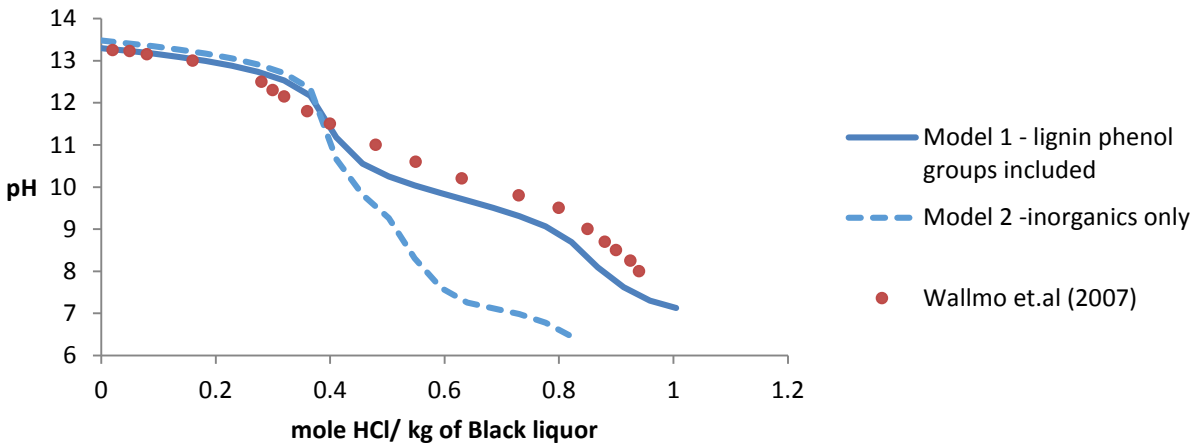

Figure 4-5: Comparison of the results for Model 1 where phenol hydroxyl groups of lignin is included and Model 2 where only inorganic compounds of BL is used for equilibrium and compared with experimental data by Wallmo et al. (2007).

The reactions occur during acid addition can be sub-divided into 3 main regions: a) hydroxide ion neutralization, b) reactions involving lignin groups c) sulfur and other reactions (Wallmo et al., 2007). These three regions can be identified in Figure 4-5. During the hydroxide ion neutralization, the change of pH is minimal due to buffering effects. In the second phase, mainly the protonation of lignin phenol groups happens. Model 1 and model 2 clearly deviates in this region having model 1 following the experimental data curve more closely. This clearly shows the importance of accounting for acid consumption by lignin phenolic groups. During the third phase, mainly sulfide and hydrosulfide ions are reacted releasing H_2S. It is important to note that pKa value of lignin changes with molecular weight giving different molecular weight fraction lignins different pKa values. Due to assumption of pKa value of 10, the pH prediction therefore only holds for the validated range of pH values (pH: 7-13). Deviations can be expected at lower pH values where lower molecular weight fractions of lignin with lower pKa values are acidified and precipitated.

4.3.4 Acid precipitation and liquor cycle mass and energy balances

The electrolyte model proposed in section 4.3.3 was used as underling equilibrium composition calculations and physical property estimation in the process simulation. The precipitation, filtration and washing operations were simulated using Mixer, Separator and flash units in Aspen Plus®. The removal of bound Na in lignin during washing steps were simulated by appropriate separation of

bound Na component into lignin cake and wash filtrate streams using Separator blocks. Design specifications were used to set cake purity (defined by bound Na removal) and precipitation yield. The composition, flow rate and pH of BL and wash filtrates and CO_2 consumption were estimated using the simulation. The specifications of the lignin biorefinery used in the simulation, were based on the data from pilot plant trials and literature (Loutfi et al., 1991), is given in Table 4-3. The BL composition used for the simulation is given in the Table 4-2. The evaporator train was simulated using Flash units with design specifications to maintain the desired solid concentration levels.

Table 4-3: Specifications of the lignin extraction process

Parameter	**Value**
Solid content of feed BL (%)	35
Process lignin yield (%)	52
CO_2 demand (t/t lignin)	0.17
H_2SO_4 demand (t/t lignin)	0.4
Water demand (t/t lignin)	13
Residual liquor retention in unwashed cake (% of total)	40
Na content of unwashed cake (%)	12
S content of unwashed cake (%)	2.0
Na content of partly washed cake (%)	3.6
S content of partly washed cake (%)	1.4
S content of fully washed cake (%)	1.3

The studied mill is a softwood Kraft pulping mill with 285 adt/d Kraft pulp capacity, however, it also produces mechanical pulp ultimately manufacturing 700 adt/d of mixed pulp. The main

parameters of the mill is given Table 4-4. Liquor cycle chemical balances were simulated including energy balances in evaporator and recovery boiler sections. The studied mill has a production bottleneck in the recovery boiler and unutilized capacities of the main chemical recovery operations were; evaporators: 14%, causticizing: 24% and lime kiln: 10%.

Table 4-4: Pulp mill parameters for mill balances

Parameter	**Value**
Kraft pulp production rate (adt/d)	285
Total pulp production rate (adt/d)	700
Effective alkali on O.D. wood (%)	14
Sulfidity (%)	22
Reduction efficiency (%)	70
Causticizing efficiency (%)	84
Wood flow rate to digester (odt/d)	619
Salt cake addition as $Na_3H(SO_4)_2$ (t/d)	6
$NaOH$ make-up (t/d)	3
BL solids flow (t/d)	487
WL flow (L/min)	617

4.4 Results and discussion

4.4.1 Implementation strategies

A portion of 28% BL has been diverted from the multiple effect evaporator train at 35% solids concentration in order to obtain a lignin extraction rate of 24 t/d. After lignin extraction, the BL

filtrate and wash filtrates are recycled back to the liquor cycle according to 4 strategies. The strategies, shown in Table 4-5, were defined according to the liquor cycle constraints in a typical Kraft pulping mills.

In strategy 1, only the BL filtrate is recycled. As a result the chemical losses accompanied with the lignin cake are higher. The pH of the BL is adjusted at the evaporator train using NaOH. The strategy 2 is same as the strategy 1 except that the pH is not re-adjusted. In strategy 3, wash filtrates, as well as the BL filtrates, are recycled at a rate of 5 t/t of lignin. It is assumed that 75% of the lignin cake chemicals are recovered at this rate. In strategy 4, the wash filtrates are recycled at a rate of 7 t/t lignin and 95% of the chemicals are recovered.

The chemical recovery efficiency of the first washing step is dependent on the characteristics of lignin cake, type of washing technique (re-slurry versus displacement washing) and the strength of the wash liquor. Table 4-5 further shows Na and S losses with the cake and calorific value of BL for each scenario. The calorific values were estimated according to the Eq. (6) proposed in section 4.3.2. The calorific value of original BL was 13.72 MJ/kg.

Table 4-5: Implementation strategies of lignin biorefinery in Kraft pulping mill

Strategy	**BL pH readjustment using NaOH**	**Amount of wash filtrates recycled (t/t lignin)**	**Chemical losses with the lignin cake (t/d)**		**Calorific value of BL (MJ/kg)**
			Na	**S**	
1	N	0	3.76	0.55	12.57
2	Y	0	3.76	0.55	12.42
3	N	5	0.94	0.37	12.32
4	N	7.5	0.18	0.33	12.25

4.4.2 Impact on Na/S balances

The Na and S are balanced differently in various mills. Usually, 6-12 kg/ADt of Na and 1.4-6.4 kg/ADt of S are added as make-up chemicals (Blackwell & Lincoln, 1998; Tran, 2008). The studied

mill has 11.2 kg/ADt of Na and 5.3 kg/ADt of S additions as make-up chemicals, which is somewhat higher than the average values. The required Na and S added as salt cake (as sodium sesquisulfate) and caustic in the studied mill as shown in Figure 4-6.

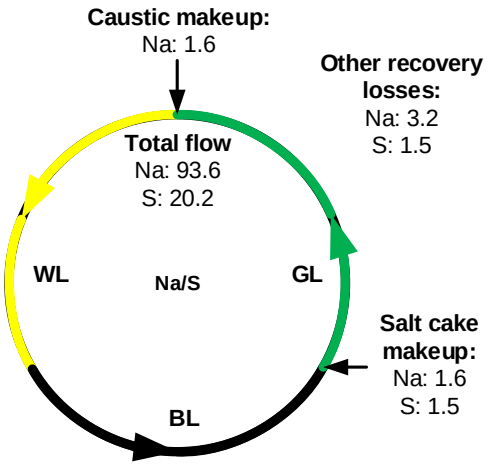

Figure 4-6: Overall Na/S balances of the liquor cycle of studied mill (without lignin biorefinery integration) (Units: t/d)

Once the lignin precipitation plant is integrated in the liquor cycle, the Na/S balances are changed resulting in new demands for make-up chemicals and purges. Figure 4-7 shows the changed Na/S balance for the considered strategies. In strategy 1, the wash filtrates are not recycled back resulting in a large loss in Na, which has been in the lignin cake as bound Na. There are also S losses with the lignin cake as bound S. The rest of the losses are from the residual liquor, which remains in the lignin cake. The unwashed lignin cake in this particular case has 12 % by wt. of Na and 2 % by wt. of S. The S loss can be adjusted by increasing the salt cake make-up, which also adjusts the loss of Na to a certain degree. However, the rest of the lost Na have to be added as caustic which increase caustic demand from 1.6 to 4.7 t/d in terms of Na. In strategy 2, caustic is added to the evaporator train to adjust the BL pH. This amount was estimated as the amount needed to bring back the total Na flow to the recovery boiler back to the original value after balancing S with addition of salt cake.

The added caustic increased BL filtrate pH up to 11.8 as predicted by the Aspen Plus® model. Further addition of caustic increases the Na_2CO_3 flow to the recausticizing section and it was therefore avoided, even though the original BL pH was 12.8. Caustic of 1.6 t/d in terms of Na at WL was needed to complete the Na balance, raising the total caustic requirement 4.8 t/d.

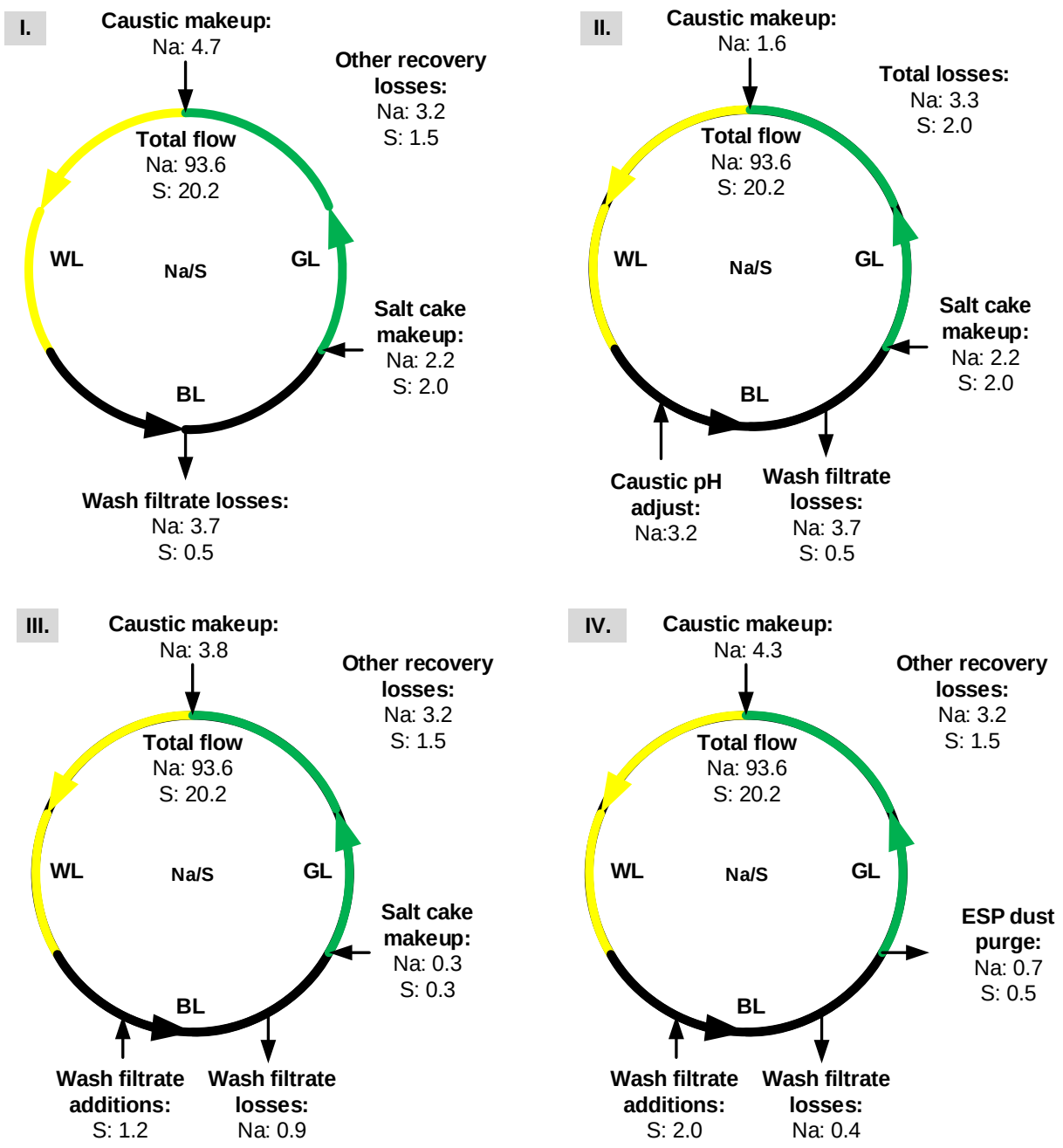

Figure 4-7: Na/S balances of the liquor cycle with integrated lignin biorefinery plant for proposed strategies (units: t/d)

In strategy 3 and 4, part of Na rich wash filtrates is recycled back to the liquor cycle. It is important to note that Na is in the form of Na_2SO_4 in wash filtrates. However, additional S is also brought to the process with wash filtrates as sulfates. In strategy 3, the additional S input can be compensated by decreasing the salt cake make-up, as salt cake input (as sodium sesquisulfate) has lower Na/S ratio than that of Na_2SO_4. Therefore, recycle of wash filtrates recovers more Na than that can be

added using sodium sesquisulfate make-up. This minimizes the loss of Na with wash filtrates and as a result the increase of caustic demand is lower (3.8 t/d in terms of Na) compared to strategy 1 and 2. In strategy 4, more wash filtrates are recycled and S input is higher than the required value. This additional S can be removed using recovery boiler ESP dust purge, which also results in a loss of Na thus increasing the caustic demand.

The total Na flow rate to the recovery boiler decreases in all strategies except strategy 2, where it is maintained by addition of caustic to the BL. This decreases in total Na flow decrease the Na_2CO_3 in the smelt resulting a proportional reduction in causticizing and lime kiln section processing requirements. This is beneficial in cases where the mill has production bottlenecks in causticizing and lime kiln sections. Table 4-6 summarizes the required chemical additions, purges and Na_2CO_3 flow rates for each strategy.

Table 4-6: Chemical additions, purges and Na_2CO_3 flow for each strategy

Implementation strategy	**Increase in caustic demand (kg/t lignin)**	**Salt cake addition (t/d)**	**ESP dust purge (t/d)**	**Decrease in Na_2CO_3 flow in smelt (%)**
1	221	8.6	0	6.4
2	223	8.6	0	0
3	146	1.2	0	4.8
4	187	0	2.5	5.2

The wash filtrate recycle and reduction of external S input (salt cake) can be used as a measure of reducing caustic demand caused by the integration of lignin biorefinery. However, the added S should not exceed the amount required by the mill (defined by sulfidity), in which is required to remove additional S by ESP purge, again increasing caustic requirement. The current Na/S balance of the mill is also important when considering wash filtrate recycle. The studied mill has higher external S input (5.3 kg/ADt) and therefore there is an opportunity to recycle a significant portion of wash filtrates without disrupting the balance of S. In a tightly balanced mill in terms of S (low

external S requirement), there may be less opportunities to recycle wash filtrates due to disruption of the S balance.

The efficiency of the first washing step (Acid wash 1) is also another factor which affect Na/S balance of a lignin biorefinery integrated Kraft mill. The efficiency increases when more chemicals can be recovered using lower quantity of acid. The sensitivity of caustic demand as a function of chemical recovery efficiency and wash liquor quantity (0.4M H_2SO_4 is used) is given in Figure 4-8. The caustic demand decreases with increasing chemical recovery efficiency and decreasing wash water requirement for the first washing step.

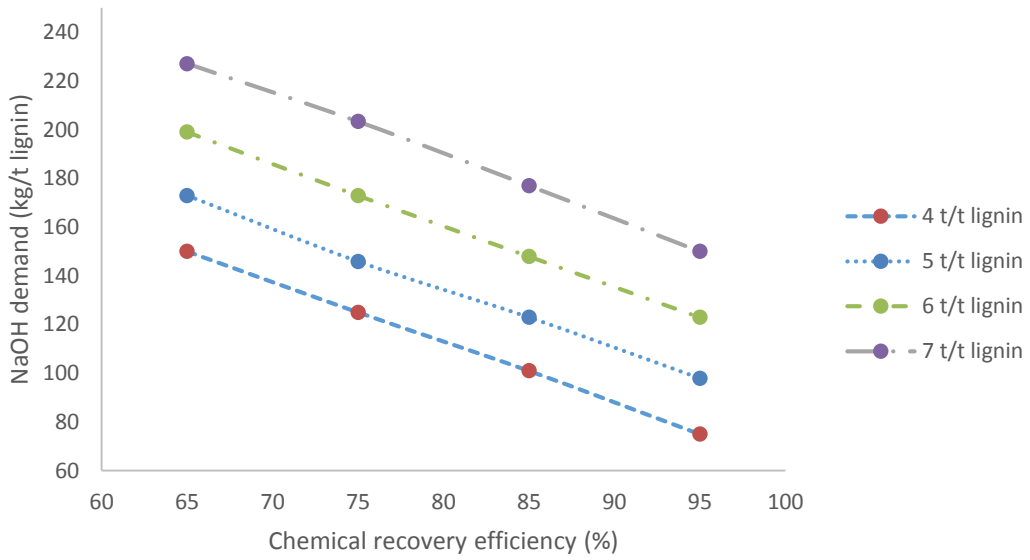

Figure 4-8: Sensitivity of the caustic demand on the chemical recovery efficiency and wash liquor consumption of first washing step (Wash liquor strength 0.4 M H_2SO_4)

In strategies 3 and 4, the liquor cycle make-up S requirement is balanced by the recycle of wash filtrates and the reduction of salt cake input. In some mills, salt cake is produced on site during ClO_2 production for pulp bleaching. Therefore, the reduction salt cake input in strategies 3 and 4 will result in excess salt cake, which can be converted into NaOH and H_2SO_4 using existing technologies such as electrochemical splitting (Cloutier & Beaudoin, 2014). However, the profitability will depend on cost of the technology, availability of salt cake in the mill as byproduct, which has been included in the Na/S balance, and the cost of NaOH and H_2SO_4.

4.4.3 Increase in steam and water demand and effluent production

The reduction of recovery boiler steam production creates a steam deficit in the mill. The increase of evaporator steam demand also contribute to the increase of global steam demand when a lignin biorefinery is implemented as given in Table 4-7. This increase arises from reduced solids content of the black liquor due to lignin removal and the additional water recycled to the black liquor stream with wash filtrates. The water demand increase is mainly caused by the required lignin wash water and BL cooling water. For strategies 3 and 4, the total steam demand is higher due to the recycle of wash filtrates. Strategies 1 and 2 have higher effluent generation due to the disposal of all the wash filtrates. The studied mill produce alkaline effluents in bleaching plant, which were not included in the chemical balance. It was assumed that these alkaline effluent were sufficient to neutralize the acidic effluents generated in the lignin plant.

Table 4-7: Steam, water demand and effluent production increase based on the implementation strategy of the biorefinery process

Strategy	**RB steam production reduction (%)**	**Evaporator train steam demand increase (%)**	**Total steam demand increase (%)**	**Water demand increase (%)**	**Additional effluent production**	
					(t/d)	**(%) of total**
1	13.1	1.1	5.5	1.5	312	0.76
2	13.1	1.1	5.5	1.5	312	0.76
3	13	4.8	6.0	1.5	184	0.44
4	13	6.8	6.2	1.5	144	0.34

The feasibility of addressing increased steam and water demands due to integration of lignin biorefinery have been demonstrated in numerous previous studies (Benali et al., 2014; Kannangara et al., 2012; Laaksometsä et al., 2009; Olsson et al., 2006). Energy and water optimization for the studied mill have been performed in our previous study (Keshthkar, 2013) and shown that steam savings up to 37% were feasible using energy optimization techniques. Water savings up to 57% are feasible.

4.4.4 Pulp production increase and implementation constraints

The lignin extraction reduces the processing demands of recovery boiler and the causticizing sections depending on the implementation strategy (Table 4-6 and Table 4-7). The demand is increased in the evaporator section for strategies 3 and 4. The BL viscosity decreases with lignin extraction, resulting in an increase in heat transfer coefficient by 4-124% (Moosavifar et al., 2009). Hence, improvements in the evaporator capacities can be expected. In this study, we have assumed an evaporator capacity improvement of 4% due to decrease of BL viscosity. In order to estimate the feasible pulp production increase, the BL flow has been increased while maintaining the same lignin extraction ratio. Table 4-8 summaries the impact of each strategy on the capacities of recovery operations.

Table 4-8: Feasible pulp production increase, lignin extraction and capacities utilized in the liquor cycle for the studied mill.

Strategy	Lignin extraction (t/d)	Pulp production increase (%)	Utilized capacity (%)			
			Evaporator train	Recovery boiler	Causticizing	Lime kiln
1	27.6	14.9	95.3	100.0	80.7	97.8
2	26.4	10	91.2	95.7	82.5	100.0
3	27.6	14.8	100.0	99.9	82.4	99.9
4	27.0	12.6	100.0	98.0	80.0	97.0

Strategy 1 provides the highest pulp production due to the absence of increase in evaporator steam demand and the reduction of lime kiln processing by the loss of Na with lignin cake. In strategy 2, the Na flow is adjusted by the re-alkalization of BL. Therefore, pulp production can only be increased up to 10% before reaching the production bottleneck at the lime kiln. Strategies 3 and 4 are limited by the evaporator steam demand increase resulting from wash liquor recycle. Further production increase might be possible, if the evaporator capacities can further be freed up by BL heat transfer coefficient decrease. In some mills, the re-adjustment of pH is necessary to prevent

increased sulfur gas emissions from BL and combustibility issues caused by reduced residual alkali of BL. Therefore, the choice of BL re-alkalization and wash filtrates recycle strategy will also be dependent on the constraints of the mill.

4.5 Conclusions

The proposed simulation approach was utilized to study the implementation of a lignin biorefinery in a Kraft pulping mill with an emphasis on process chemistry and Na/S balances. For a Kraft pulping mill with 285 ADt/d Kraft pulp capacity, a lignin extraction ratio of 15% was feasible according to the recovery boiler calorific value constraints resulting in a lignin biorefinery plant of 24 t/d in a mill. Four strategies of Na/S balance were analyzed and following conclusions have been made with regard to the implementation of lignin biorefineries in the studied Kraft pulping mill.

- The unwashed lignin cake is enriched with Na (around 12% by wt.) and hence the generated wash filtrates contain a significant amount of Na mixed with S from H_2SO_4 and diluted with water. Therefore, recycling of the most concentrated wash filtrates (from first washing step) should be considered to minimize the loss of Na.
- Additional S that is introduced with recycled wash filtrates, can be balanced by reducing the S make-up (salt cake in the mill studied) or increasing ESP purge, which also removes Na. The additional make-up caustic demand reached a minimum of 146 kg/t lignin for this case when maximum amount of wash filtrates was recycled before increasing the ESP purge. As increasing ESP purge increases the make-up caustic demand. Adding extra S with wash filtrates to the liquor cycle than required by the mill sulfidity is not, hence, recommended. Mills with larger external S requirement would be able handle more wash filtrates than tightly balanced mills in terms of S.
- The sensitivity analysis revealed that the minimum caustic demand is a function of the chemical recovery efficiency and wash liquor demand of the first washing step and that it can be decreased below 100 kg/t lignin by improving the washing efficiency. Therefore, improving the washing operation, to achieve highest chemical removal with minimum amount of acid, should be considered to minimize the disruption of Na/S balances.
- Since most Kraft mill liquor cycles are also limited by other operations such as evaporator train, causticizing and lime kiln, the recycling strategies should balance the impact on other

recovery operations. The recycle of water with wash filtrates increases the evaporator train load, re-adjusting the pH of BL in evaporators can increase the causticizing and lime kiln loads and recovery of Na with wash filtrate recycle can decrease the extent of reduction of causticizing and lime kiln loads. Due to these impacts, Kraft pulping mills with limited thermal capacities in recovery boiler and large unitized capacities in the rest of the liquor cycle are ideal for implementation of lignin biorefineries with pulp production increase. For the studied mill, a pulp production increase up to 14.9% was feasible without considering other liquor cycle bottlenecks.

- For the studied mill, a strategy of 5 t/t of lignin wash filtrate recycle with no BL pH adjustment in the evaporators balanced the disruption of Na/S balance, evaporator steam demand increase and chemical loads to causticizing loop and lime kiln, providing a minimum caustic demand at 146 kg/t lignin and highest pulp production increase at 14.8%. When applying to this strategy to another mill, the ability to accommodate external S, the need to re-alkalize black liquor, available capacities in evaporator train and causticizing loop have to be considered.

Although the estimated values of lignin extraction, caustic make-up demand and pulp production increase are specific to the studied Kraft pulping mill, the conclusions can be used as general guidelines in implementing lignin biorefineries in Kraft pulping mills. The constraints imposed by each mill have to be taken into account together with changed mill balances in order obtain successful biorefinery implementations.

4.6 Acknowledgements

This work was financially supported by the BioFuelNet Canada. The authors are grateful to industrial partners for providing the data used in the study.

4.7 References

Alen, R., Patja, P., & Sjöström, E. (1979). Carbon dioxide precipitation of lignin from pine kraft black liquor. *Tappi, 62*(11), 108-110.

Andersson, P. (2014). *A dynamic Na/S balance of a kraft pulp mill.* Karlstad University.

Benali, M., Périn-Levasseur, Z., Savulescu, L., Kouisni, L., Jemaa, N., Kudra, T., & Paleologou, M. (2014). Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp

mill: Optimal resources integration and economic viability assessment. *Biomass and Bioenergy, 67*(0), 473-482.

Blackwell, B., & Lincoln, D. (1998). Sodium/sulphur/chlorine balance demonstrated low liquor losses at a kraft mill. *Pulp and Paper Canada, 99*(1), 74-78.

Bozell, J., Holladay, J., Johnson, D., & White, J. (2007). Top value added Chemicals from Biomass.Volume II–Results of Screening for Potential Candidates from Biorefinery Lignin, US Department of energy, report PnnL-983. In P. N. N. Laboratory (Ed.), *http://www1.eere.energy.gov/bioenergy/pdfs/pnnl-16983.pdf*.

Cloutier, J.-N., & Beaudoin, L. (2014, 8-13 June, 2014). *New source of caustic for Kraft mills from the electrolysis of sodium sulphate - preliminary economics.* Paper presented at the International Chemical Recovery Conference, Tampere, Finland.

Dahlin, P. (2015). *Na/S balances at Skoghall mill 2015: Balances after reconstruction of the fiber line.* (Master), Karlstad University.

Hamaguchi, M., & Vakkilainen, E. (2010, 12-15 October). *The influence of lignin removal on the energy balance of future pulp mills.* Paper presented at the XXI TECNICELPA Conference and Exhibition, Lisbon, Portugal.

Kannangara, M., Marinova, M., Fradette, L., & Paris, J. (2012). *Lignin recovery by acid precipitation in a kraft mill: An energy perspective*, 740 rue Notre-Dame ouest, Bureau 810, Montreal, Quebec, H3C 3X6, Canada.

Keshthkar, J. (2013). *Steam and water combined analysis, integration and efficiency enhancement in Kraft pulping mills.* (PhD), Ecole Polytechnique Montreal.

Kouisni, L., Holt-Hindle, P., Maki, K., & Paleologou, M. (2012). The lignoforce system: A new process for the production of high-quality lignin from black liquor. *J-FOR: The Journal of Science and Technology for Forest Products and Processes, 2*, 6-10.

Laaksometsä, C., Axelsson, E., Berntsson, T., & Lundström, A. (2009). Energy savings combined with lignin extraction for production increase: case study at a eucalyptus mill in Portugal. *Clean Technologies and Environmental Policy, 11*(1), 77-82.

Lockhart, J. (2008). *Precipitator dust purification for Kraft mill chloride reduction.* Paper presented at the Black liquor recvoery boiler advisory committe Conference, Atlanta, United States.

Loutfi, H., Blackwell, B., & Uloth, V. (1991). Lignin recovery from kraft black liquor: preliminary process design. *Tappi Journal, 74*(1), 203-210.

Moosavifar, A., Sedin, M., & Theliander, H. (2009). Changes in viscosity and boiling point elevation of black liquor when a fraction of lignin is removed - Consequences in the evaporation stage. *Appita Journal, 62*(5), 383-390.

Olsson, M. R., Axelsson, E., & Berntsson, T. (2006). Exporting lignin or power from heat-integrated kraft pulp mills: A techno-economic comparison using model mills. *Nordic Pulp and Paper Research Journal*.

Perin-Levasseur, Z., Benali, M., & Paris, J. (2010). *Lignin Extraction Technology Integrated in a Kraft Pulp Mill : Implementation Strategy.* Paper presented at the 3rd International

Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Lausanne, Switzerland.

Saturnino, D. M. (2012). *Modeling of Kraft Mill Chemical Balance.* University of Toronto.

Silva, E. A. B. d., Zabkova, M., Araújo, J. D., Cateto, C. A., Barreiro, M. F., Belgacem, M. N., & Rodrigues, A. E. (2009). An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chemical Engineering Research and Design, 87*(9), 1276-1292.

Smook, G. A. (1992). *Handbook for pulp and paper technologists* (Third Edition ed.). Vancouver: Angus Wilde Publications.

Stevens, F., Grace, T., & Leopold, B. (1989). *Alkaline pulping: Pulp and paper manufacture*: Technical Section, Canadian Pulp and Paper Association.

Tomani, P. (2010). The lignoboost process. *Cellulose Chemistry and Technology, 44*(1-3), 53-58.

Tran, H. (2008, 7-10 Januray, 2008). *The Kraft Recovery Process.* Paper presented at the Tappi Kraft Recovey Short Course, St. Petersburg, Florida, United States.

Uloth, V. C., & Wearing, J. T. (1989). Kraft lignin recovery: acid precipitation versus ultrafiltration, Part II: Technology and economics. *Pulp & Paper Canada, 90*(10), 34-37.

Vakkilainen, E., & Valimaki, E. (2009). *Effect of lignin separation to black liquor and recovery boiler operation*, Memphis, TN, United states.

Vakkilainen, E. K. (2000). Estimation of elemental composition from proximate analysis of black liquor. *Paperi ja Puu/Paper and Timber, 82*(7), 450-454.

Valimaki, E., Niemi, P., & Haaga, K. (2010). *A case study on the effects of lignin recovery on recovery boiler operation.* Paper presented at the TAPPI/PAPTAC International Chemical Recovery Conference, Williamsburg, VA, United states.

Wallmo, H., Richards, T., & Theliander, H. (2007). Lignin precipitation from kraft black liquors: kinetics and carbon dioxide absorption. *Paperi ja puu, 89*(7-8), 436-442.

Wising, U., Algehed, J., Berntsson, T., & Delin, L. (2006). Consequences of lignin precipitation in the pulp and paper industry.

Wooley, R., & Putsche, V. (1996). Development of an ASPEN PLUS Physical Property Database for Biofuels Components. Golden,CO,: National Renewable Energy Laboratory.

Chapter 5 ARTICLE 3: EFFECT OF MIXING HYDRODYNAMICS ON THE PARTICLE AND FILTRATION PROPERTIES OF PRECIPITATED LIGNIN

Miyuru Kannangara, Mariya Marinova, Louis Fradette, and Jean Paris

Research Unit on Energy Efficiency and Sustainable Development of the Forest Biorefinery, Department of Chemical Engineering, Polytechnique Montreal, C.P. 6079, succ. Centre-Ville, Montréal, QC, Canada H3C 3A7

Abstract

The effects of mixing hydrodynamics on the particle and filtration properties of precipitated lignin from black liquor has been investigated. The hydrodynamics were varied in terms of turbulent shear rate and impeller flow pattern in the stirred tank. The precipitated lignin flocs were characterized in terms of particle size, size distribution, and particle shape. Our findings showed that the effect of hydrodynamics on the size and shape of primary lignin particles were negligible. However, as lignin primary particles aggregate into larger flocs, the impact of hydrodynamics became increasingly important. More compact and smaller lignin flocs were produced at higher turbulent shear levels during black liquor pH reduction (acidification step). Upon further mixing (ageing step), these flocs aggregated into much larger flocs as the level of turbulence was reduced after the acidification step. They had narrow size distributions. The size of the final flocs varied mainly with the turbulent shear rate, minimum shear rate producing largest particles. However, low shear acidification produced loose particles with wide size distributions and lower strength, making them susceptible to breakage due to impeller action. The low shear impeller showed better aggregation with loose particles. Lignin flocs with higher compactness and size showed better filtration and washing properties. Optimal hydrodynamic conditions led to production of lignin with good filtration and washing properties at 1.83E+09 m/kg specific filtration resistance, 243 kg/h.m^2 lignin filtration rate and 0.09% ash content. The reproducibility of the results was validated using black liquor samples from three Kraft pulping mills.

Keywords

Lignin precipitation, Kraft process, hydrodynamics, particle properties, filtration

5.1 Introduction

Lignin, one of the most abundant natural polymers on earth, is currently being investigated as a feedstock for manufacture of bio-based products and chemicals. Pulp and paper industry produces around 20 million tons of lignin annually, however only 2% (1.1 million tons) of this lignin is being used for applications other than heat and power generation. The amount of lignin recovered from Kraft pulping mills are even lower, totaling to an estimated 100,000 tons annually. Lignin is entrained in the residual black liquor stream of Kraft pulping mills, which is combusted to generate steam and recover pulping chemicals. The extraction of lignin from black liquor is emerging as potential lignin biorefinery pathway, including recent industrial installations. Acid precipitation is one of the most promising methods for lignin recovery from Kraft pulping mills in terms of technological maturity and economics (Benali et al., 2014; Uloth & Wearing, 1989a).

A flow diagram of the acid precipitation process is given in Figure 5-1: Flow diagram of the acid precipitation process.. The incoming black liquor is acidified to a pH of 9 to 10 (acidification step) to precipitate lignin. Resulting lignin slurry is further agitated (ageing step) for a residence time of 30 to 90 min to complete the aggregation of lignin. The slurry is then filtered, and the cake is washed with H_2SO_4 and water to reduce the ash content (Kouisni et al., 2012; Loutfi et al., 1991; Wallmo, Richards, et al., 2009).

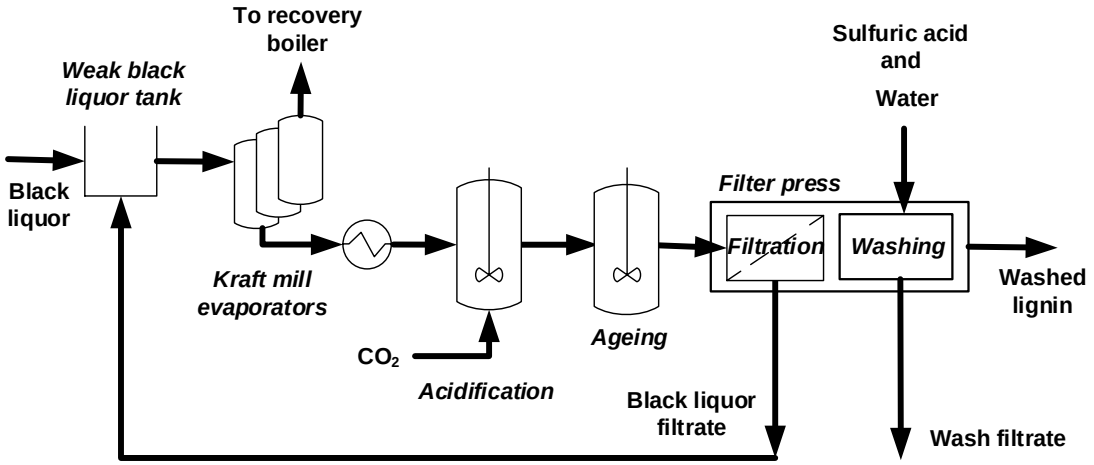

Figure 5-1: Flow diagram of the acid precipitation process.

Lignin in black liquor is a complex colloidal system. At high pH values, the phenolic and carboxyl groups of lignin molecules are dissociated, providing a negative surface charge, thus maintaining the colloidal stability. As the pH decreases, the surface charges are neutralized, destabilizing the lignin colloids, making them to coagulate into solid macromolecule particles. The aggregation of lignin in aqueous solutions has been found to be governed by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which describes the colloidal stability as balance between attraction and electrostatic repulsion forces (Norgren et al., 2002; Norgren et al., 2001). As a result, the amount of lignin precipitated is mainly influenced by the solution pH, temperature and salt concentration (Norgren et al., 2002; Norgren et al., 2001). Lignin aggregation under Brownian motion, absence of agitation, have been reported to produce lignin particle with fractal dimensions varying from 1.9 to 2.45 and sizes in the range of 100 nm up to 1-2 µm (Norgren et al., 2002).

Although, higher yields can be obtained by adjusting the pH, temperature and black liquor solids content, the lignin precipitation process can only be conducted in a narrow range of conditions to be able to obtain filterable lignin. The precipitation pH, temperature and black liquor total solids content generally have to be in the range of 9 to 10, 60 to 80°C and 30-40%, respectively (Loutfi et al., 1991; Ohman & Theliander, 2007; Wienhaus, Bernaczyk, & Pecina, 1990). Lignin particles produced outside these ranges have been described as very fine or soft and tacky, making filtration difficult (Loutfi et al., 1991). The changes in the particle properties arise from varying the molecular surface properties of lignin as well as solution conditions. Low molecular weight lignin fractions precipitate at lower pH values, producing finer particles with less active sites for particle-particle aggregation. The temperature decreases the surface charges of lignin, providing better aggregation, however, temperatures higher than 80-85°C produces lignin in liquid state (Loutfi et al., 1991; Norgren & Lindstrom, 2000b; Zhu et al., 2014).

The reported specific filtration resistances of lignin cake were generally high, varying in the range of 1E+10 to 1E+12 m/kg while lowest recorded filtration resistance was around 8E+09 m/kg for softwood black liquors. The filtration and washing equipment are one of the most capital intensive in acid precipitation plants due to the high filtration resistance, amounting to ~30% of the total capital expenditure (Diffo, 2013; Gooding, 2012). Therefore, there are incentives in optimizing the efficiency of lignin filtration.

Although, the lignin surface properties and the physicochemical properties of the solution tend to dominate the colloidal aggregation, the hydrodynamic conditions affect every aspect of this phenomenon including initial aggregation, growth and breakage of particles, determining the final particle size and structure (Spicer, Keller, & Pratsinis, 1996; Spicer et al., 1998). The filtration and dewatering efficiencies are heavily dependent on the size, structure and distribution of the particles (Jarvis, Jefferson, Gregory, & Parsons, 2005; Spicer et al., 1998; Xu, W. & Gao, 2012). The hydrodynamic flow pattern and shear rate are two main parameters that determine the hydrodynamic state of a stirred tank. The flow pattern mainly depends on the hydrodynamic design of the system including impeller type, diameter and positioning. The level of shear in the stirred tank varies from impeller zone to smallest turbulent eddy fluctuations creating a complex shear field (Kresta, 1998; Paul, Atiemo-Obeng, & Kresta, 2003).

Despite the relevance of hydrodynamic the conditions, the effect of hydrodynamics on the lignin precipitation has not received much attention. The published studies investigated, among other parameters, the effect of agitation rate on the filtration resistance, reporting that slower agitation speeds during the acidification and ageing steps decrease the filtration resistance (Howell & Thring, 2000; Wallmo, Richards, et al., 2009). However, more in depth studies are required to understand the effect of fundamental hydrodynamic quantities on the properties of the precipitated lignin. To produce high purity lignin at low production costs, it is necessary to optimize the hydrodynamics of the lignin precipitation process, so that it facilitates better filtration and washing of lignin.

Within this context and focusing on the fundamental and technological aspects, the goals of the present work were to investigate the effects of turbulent shear rate and hydrodynamic flow pattern on the acid precipitation process including particle and filtration properties of precipitated lignin. The precipitation was carried out using two different impeller systems: Pitched blade turbine (PBT) and Maxblend^{TM} (MB) mixing assemblies. They were operated at different power levels to vary the turbulent shear rates. The lignin particles were characterized in terms of size, shape and distribution. Filtration and washing properties of the precipitated lignin were characterized in terms of specific filtration resistance of lignin cake, washing time, and ash content of lignin. The lignin yield was also estimated. The reproducibility of the results were confirmed using black liquor from three Kraft pulping mills. All the black liquors used in the study were softwood liquors.

5.2 Materials and methods

5.2.1 Experimental setup

All the experiments were carried out in an open 2 L vessel with standard baffles (T/10). Heating was provided by a circulating hot water bath with a temperature controller connected to the outer jacket of the vessel. The CO_2 was introduced using a porous sparger tip located at the bottom of the vessel. The CO_2 flow rate was measured and adjusted using a rotameter placed between the sparger and the CO_2 supply. The black liquor was mixed using a two-stage, four-bladed, 45°-angle PBT or a straight MB impeller. The dimensions and positioning of the impellers are shown in Figure 5-2. The optimal positioning of MB impeller, which was very close to the tank bottom, could not be achieved due to the presence of the sparger tip. A mixer (Caframo BDC 2002) with 1 RPM accuracy was used to mix the black liquor. A standard vacuum filtration setup consisting of a 15 cm-diameter Buchner funnel, a 2-L filtration flask, and 15 cm-diameter, Grade 113 Whatman filter discs were used to filter and wash the precipitated lignin at a vacuum pressure of 70 kPa.

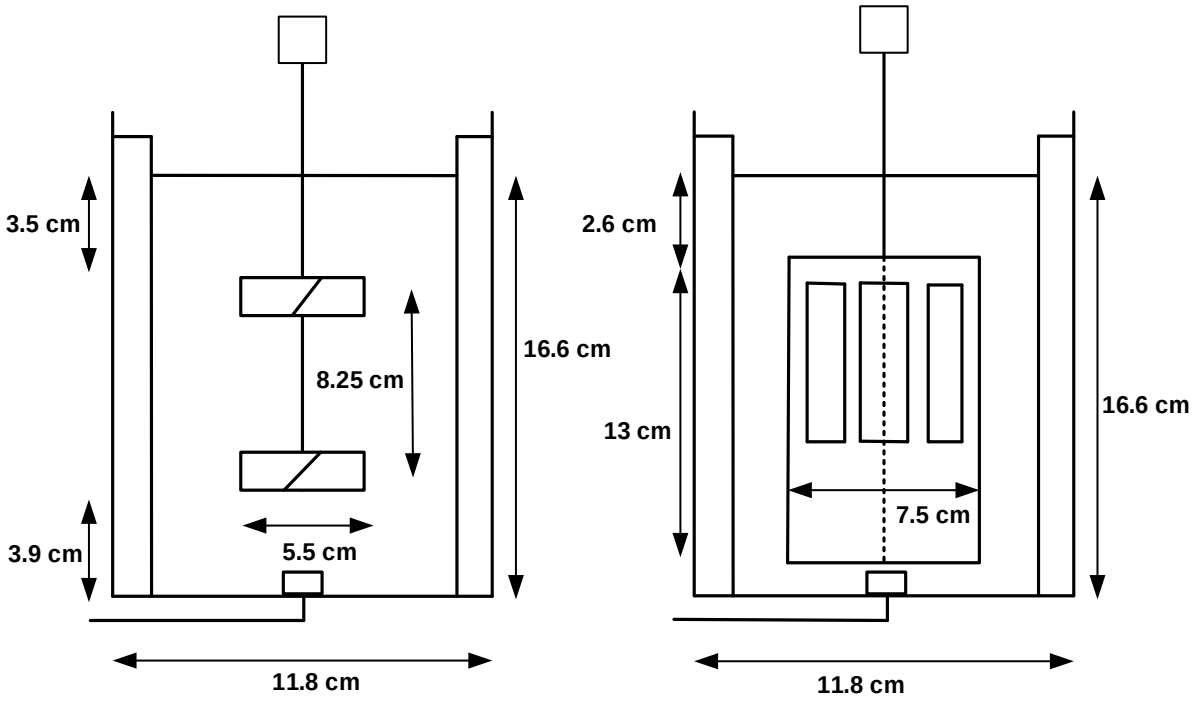

Figure 5-2: Two-stage pitched-blade turbine (PBT) and Maxblend (MB) impeller assemblies and their dimensions.

5.2.2 Black liquor samples

Four softwood black liquor samples (A, B, C and D) were received from Canadian Kraft pulping mills, which had solids concentrations ranging from 46% to 52%. Liquor A and D had been subjected to oxidation pre-treatment. All the liquors were diluted with deionized water to 30% dissolved solids level and were pre-filtered using Grade 113 Whatman filter discs to remove suspended solids such as fibers, dregs, and soap. The study was performed using a Liquor A. The reproducibility of the results for liquor A was evaluated with black liquors B, C, and D. The characteristics of the four liquors are given in Table 5-1. The characterization methods are described in section 5.2.3. The values reported are averages of four repetitions.

Table 5-1: Properties of the black liquor samples.

Properties / **Liquor**	**A**	**B**	**C**	**D**
Total solids (%)	30	30	30	30
UV lignin (% total solids)	36.3	41.8	38.5	38.3
Klason lignin (% total solids)	29.5	32.5	30.1	30.2
Acid-soluble lignin (% total solids)	4.8	7.5	5.4	5.3
Inorganics or ash (% total solids)	34.2	27.3	28.2	28.3
Organics (% total solids)	65.8	72.7	71.8	71.7
Na (% total solids)	17.5	18.3	22.7	22.5
Residual alkali (g/L)	6.2	3.4	17.1	18.1
Sulfide content (g/L)	1.65	7.5	19.3	1.2
pH at room temperature	13.0	12.9	13.3	13.4
Dynamic viscosity (mPas)	7	8	9	9

5.2.3 Characterization of the black liquors, filtrates, and lignin samples

The total solids content was estimated by drying a known amount of liquor or lignin at 105°C based on the CPPA J.15 (II) standard test procedure. The UV lignin content was determined using a Biochrom Ultrospec UV spectrophotometer at a wavelength of 280 nm. Black liquor (2 g) was dissolved in 100 ml of 0.1 M NaOH and was diluted to absorbance at 280nm of 0.3-0.8 using an absorption coefficient of 23.7 $dm^3g^{-1}cm^{-1}$.

The Klason lignin content and acid soluble lignin content were determined using the procedure described in (Zhu et al., 2014). In this method, 3 mL of 72% sulfuric acid was added to a 1.2 g sample of black liquor. The sample was kept in a water bath at 30°C for 1 hour. The sample was diluted with deionized water (84 g), was hydrolyzed at 125°C in an autoclave for 1 h and was then filtered to recover the Klason lignin. The dry weight was determined gravimetrically. The filtrate was diluted by a factor of 1/100 and the acid soluble lignin content was determined using a Biochrom Ultrospec UV spectrophotometer at a wavelength of 205 nm using an absorption coefficient of 110 $dm^3g^{-1}cm^{-1}$.

The ash content of the black liquor was determined by heating a known quantity of residue from total solids content determination at 950°C for 24 h. The measuring remaining inorganic residue (ash) the in the sample was measured as described in (Holmqvist, Wallberg, & Jonsson, 2005; Wallberg, Jonsson, & Wimmerstedt, 2003). The lignin ash content was determined by heating a known dry weight of lignin in a furnace at 550°C until a constant weight was obtained. The sulfide content of black liquor was determined using the CPPA J.15 (VI) standard test procedure. The residual effective alkali content was determined using the method recommended in (Radiotis, Sullivan, MacLeod, Syed, & O'Hagan, 2007). The viscosity measurements were performed with a Bohlin Visco88 viscometer.

5.2.4 Experimental Procedure

The filtered black liquor at 30% dissolved solids (1.8 L) was poured into the vessel with the selected impeller (PBT or MB) and heated to 75°C temperature while agitating. CO_2 sparging (1 L/min) was started and the mixing speed was adjusted to the desired level in order to apply the required power to the fluid. The pH during acidification was measured periodically using a MetroHM Unitrode glass pH electrode. The CO_2 sparging was stopped when the pH reached 9.8 ± 0.5. This

pH reduction step corresponds to the black liquor acidification operation given in Figure 5-1. The mixing was continued for 1 hour at the desired speed and 75°C temperature and this step corresponds to the ageing operation of the process. The agitation rates during the acidification and ageing operations are set to adjust the turbulent shear levels and it is discussed in section 5.2.5. The pH and temperature values were chosen from pre-trial tests to produce filterable, washable lignin. Lignin slurry samples (5 mL) were withdrawn during ageing step at 0, 5, 15, 30, and 60 min time intervals. The samples were filtered using 15 cm diameter Grade 113 Whatman filter discs prior to characterizing the particle properties.

After the ageing phase, the lignin slurry was cooled to about 55°C. It was then filtered, and the filtrate volume versus time was recorded. The filtrate was analyzed for total solids, UV lignin content, and viscosity. The filter cake was washed with 1 L of 0.4 M H_2SO_4 and 200 mL of water poured on top of the cake. The total washing time and weight of the wet lignin cake were recorded. The cake was air-dried at room temperature for 24 h and then oven-dried at 105°C overnight to determine its dry weight.

5.2.5 Characterization of the hydrodynamic conditions in the stirred tank

The turbulent shear rate in the stirred tank was characterized by the average dissipation rate of the turbulent kinetic energy ($\langle\varepsilon\rangle$), estimated by the ratio ($P/\rho V$), where P is the total power input, ρ is the density of black liquor and V is the volume of the stirred tank. P was estimated using the power number (N_P) of the impeller.

$$P = N_P \rho N^3 D^5 \qquad [1]$$

The quantities, N and D, are the agitation rate and the impeller diameter. The N_P values were 2.2 for the two-stage PBT assembly and 6.1 for the MB impeller (Hidalgo-Millán et al., 2012; Paul et al., 2003). The two impellers have largely different power numbers (N_P) and therefore they created significantly different impeller speeds and hence different shear rates in the impeller zone, in addition to the differences in the created flow patterns.

The dissipation rate of turbulent kinetic energy (ε) is the primary parameter used in characterizing the turbulence, including length, time and velocity scales. The average $\langle\varepsilon\rangle$ does not characterize the local dissipation rates hence it does not take into account the variations of the shear field generated by the flow fields of two impellers considered. However, the average turbulent shear

rates in the liquid bulk were similar when both assemblies were operated at the same $P/\rho V$ and thus provided a base for comparing the performance of two impeller systems, consistent with the previous studies (Hidalgo-Millán et al., 2012; Spicer et al., 1996). As ρ is constant for the given system, the specific power input (P/V) was used as the characterization parameter for the turbulent shear rate, which is often applied in hydrodynamic system scale up.

The specific power levels chosen for the present study were 1.029, 0.107, 0.011, and 0.003 kW/m^3. Black liquor acidification, which requires a high level of pumping and turbulence to disperse the CO_2, was performed at 1.029 and 0.107 kW/m^3. The lower power levels, 0.107, 0.011, and 0.003 kW/m^3, were used during the lignin slurry ageing operation to minimize particle breakage. The power levels generated Reynolds numbers ranging from 626 to 5679 and RPMs ranging from 40 to 674 as shown in Figure 5-2. The experimental conditions were replicated twice or three times, and average values are reported.

Table 5-2: The power levels and corresponding to the Reynolds numbers and RPMs for the PBT and MB impeller assemblies.

Power level (kW/m^3)	**PBT**		**MB**	
	RPM	**Re**	**RPM**	**Re**
0.003	93	783	40	626
0.011	148	1247	63	987
0.107	317	2671	135	2115
1.029	674	5679	287	4497

5.2.6 Characterization of specific filtration resistance and lignin yield

The integrated form of the constant pressure filtration equation was used to determine the specific resistance of the filter cakes. The gradient of this equation was used to calculate the specific filtration resistance ($\boldsymbol{\alpha}$) of the cake.

$$\frac{t}{V} = \frac{K_1}{2} V + K_2 \qquad [2]$$

$$K_1 = \frac{\alpha c \mu}{A^2 \Delta p} \quad [3]$$

$$K_2 = \frac{\mu R_M}{A \Delta p} \quad [4]$$

The quantity V is the filtrate volume, t is the corresponding time taken to collect the filtrate volume, c is the solids concentration of the slurry, μ is the dynamic viscosity of the filtrate, A is the filtration area, Δp is the pressure difference of filtration, and R_M is the filtration resistance of the medium. The solid concentration of the slurry was estimated using the amount of dry lignin recovered. The lignin yield was computed as the amount of dry lignin recovered from the total lignin in the black liquor. The UV lignin content was used to estimate the total lignin in the black liquor.

5.2.7 Characterization of particle size distributions and structures

A laser diffraction instrument (Mastersizer 3000, Malvern, UK) was used to determine the particle size distribution of the lignin samples. The wet lignin particles were dispersed using a Hydro EV wet dispersion unit (Malvern, UK). A 3 M NaCl solution (500 mL) with the pH adjusted to the precipitation level was used as a dispersant. DV_{50}, the median particle size of the volume distribution, and $D_{3,2}$, the Sauter median diameter, were used as size characterization parameters.

The mass fractal dimension (D_f), which is a measure of compactness of a fractal structure, has been used to determine the compactness of precipitated lignin particles. The light scattering data from the Mastersizer was used in this method to estimate the fractal dimensions of aggregates, as described in the literature (Bo et al., 2012; Guan, Waite, & Amal, 1998; Jarvis, Jefferson, & Parsons, 2005). The total scattered light intensity (I) is related to scattering vector (Q) by power law with D_f as coefficient. Q was computed as given in Eq.6 (Guan et al., 1998).

$$I \propto Q^{-D_f} \quad [5]$$

$$Q = \frac{4n\pi \sin(\theta/2)}{\lambda} \quad [6]$$

where θ is the scattering angle, λ is the wave length of radiation in vacuum, n is the refractive index of the dispersant. D_f is determined by the slope of the log I vs log Q plot.

The structures of selected precipitated lignin samples were observed by scanning electron microscopy (SEM). The samples were prepared by dispersing the sample in water, drying and metal coating for conduciveness.

5.3 Results and Discussion

5.3.1 Effect of hydrodynamic conditions on particle properties

5.3.1.1 Evolution of particle size during ageing operation

5.3.1.1.1 Acidification power level of 1.029 kW/m^3

Three ageing power levels (0.107, 0.011, and 0.003 kW/m^3) were used in the experiments performed with a 1.029 kW/m^3 acidification power. As shown in Figure 5-3, the initial particle size (ageing time = 0) was around 11 µm and the size increased rapidly, during the first 15 min of the ageing operation. The rapid growth indicates more particle-to-particle aggregation than breakage. After a certain size, which seems to be dependent on the power level, was reached, particle growth slowed down considerably, suggesting that the rates of particle-to-particle aggregation and particle breakage due to have become similar. The final particle size was dependent on the ageing power level, albeit it was not affected by the type of impeller. This indicates that the turbulent shear rate controlled the particle growth and the local shear fields created by the impeller flow patterns did not play a major role in aggregation and breakage. The lowest specific power, which created the lowest turbulent shear rate, produced the largest particle size. The values of DV_{50} and $D_{3,2}$ paralleled the particle growth rate. The size difference between these two properties ranged from 2 to 4 µm, indicating narrow size distributions.

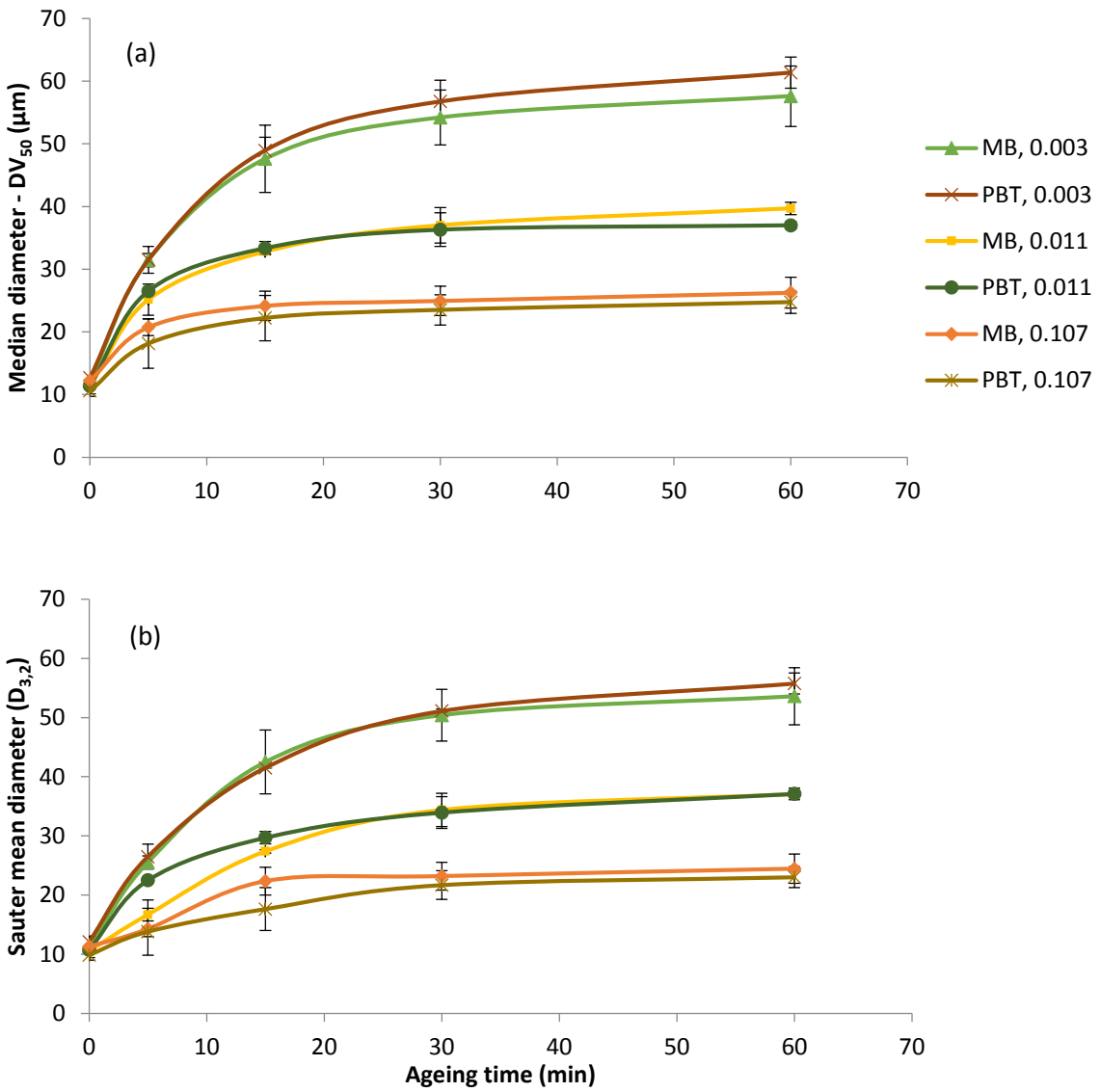

Figure 5-3: Changes in particle size during the ageing operation using the 0.003, 0.011, and 0.107 kW/m^3 ageing power levels for flocs acidified at 1.029 kW/m^3 acidification power level with the MB and PBT impeller assemblies. (a) Median diameter (DV_{50}) (b) Sauter mean diameter ($D_{3,2}$).

5.3.1.2 Acidification power level of 0.107 kW/m^3

For black liquor acidified at 0.107 kW/m^3 power level, two ageing power levels (0.107 and 0.011 kW/m^3) were investigated. The particle size at the beginning of the ageing operation was around 19 µm as shown in Figure 5-4. A size increase was less obvious with the 0.107 kW/m^3 ageing power level but size reached 37 or 44 µm with the 0.011 kW/m^3 ageing power, depending on the type of impeller. The MB impeller produced larger sizes while PBT produced smaller sizes. The DV_{50} size values were comparable with the values at the 1.029 kW/m^3 acidification power, but $D_{3,2}$

size values were relatively smaller. The average difference between DV_{50} and $D_{3,2}$ was higher (~7 µm), indicating broader particle size distributions. Unlike with 1.029 kW/m^3 acidification power, the particle size growth depended on the impeller type with 0.107 kW/m^3 acidification power, indicating an effect of the flow pattern generated by the impeller on the aggregation of the lignin particles.

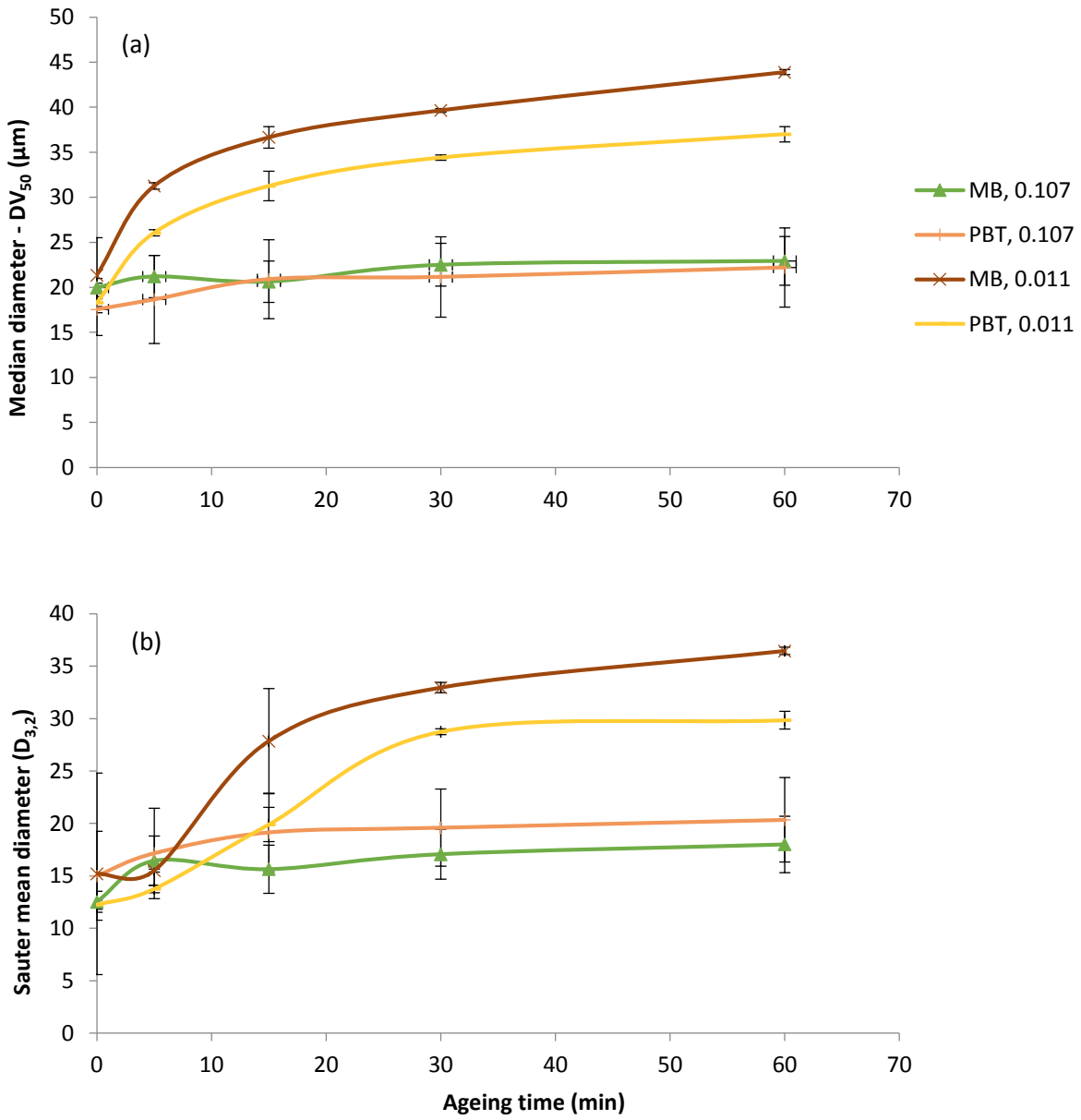

Figure 5-4: Changes in particle size during the ageing operation using the 0.011, and 0.107 kW/m^3 ageing power levels for flocs acidified at 0.107 kW/m^3 acidification power level with the MB and PBT impeller assemblies. (a) Median diameter (DV_{50}) (b) Sauter mean diameter ($D_{3,2}$).

5.3.2 Size distribution

Figure 5-5(a) shows the volume weighted size distribution at the beginning of the ageing operation (t = 0) for acidification at 1.029 and 0.107 kW/m^3 for both impellers. The 1.029 kW/m^3 acidification produced a narrow distribution with a lower median value.

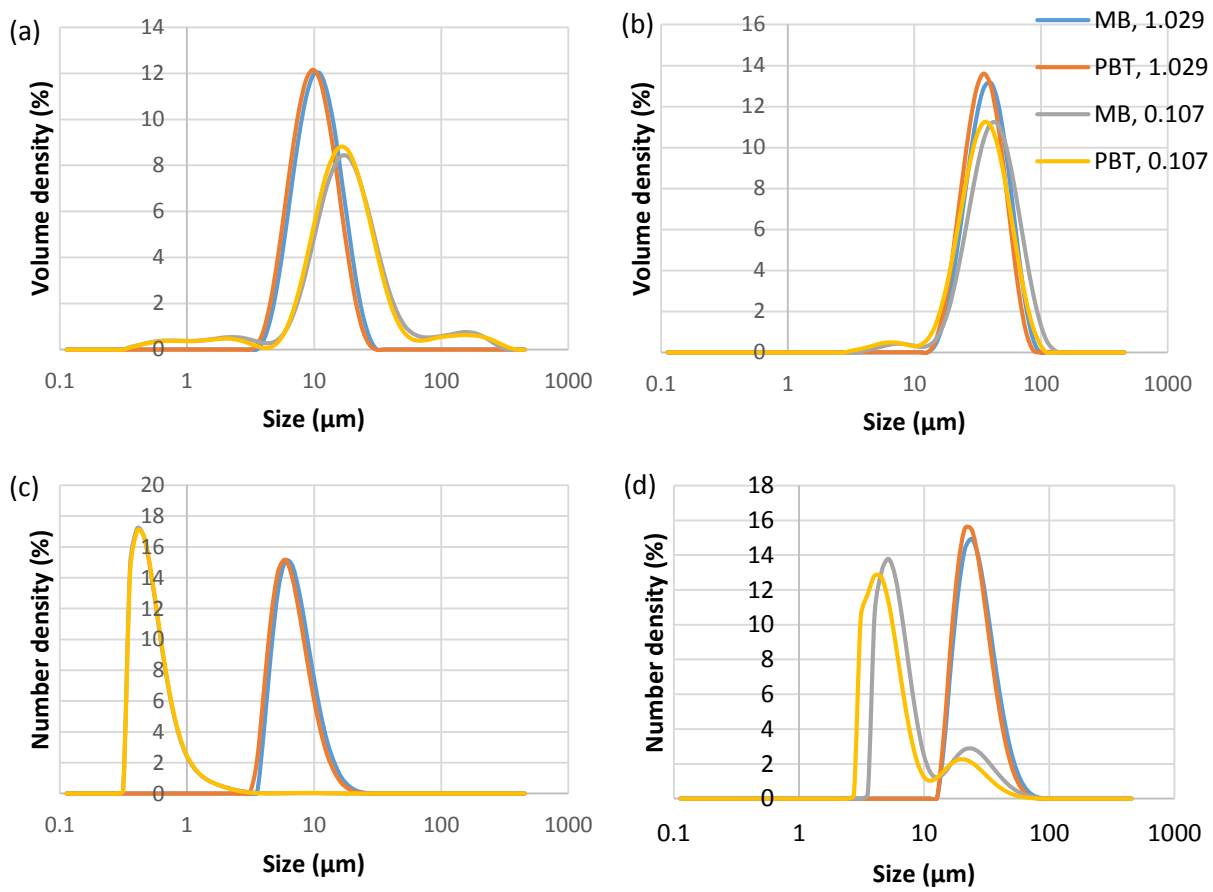

Figure 5-5 : Volume weighted and number weighted distributions for PBT and MB mixing assemblies at the start (t = 0) and end (t = 60 min) of the ageing operation for the 1.029 kW/m^3 and 0.107 kW/m^3 acidification power levels and the 0.011 kW/m^3 ageing power level. (a) Volume weighted distribution (t = 0). (b) Volume weighted distribution (t = 60 min). (c) Number weighted distribution (t = 0). (d) Number weighted distribution (t = 60 min).

A distribution without tails indicates the absence of finer or much larger particles than the median size. In contrast, lignin precipitated at 0.107 kW/m^3 acidification had wider size distribution and higher median size (Figure 5-5(a)). It also had tails on both sides, suggesting the presence of finer and much larger particles than the median size. The difference in size distribution as a function of

the type of impeller was negligible. The corresponding number weighted distribution (at t = 0) given in Figure 5-5(c), shows that there were a large number of fine particles present in the sample obtained at 0.107 kW/m^3 acidification power. The number weighted size distribution at 1.029 kW/m^3 acidification power did not indicate a presence of small particles. The presence of fine particles, albeit it does not represent a significant volume of the particles, can be detrimental to filtration.

The median sizes of the volume weighted and number weighted size distributions increased during the ageing operation, as given in Figure 5-5(b) and Figure 5-5(d). The median of the volume weighted size distribution at the end of ageing operation (t = 60) was similar for both 1.029 and 0.107 kW/m^3 acidification power levels. However, fine particles were still present in the sample acidified at 0.107 kW/m^3 power. The size of this fine particles, however, was not the same as the size of the fine particle fraction shown in Figure 5-5(c), where the fine particles are smaller than 1 µm. A difference as a function of the impeller can also be observed in Figure 5-5(d). The MB impeller system produced slightly higher median size than the PBT system at 0.107 kW/m^3 acidification.

5.3.3 Aggregate structure

The discussion regarding particle growth and size distributions revealed that lignin precipitated at 1.029 and 0.107 kW/m^3 acidification power levels showed considerably different aggregation behaviors during the ageing step and size distributions. The particle structures was analyzed in order to explain the observed differences.

Figure 5-6 shows the distribution of estimated fractal dimension (D_f) values in the beginning and at the end of ageing operation. The obtained D_f values mostly overlap for the investigated acidification power levels. In the beginning of the ageing operation, the D_f values varied from 2.3 to 2.65 while its variation was from 2.15 to 2.5 at the end of the ageing operation. Except this gradual decrease of D_f during the ageing operation, a considerable difference according to acidification power level could not be found.

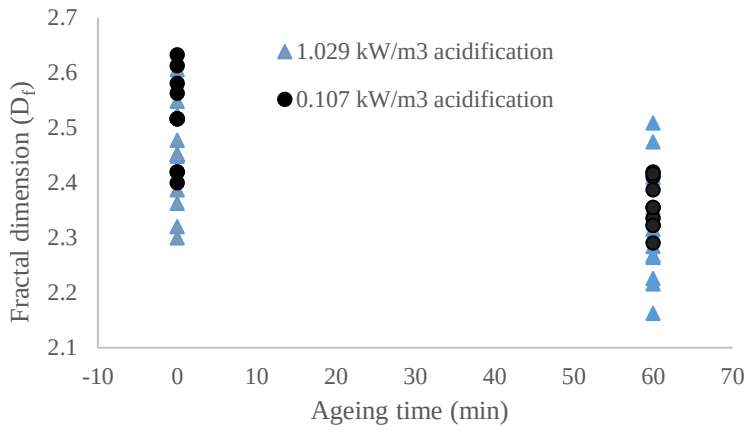

Figure 5-6: Fractal dimension (D_f) of the lignin flocs at the start and end of the acidification step.

Figure 5-7 shows the SEM images of precipitated lignin at the beginning of ageing step for both 1.029 and 0.107 kW/m^3 acidification power at 6000 magnification. In both images, the lignin flocs seem to be formed by the aggregation of many similar primary particles of 1-2 µm diameter. However, the structure of floc itself was considerably different. The lignin flocs produced at 1.029 kW/m^3 acidification (Figure 5-7(a)), albeit their small size, were compact, spherical and more uniform in size and shape than the flocs produced at 0.107 kW/m^3 acidification (Figure 5-7(b)). The lignin flocs produced at 0.107 kW/m^3 acidification were larger, however, having a loosely bound irregular structure with less compactness.

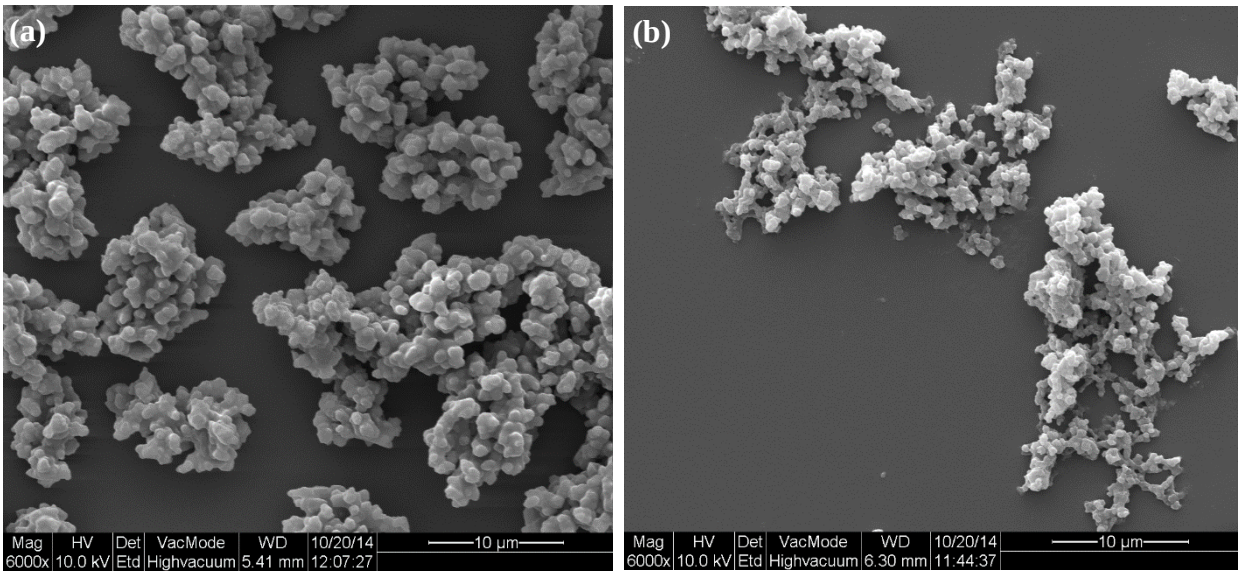

Figure 5-7: SEM images showing the size, distribution, and structure of precipitated lignin at 6000x magnification at the start of the ageing operation (t = 0). (a) 1.029 kW/m^3 acidification power level, (b) 0.107 kW/m^3 acidification power level.

The structural difference of lignin flocs at different acidification power levels, which was observed in SEM images, could not be identified using D_f values. According to Figure 5-7, the lignin flocs seem to have two level structures, where they are formed from the aggregation of many primary particles with distinct size and shape. Light scattering methods have been reported to provide poor D_f value estimations for flocs with two level structure (Ibaseta & Biscans, 2010). The D_f values of such flocs tend to measure to structure of the primary particles rather than the floc itself. The range of estimated D_f = 2.15-2.65 is consistent with the D_f = 1.9-2.45 of lignin particles reported in the literature, aggregated under the Brownian motion with sizes of 1-2 µm (Norgren et al., 2002). The similarity of D_f values and sizes of primary particles obtained under turbulent conditions in this study and Brownian motion in the literature, suggests that the hydrodynamic conditions did not have a large impact on the formation of primary lignin particles.

The length of turbulent eddy fluctuations, defined as the length scale $(\upsilon/\langle\varepsilon\rangle)^{\frac{1}{4}}$ where υ is the kinematic viscosity and $\langle\varepsilon\rangle$ is the mean dissipation rate of kinetic energy, was 125 µm for the power level 1.029 kW/m^3.. This could possibly explain the negligible effect of hydrodynamic conditions on the size and shape of the primary particles, of which the size is at 1-2 µm range, much smaller than turbulent length scale.

However, the impacts of hydrodynamics becomes increasingly important as the flocs grow in size, as seen in Figure 5-7. The weak bonds between lignin flocs can be broken, causing them to disintegrate. However, the disintegrated flocs aggregate again due to the high collisions. If the bonds are not strong enough to withstand the shear forces, the flocs disintegrate once again. This interplay of aggregation and breakage evolve the structure and size of the final flocs. As a consequence, the flocs generated at higher shear levels (1.029 kW/m^3) tend to have small and compact structures. Compact aggregates have been reported to have higher strength, as the primary particles are held together by many more bonds (Jarvis, Jefferson, Gregory, et al., 2005; Spicer et al., 1998). On the hand, the flocs generated at low shear levels had larger sizes and loose structures.

The compact and small flocs generated at the end of high shear acidification step evolved into larger particles, final size of which depending on the shear level during the ageing step. The size increase was independent on the impeller type and size distributions were narrow without fine particles, as shown in Figure 5-3 and Figure 5-5(c). Figure 5-5(c) shows the SEM images of lignin flocs at the start and the end of ageing operation. From Figure 5-8(a) and Figure 5-8(c), it seems

the small and compact flocs have aggregated together to form compact and large flocs, maintaining the compact structure of the floc. The narrow size distribution and negligible impact by the impeller type could be attributed to the strength of the compact flocs, which are harder to break under impeller shear field.

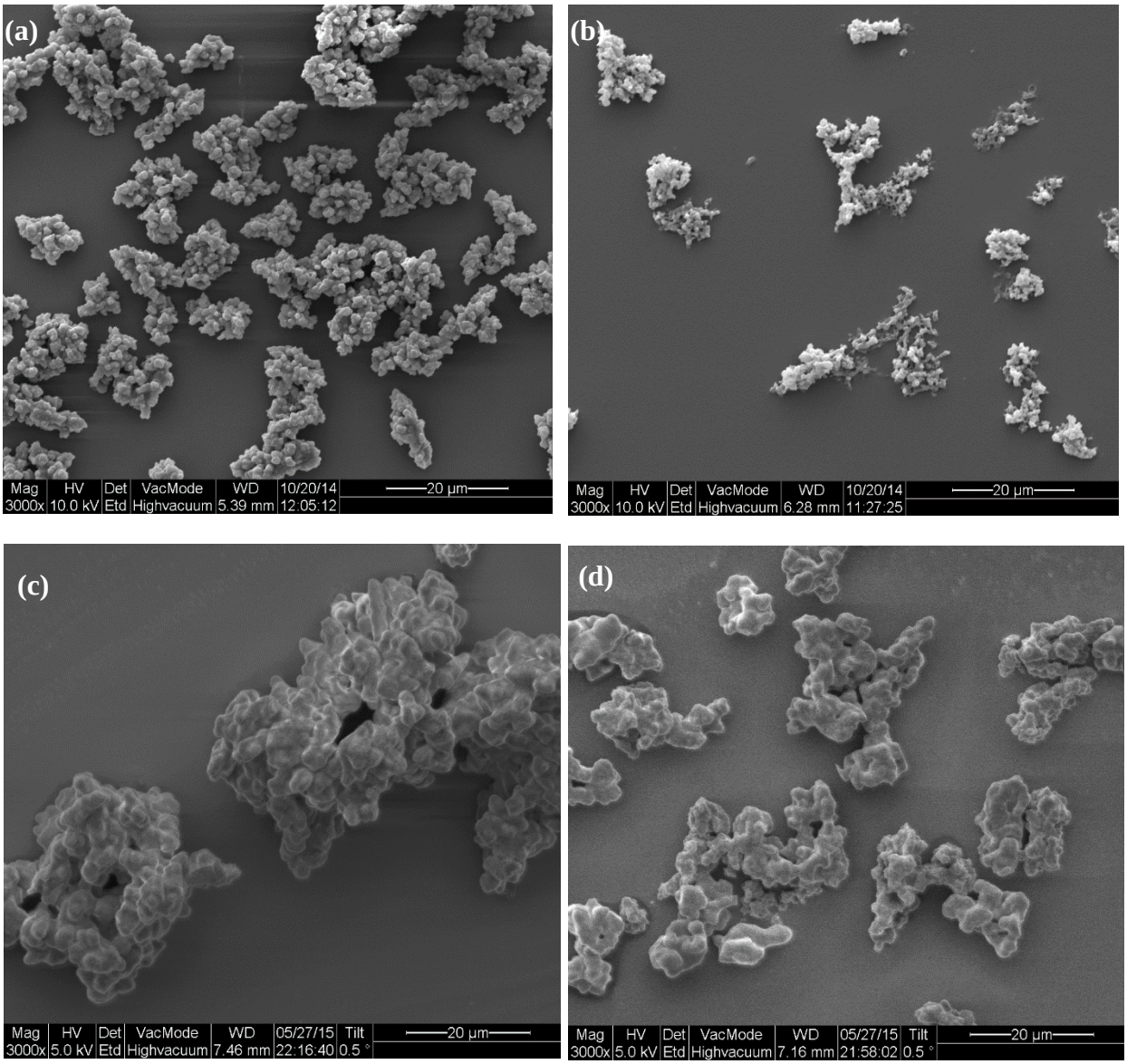

Figure 5-8: SEM images showing the size, distribution, and structure of precipitated lignin at 3000x magnification. (a) 1.029 kW/m^3 acidification power level (at the start of the ageing operation), (b) 0.107 kW/m^3 acidification power level (at the start of the ageing operation), (c) 1.029 kW/m^3 acidification power level (at the end of the ageing operation), (d) 0.107 kW/m^3 acidification power (at the end of the ageing operation).

Large but loose flocs produced by low shear acidification aggregated into larger particle during ageing step, having wide size distributions with fine particle fraction. The particle sizes were influenced by the type of impeller, as illustrated in Figure 5-4. As shown in Figure 5-8(c) and Figure 5-8(d), the flocs have grown with time but they still contain the loose structures similar to the structures in the beginning of the ageing operation. As a consequence, these flocs are weaker and they are more susceptible to breakage due to impeller action, generating fine particle and wider size distributions. Hence, low shear impellers such as MB would minimize the particle breakage and generate larger sizes, as indicated in Figure 5-4.

5.4 Effect hydrodynamic conditions on filtration, washing and yield

5.4.1 Filtration resistance

The different acidification and ageing power levels used resulted in large differences in the filtration resistance of the lignin cakes as shown in Figure 5-9. Filtration resistance was relatively lower and its variation as a function of the impeller was minimal for the trials performed at high shear acidification. This can be expected as more compact particles with narrow size distributions were obtained at high shear acidification. The filtration resistance decreased with the decrease in the ageing power, resulting in lowest resistance of 1.83E+09 m/kg with 0.003 kW/m^3 ageing.

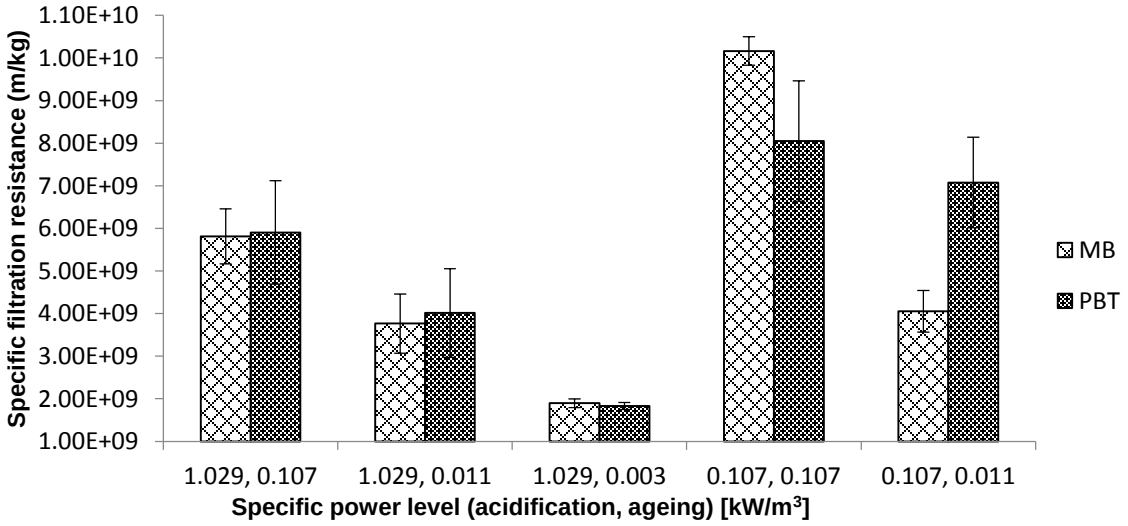

Figure 5-9: Filtration resistances of precipitated lignin cakes for the two impeller assemblies at different acidification and ageing power levels.

The values for the filtration resistances closely tracked the results for the particle size distributions. The $D_{3,2}$ was highest at 55.7 µm for the lowest filtration resistance. The highest filtration resistance of 1.02E+10 m/kg was observed for the lowest particle size of 17.9 µm.

5.4.2 Lignin yield

The lignin yields varied from 33% to 50% for the investigated conditions, as shown in Figure 5-10. The highest yields were obtained at 1.029 kW/m^3 acidification. The yields increased as the ageing power decreased. A significant difference in yield as a function of the impeller was not observed. The lowest acidification power level (0.107kW/m^3) generated the lowest yields. The size of particle could be related to yield as larger particles are more likely to be retained by the filter paper during filtration and washing than smaller particles. In addition, lignin can be dissolved during washing due to the disintegration of the lignin particles caused by the changes in ionic strength (Ohman & Theliander, 2006; Ohman et al., 2007a). Less compact and weaker lignin structures are more likely to be broken into much smaller particles and escape during washing, thus reducing the yield.

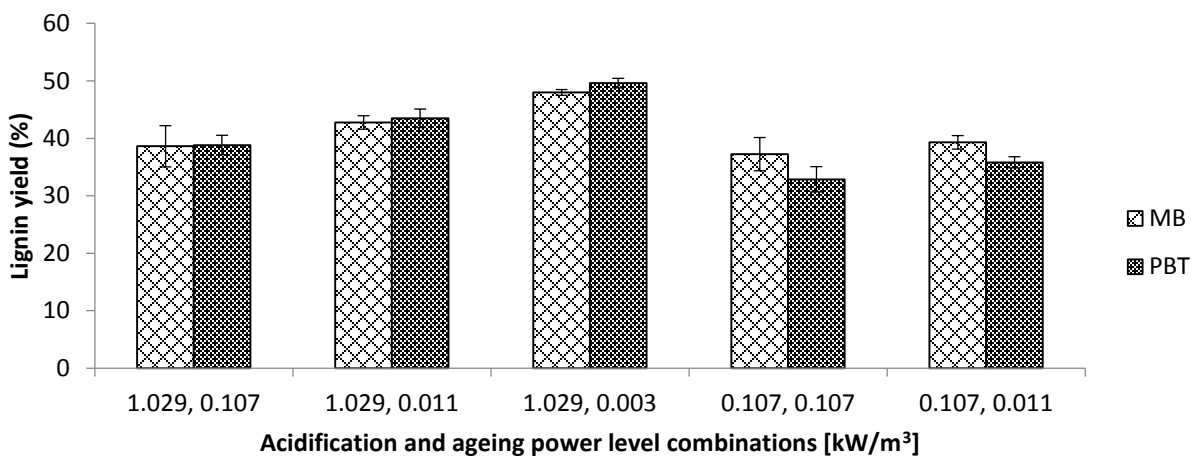

Figure 5-10: Lignin yields (%) for the two impeller systems and five different acidification and ageing power level combinations.

5.4.3 Washing time and ash content

All the lignin cakes from the liquor A sample could be readily washed. The ash content of the washed lignin cakes ranged from 0.09% to 0.25%, indicating that they had been well washed. The time to wash 100g of lignin changed significantly depending on the experimental conditions as

given in Figure 5-11. It followed the trend observed for filtration (Figure 5-9). All the trials performed at the 1.029 kW/m^3 acidification power level resulted in lower washing times. The flocs generated at a high acidification power level (1.029 kW/m^3) were stronger due to compactness, as mentioned in section 5.3.3 and could be less likely to disintegrate during washing, resulting in a lower cake resistance and a shorter washing time.

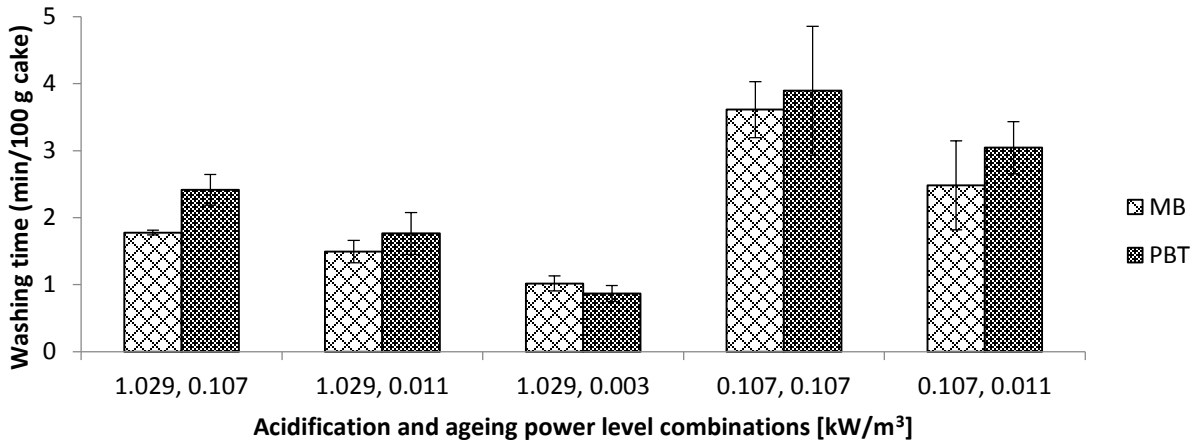

Figure 5-11: Washing times (min/100 g of lignin (dry basis)) for the MB and PBT assemblies for different acidification and ageing power level combinations.

5.4.4 Lignin filtration rate

Lignin filtration rate is defined as the amount of lignin (dry basis) that can be filtered and washed per unit time and unit area and can be used when designing filtration and washing equipment. Table 5-3 shows the estimated lignin filtration rates as function of the power level. A difference of a factor of three in the lignin filtration rate was obtained as a function of the acidification and ageing power levels. The 1.029, 0.003 kW/m^3 power level combination provided the highest rate of lignin production (244 kg/h.m^2) while the lowest (86 kg/h.m^2) was obtained with the 0.107, 0.107 kW/m^3 power level combination. This difference indicates that filtration and washing equipment size can be considerably reduced by choosing the appropriate turbulent shear levels during the acidification and ageing steps of the acid precipitation process.

Table 5-3: Average rates of lignin filtration for the power levels used.

Power level (kW/m^3)		**Rate of lignin filtration (kg/h.m^2)***
Acidification	Ageing	
1.029	0.107	86
1.029	0.011	140
1.029	0.003	244
0.107	0.107	65
0.107	0.011	82

* The filtration rate represents the averages of PBT and MB impeller types at the power levels considered.

5.5 Verification of the reproducibility of the results using black liquors from other Kraft pulping mills

Significant variations in particle size distribution, shape, and process performance as a function of mixing power level were discussed in sections 5.3.1 and 5.4. However, the composition of black liquors varies from mill to mill. As such, it is important to confirm the reproducibility of the results using three batches of black liquors from different origins. Table 5-4 summarizes the particle sizes obtained for the A B, C, and D liquors. As expected, the highest particle sizes were obtained with the 1.029, 0.0.003 kW/m^3 power level combination for all the liquors. The particle sizes produced by the 1.029, 0.107 and 0.107, 0.107 kW/m^3 power level combinations were similar, with the exception of $D_{3,2}$ for liquors C and D, which had much smaller values, indicating the presence of fine particles.

Table 5-4: Particle sizes at the end of the ageing operation for black liquors A, B, C, and D for three acidification and ageing power level combinations.

	Final particle sizes at selected acidification and ageing power levels (µm)					
	1.029, 0.107 kW/m^3		**1.029, 0.003 kW/m^3**		**0.107, 0.107 kW/m^3**	
	DV_{50}	**$D_{3,2}$**	**DV_{50}**	**$D_{3,2}$**	**DV_{50}**	**$D_{3,2}$**
Liquor A	24.7	23.0	61.3	55.7	22.2	20.6
Liquor B	19.4	18.1	52.5	49.0	25.8	21.8
Liquor C	23.8	21.9	63.4	59.2	15.2	7.0
Liquor D	23.2	20.6	73.7	69.1	27.0	10.8

Table 5-5 summarizes the key process performance parameters for liquors A, B, C and D. Filtration and washing were faster for the cakes with the 1.029, 0.003 kW/m^3 power level combination, indicated by the specific filtration resistances, washing times, and rates of lignin filtration. All the cakes were well washed and had a very low ash content, which ranged from 0.1% to 0.55%. The lignin slurries produced using the 1.029, 0.107 kW/m^3 power level combination took more time to filter and wash and the ash content of the cakes was higher.

Filtration was very slow for the 0.107, 0.107 kW/m^3 power level combination. The cakes from liquors B and D became completely plugged when the wash water was added, forcing us to abandon the experiment. These results confirm the observed impact of hydrodynamics on the acid precipitation process using black liquor A and its applicability to black liquors from different origin. However, large differences in optimal performance have been observed depending on the black liquor origin.

Table 5-5: Process performance parameters for selected specific power levels for liquors A, B, C, and D.

Power level (kW/m^3) (Acidification, ageing)		**Filtration resistance (m/kg)**	**Yield (%)**	**Washing time (min)**	**Ash content (%)**	**Rate of lignin filtration (kg/h.m^2)**
Liquor A						
1.029	0.107	5.90E+09	38.8	2.4	0.25	83
1.029	0.003	1.83E+09	49.6	1.0	0.10	256
0.107	0.107	8.05E+09	32.8	3.7	0.15	62
Liquor B						
1.029	0.107	2.12E+10	40.0	10.2	1.74	32
1.029	0.003	4.86E+09	42.0	1.5	0.16	167
0.107	0.107	2.23E+11	-	-	-	-
Liquor C						
1.029	0.107	2.33E+10	41.3	20.2	7.50	20
1.029	0.003	3.49E+09	37.2	3.0	0.55	81
0.107	0.107	2.64E+10	41.5	24.6	10.8	16
Liquor D						
1.029	0.107	2.46+10	38.9	21.7	5.10	22
1.029	0.003	3.45+09	37.8	1.4	0.33	211
0.107	0.107	3.35E+11	-	-	-	-

5.6 Conclusions

The effects of mixing hydrodynamics during precipitation on the lignin particle and filtration properties was evaluated. The hydrodynamics were varied using Pitched blade turbine (PBT) and Maxblend^{TM} (MB) impeller assemblies and different mixing power levels during acidification and ageing steps.

The impact of the mixing hydrodynamics on the size and shape of primary lignin particles, having sizes ranging 1-2 µm and fractal dimensions D_f=2.15-2.65, was negligible. As primary lignin particles aggregate into larger lignin flocs, the impact of hydrodynamics conditions became increasingly important. Considerably different mixing power levels during the acidification step exposed the aggregation of primary lignin particles into lignin flocs to largely different shear rates. At high shear rates, flocs tend to acquire more compact structures due to intensive breakage and aggregation under higher shear stresses, which eventually produced stronger flocs. On the other hand, low shear rates allowed flocs to have larger sizes but their structures were loose.

It was shown that both compact and loose flocs generated in the acidification step could be aggregated into much larger flocs during the ageing step, using reduced ageing power levels. Lowest aging power level produced largest lignin flocs. However, large differences in structure and size distribution were observed according to the condition of the initial flocs. The growth of the compact flocs during ageing step was similar for both types of impellers and the size distributions were narrow. The floc growth depended mainly on the turbulent shear rate.

However, the growth of loose flocs depended on the type of the impeller and the size distributions were wide with a fraction of fine particles. These differences arose from the strength of the initial flocs, where compact flocs were less susceptible to breakage by impeller action than loose flocs. As a consequence, MB impeller showed better aggregation with loose flocs because it created relatively low shear in the impeller zone.

The more compact and larger flocs showed better filtration and washing properties. Higher shear during acidification and lower shear during ageing, independent of the type the impeller, led to lowest filtration resistance of 1.83E+09 m/kg and highest filtration rate of 256 kg/h.m^2. The tests performed on black liquor samples from the other mills confirmed the above findings. However,

these confirmation tests resulted in largely different filtration performances and in the ability to efficiently wash the cakes.

5.7 Acknowledgements

This work was financially supported by the BioFuelNet Canada. The authors are grateful to Prof. Oumarou Savadogo and FPInnovations for providing the experimental facilities and setups and to Jalil Baria for assistance with the experiments. We also thank the Kraft pulping mills for providing the black liquor samples

5.8 References

Benali, M., Périn-Levasseur, Z., Savulescu, L., Kouisni, L., Jemaa, N., Kudra, T., & Paleologou, M. (2014). Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment. *Biomass and Bioenergy, 67*(0), 473-482.

Bo, X., Gao, B., Peng, N., Wang, Y., Yue, Q., & Zhao, Y. (2012). Effect of dosing sequence and solution pH on floc properties of the compound bioflocculant–aluminum sulfate dual-coagulant in kaolin–humic acid solution treatment. *Bioresource Technology, 113*(0), 89-96.

Diffo, C. (2013). Lignin Biorefinery Technology and Markets. Retrieved from http://www.reseauvco.ca/fileadmin/vco/documents/Webinairs/PowerPoint_Presentation.pdf

Gooding, C. (2012). *Comparison of the LignoBoost™ and SLRP™ Lignin Recovery Processes.* Paper presented at TAPPI International Bioenergy & Bioproducts Conference, Savannah, United States.

Guan, J., Waite, T. D., & Amal, R. (1998). Rapid Structure Characterization of Bacterial Aggregates. *Environmental Science & Technology, 32*(23), 3735-3742. doi: 10.1021/es980387u

Hidalgo-Millán, A., Zenit, R., Palacios, C., Yatomi, R., Horiguchi, H., Tanguy, P. A., & Ascanio, G. (2012). On the hydrodynamics characterization of the straight Maxblend® impeller with Newtonian fluids. *Chemical Engineering Research and Design, 90*(9), 1117-1128.

Holmqvist, A., Wallberg, O., & Jonsson, A.-S. (2005). Ultrafiltration of kraft black liquor from two Swedish pulp mills. *Chemical Engineering Research and Design, 83*(8 A), 994-999. doi: 10.1205/cherd.04204

Howell, J. F., & Thring, R. W. (2000). Hardwood lignin recovery using generator waste acid. Statistical analysis and simulation. *Industrial & engineering chemistry research, 39*(7), 2534-2540.

Ibaseta, N., & Biscans, B. (2010). Fractal dimension of fumed silica: Comparison of light scattering and electron microscope methods. *Powder Technology, 203*(2), 206-210.

Jarvis, P., Jefferson, B., Gregory, J., & Parsons, S. A. (2005). A review of floc strength and breakage. *Water Research, 39*(14), 3121-3137.

Jarvis, P., Jefferson, B., & Parsons, S. A. (2005). Breakage, Regrowth, and Fractal Nature of Natural Organic Matter Flocs. *Environmental Science & Technology, 39*(7), 2307-2314. doi: 10.1021/es048854x

Kouisni, L., Holt-Hindle, P., Maki, K., & Paleologou, M. (2012). The lignoforce system: A new process for the production of high-quality lignin from black liquor. *J-FOR: The Journal of Science and Technology for Forest Products and Processes, 2* 6-10.

Kresta, S. (1998). Turbulence in stirred tanks: Anisotropic, approximate, and applied. *The Canadian Journal of Chemical Engineering, 76*(3), 563-576. doi: 10.1002/cjce.5450760329

Loutfi, H., Blackwell, B., & Uloth, V. (1991). Lignin recovery from kraft black liquor: preliminary process design. *Tappi Journal, 74*(1), 203-210.

Norgren, M., Edlund, H., & Wågberg, L. (2002). Aggregation of lignin derivatives under alkaline conditions. Kinetics and aggregate structure. *Langmuir, 18*(7), 2859-2865.

Norgren, M., Edlund, H., Wågberg, L., Lindström, B., & Annergren, G. (2001). Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: phase behaviour. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 194*(1–3), 85-96.

Norgren, M., & Lindstrom, B. (2000). Physico-chemical characterization of a fractionated kraft lignin. *Holzforschung, 54*(5), 528-534. doi: 10.1515/HF.2000.089

Ohman, F., & Theliander, H. (2006). Washing lignin precipitated from kraft black liquor. *Paperi ja Puu, 88*(5), 287-292.

Ohman, F., & Theliander, H. (2007). Fitration properties of lignin precipitated from black liquor. *Tappi Journal, 6*(7), 3-9.

Ohman, F., Wallmo, H., & Theliander, H. (2007). A novel method for washing lignin precipitated from kraft black liquor - Laboratory trials. *Nordic Pulp and Paper Research Journal, 22*(1), 9-16.

Paul, E. L., Atiemo-Obeng, V., & Kresta, S. M. (2003). *Handbook of Industrial Mixing: Science and Practice*: Wiley.

Radiotis, T., Sullivan, J., MacLeod, M., Syed, S., & O'Hagan, T. (2007). *Improved methods for measuring residual effective alkali in kraft black liquors part 2: Comparison of titration methods.* Paper presented at Engineering, Pulping and Environmental Conference 2007, TAPPI, October 21, 2007 - October 24, 2007, Jacksonville, FL, United states (Vol. 4, pp. 2388-2436).

Spicer, P. T., Keller, W., & Pratsinis, S. E. (1996). The Effect of Impeller Type on Floc Size and Structure during Shear-Induced Flocculation. *Journal of Colloid and Interface Science, 184*(1), 112-122.

Spicer, P. T., Pratsinis, S. E., Raper, J., Amal, R., Bushell, G., & Meesters, G. (1998). Effect of shear schedule on particle size, density, and structure during flocculation in stirred tanks. *Powder Technology, 97*(1), 26-34.

Uloth, V. C., & Wearing, J. T. (1989). Kraft lignin recovery: acid precipitation versus ultrafiltration, Part II: Technology and economics. *Pulp & Paper Canada, 90*(10), 34-37.

Wallberg, O., Jonsson, A.-S., & Wimmerstedt, R. (2003). Fractionation and concentration of kraft black liquor lignin with ultrafiltration. *Desalination, 154*(2), 187-199. doi: 10.1016/S0011-9164(03)80019-X

Wallmo, H., Richards, T., & Theliander, H. (2009). An investigation of process parameters during lignin precipitation from kraft black liquors: A step towards an optimised precipitation operation. *Nordic Pulp and Paper Research Journal, 24*(2), 158-164.

Wienhaus, O., Bernaczyk, H., & Pecina, H. (1990). Research into the precipitation of lignin from sulfate black liquors, particularly by carbon dioxide. *Das Papier, 44*(11), 563-569.

Xu, W., & Gao, B. (2012). Effect of shear conditions on floc properties and membrane fouling in coagulation/ultrafiltration hybrid process—The significance of Alb species. *Journal of Membrane Science, 415–416*(0), 153-160.

Zhu, W., Westman, G., & Theliander, H. (2014). Investigation and characterization of lignin precipitation in the lignoboost process. *Journal of Wood Chemistry and Technology, 34*(2), 77-97. doi: 10.1080/02773813.2013.838267

Chapter 6 ACID PRECIPITATION OF LIGNIN FROM BLACK LIQUOR: OPTIMIZATION OF FILTRATION PERFORMANCE AND YIELD USING TAGUCHI METHOD

6.1 Introduction

The pulp and paper industry in Canada has been facing difficult economic conditions since the last decade due to falling demand for traditional paper commodities and international competition; this has caused mill closures and capacity reductions. Pulp and paper companies are re-evaluating their business models and considering the manufacture of novel bioproducts and biochemicals using biorefinery technologies. In this context, the extraction of lignin from the residual black liquor stream of Kraft pulping mills and its conversion to novel products, such as phenolic resins, carbon fibers and polyurethane foams has gained much attention in the research community and in industry.

In the delignification step of Kraft pulping, lignin is removed from wood at high alkaline and high temperature conditions to produce pulp. The removed lignin is entrained in the residual liquor, called black liquor (BL), during the washing of the pulp. BL consists of degraded lignin and hemicelluloses and spent delignification chemicals. It has a high calorific value and in a Kraft process, it is concentrated and combusted in the recovery boiler to generate steam and power and to regenerate the delignification chemicals (Smook, 1992b; Stevens et al., 1989).

Acid precipitation is a promising way of extracting lignin from black liquor (Kouisni et al., 2012; Loutfi et al., 1991; Ohman et al., 2007a). In this method, lignin is precipitated by acidifying black liquor using CO_2 (acidification step) and the slurry is further agitated for 30-90 min (ageing step) and then filtered. The produced cake is washed with H_2SO_4 and water to reduce the ash content of lignin (Loutfi et al., 1991).

The lignin precipitation involves the neutralization of surface charges of lignin molecules, which is mainly due to dissociated phenolic hydroxyl and carboxyl groups, inducing its coagulation into solid particles, during the acidification step. These primary particles further aggregate into larger lignin particle structures by mutual contact (Norgren et al., 2002; Norgren et al., 2001). The aggregation of lignin in aqueous solutions has been explained using DLVO (Derjaguin Landau

Verwey Overbeek) theory, which describes colloidal stability as a balance between attraction forces and electrostatic repulsion forces arising from the electrical double layer (Norgren et al., 2002; Norgren et al., 2001; Norgren & Lindstrom, 2000a, 2000b). As a result, the process operating conditions, including the precipitation pH, temperature, ionic strength of the black liquor and mixing conditions influence the precipitation process.

The percentage of the total lignin that is precipitated out in the black liquor (lignin yield) can be enhanced by decreasing the precipitation pH, however, filterable lignin can only be obtained in a narrow range of pH values starting from 9 to 10.8 (Howell & Thring, 2000; Loutfi et al., 1991; Ohman & Theliander, 2007; Theliander, 2010; Zhu et al., 2014). The lignin yield increases with decreasing temperature although readily filterable lignin is only produced at temperatures from 60 to 80°C (Loutfi et al., 1991; Theliander, 2010; Wallmo, Richards, et al., 2009). The lignin particles precipitated outside of the optimum ranges of pH and temperature have been reported to be very fine or soft and tacky making it difficult to filter and wash them (Loutfi et al., 1991). The black liquor concentration, which is suitable for lignin precipitation, was reported to be between 30 to 40% total solids(Loutfi et al., 1991). Dilute liquor results in lower yields but concentrated liquor is difficult to handle and produces fine lignin particles (Alen et al., 1979; Loutfi et al., 1991). Higher residence times and lower agitation rates during the ageing operation were also reported to decrease the filtration resistance of the lignin cake (Wallmo, Richards, et al., 2009).

High value lignin applications such as carbon fibers require a lignin ash content lower than 0.1% (Luo et al., 2011). Recent efforts in lignin precipitation process development have been focused on producing low ash lignin by improving the filtration and washing steps. It has been reported that gradients of ionic strength are created during washing the cake, causing the lignin to re-dissolve and plug the cake (Ohman & Theliander, 2006; Ohman et al., 2007a). Re-slurring of the lignin cake using sulfuric acid was proposed, followed by re-filtration and displacement washing to overcome this drawback. Black liquor oxidation prior to acidification has been reported to produce larger lignin particles, resulting in easier filtration and washing and low ash lignin product (Kouisni et al., 2012).

To produce high purity lignin with low production costs, the lignin precipitation process, which is influenced by many parameters, has to be carefully optimized. The application of statistical design of experiments (DOE) can be highly useful in such a situation. In DOE, the parameters are

simultaneously varied in order to obtain valid and objective information using planned experimental trials. Taguchi orthogonal array DOE has been widely used in industrial product and process design and optimization. In this method, a large number of factors can be investigated using a minimum number of experiments. Orthogonal arrays (OA), in which each pair of factors is tested at least once in a balanced manner, are used in this method and this help to identify the main effects of the investigated parameters. The method uses signal-to-noise (S/N) ratios, which incorporate average factor effects as well as the variation in equal priority, to find out the optimum factor levels. The method also facilitate performing the analysis of variance (ANOVA), which estimates the significance and relative influence of each parameter.

To the best of our knowledge, no such systematic investigation studying the effects of operating conditions of lignin precipitation process has been published. The objective of this work was to determine the optimum operating conditions of the acid precipitation process that achieve higher filtration performance and yield, thus producing low ash lignin product. Oxidized softwood black liquor was used in this work. The investigation was carried out in the following sequence: (1) Preliminary trials to screen and determine the range of main operating conditions; (2) Experimental investigation using Taguchi design OA design; (3) Statistical analysis using S/N ratios and ANOVA; (4) Verification of optimal conditions using confirmation experiments. The overall optimum process operating ranges have been discussed.

6.2 Methodology

6.2.1 Experimental work

6.2.1.1 Experimental setup

The experiments were carried out in an open vessel of 2 L capacity and 11.8 cm inside diameter. The vessel was fitted with standard baffles (T/10). A schematic of the setup with dimensions is given in Figure 6-1. The vessel was heated by a circulating hot water bath with temperature control connected to the outer jacket of the vessel. CO_2 was injected into the tank by a sparger tip located at the bottom of the vessel. A four bladed and 45° angle pitched blade turbine (PBT) with diameter 5.5 cm was used for the agitation. The impeller was placed 3.9 cm above the bottom of the tank. The filtration was performed using a standard vacuum filtration setup consisting of a Buchner

funnel of 15 cm diameter and a filtration flask. A filter paper (Whatman grade 131) with diameter of 15 cm was used for the filtration at a vacuum of 70 kPa.

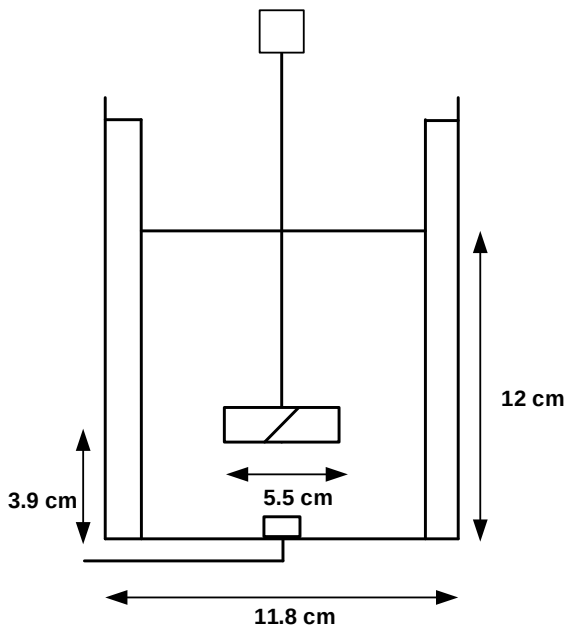

Figure 6-1: The stirred tank setup used for the experiments.

6.2.1.2 Experimental procedure

Oxidized softwood black liquor at 48% solids content was supplied by a Canadian Kraft pulping mill. This liquor was diluted to the required solids content and filtered to remove any suspended solids. A 1.3 L volume of black liquor was added to the vessel and agitation was started to heat up the black liquor solution. After the desired temperature was achieved, the CO_2 sparging (1.5 L/min flow rate) and pH measurement were started. The pH measurement was performed using MetroHM unitrode combination electrode with temperature correction. Therefore, the pH values were recorded at precipitation temperature. After the precipitation pH reached the desired level, the CO_2 sparging was stopped and the lignin slurry was further agitated at the same temperature. The slurry was cooled down to about 55°C and filtered. The filtration volume versus time was recorded. The filter cake was washed by pouring 1000 mL of 0.4 M sulfuric acid and then 200 mL of water on top of the cake. The complete washing of the cake was determined by the visual observation of the color of the wash filtrate. Once the color of wash filtrate reached clear to light yellow, the washing step was assumed to be complete. The amount of wash water was enough to completely wash the

cakes generated in all the experiments. The washed cake was air dried for 24 hours and weighed. Samples of the cake were oven dried at 105°C to determine solid content. Samples of the oven dried cake was analyzed for ash content.

6.2.2 Black liquor, filtrate and lignin characterization

The properties of the black liquor are given in Table 6-1. The solid content black liquor, filtrate and lignin were determined by oven drying a sample of known quantity at 105°C until a constant weight was obtained according to the CPPA J.15 (II) standard test procedure. The UV lignin content of the black liquor and filtrates were analyzed by using Biochrome Ultraspec UV spectrophotometer at wave length of 280 nm. A liquor sample (2 g) was taken and dissolved in 100 mL of NaOH and diluted to an OD_{280} of 0.3-0.8. An absorption coefficient of 23.7 $dm^3g^{-1}cm^{-1}$ was used. The Klason and acid-soluble lignin content were determined by using a procedure described in the literature (Zhu et al., 2014). The ash content of black liquor was determined by igniting a known weight of black liquor at 950°C and weighing the inorganic residue (Holmqvist et al., 2005; Wallberg et al., 2003). The ash content of lignin was determined by igniting a known quantity of oven dried lignin at 525°C until a constant weight was obtained and weighing the remaining ash. The residual alkali content was determined according to a procedure described in literature (Radiotis et al., 2007). Sulfide content of black liquor was determined according to the CPPA J.15 (VI) standard test procedure. The lignin particle sizes were characterized using a laser refraction instrument (Mastersizer 3000), in which the particles were dispersed in 3M NaCl solution with pH adjusted to the precipitation pH.

Table 6-1: Properties of oxidized black liquor used in this work.

Parameter	**Value**
Total solids (%)	30
UV lignin (% total solids)	38.9
Klason lignin (% total solids)	32.6
Acid soluble lignin (% total solids)	4.5
Inorganics or ash (% total solids)	40.1
Organics (% total solids)	59.9
Na (% total solids)	18.8
Residual alkali (g/L)	8.0
Sulfide content (g/L)	1.72
pH at room temperature	12.6
Dynamic viscosity (mPas)	7

6.2.3 Calculation of lignin yield and filtration resistance

The lignin yield was computed as amount of pure lignin (dry basis) recovered from the total lignin in the original black liquor. UV lignin content was used to estimate the total amount of lignin in the black liquor. The filtration resistance (**α**) was estimated using the gradient of the filtration equation given in Eq.1.

$$\frac{t}{V} = \frac{K_1}{2} V + K_2 \qquad (1)$$

$$K_1 = \frac{\boldsymbol{\alpha} c \mu}{A^2 \Delta p} \quad (2)$$

$$K_2 = \frac{\mu R_M}{A \Delta p} \quad (3)$$

V is the filtrate volume and t is the time taken to collect this filtrate volume. μ is the dynamic viscosity of the filtrate, A is the filtration area, c is the solids concentration of the slurry, Δp is the filtration pressure difference, and R_M is the filtration resistance of the medium.

6.2.4 Mixing tank characterization

The level of turbulence in the mixing tank was characterized by the specific power generated by the impeller. The specific power input for a given agitation rate was calculated by the power number (N_P), as given in Eq. 4.

$$P = N_P \rho N^3 D^5 \quad (4)$$

The quantities, P, ρ, N and D are the specific power input, the density of the black liquor, the agitation rate and impeller diameter, respectively. N_P of the pitched blade turbine was taken as 1.27 (Paul et al., 2003). Table 6-2 gives the RPMs and Re numbers at the specific power levels used in the study.

Table 6-2: The specific power levels, RPMs and Re numbers of operation.

Power level (kW/m^3)	**RPM**	**Re**
0.001	72	492
0.005	122	830
0.010	154	1052
1.080	730	4989

6.3 Statistical analysis

The Minitab® 17 statistical software was used for the analysis of the experimental data.

6.3.1 S/N ratio computation

The S/N ratio is defined as the ratio of the mean of a response (signal, S) to its standard deviation (noise, N). It is calculated using the logarithmic value of the sum of mean squared deviation, which is defined according to the required optimization criteria of the response variable: smaller is better, larger is better and nominal is best. The calculations are given in equations 5, 6 and 7.

Smaller: $S/N = -10\, log\left(\frac{1}{n}\sum_{i=1}^{n} Y_i^2\right)$ (5)

Larger: $S/N = -10\, log\left(\frac{1}{n}\sum_{i=1}^{n} \frac{1}{Y_i^2}\right)$ (6)

Nominal: $S/N = -10\, log\left(\frac{1}{n}\sum_{i=1}^{n} (Y_i - Y_i)^2\right)$ (7)

Where n is the number of repetitions and Y_i is the value of the response for the ith repetition. Y_o is the nominal value of the response. The level that generates the highest S/N ratio is considered as the optimal level of a factor, which provides minimization, maximization or a nominal value of a response variable. The calculation of the S/N ratio captures the variability of the data, assigning factors with low variability higher S/N ratio values. Therefore, the optimum factor levels obtained reflect more robust operating conditions.

6.3.2 Analysis of variance (ANOVA) computation

ANOVA is used to determine the statistical significance of factor effects relative to the random variation of the process. The sum of squares (SS) is first calculated followed by the mean sum of squares (MS), given by the division of SS by the degrees of freedom (DOF). MS is used in the estimation of the F value, which is used in significance testing.

The sum of squares of factor A (SS_A) is given by equation 8, where Y_{A_i} is the observation of this factor for level i, n_{A_i} is the number of observations for level i, m_A is the number of replicates, T is the sum of all the observations in the experimental program and, N is the number of total

experimental trials. The calculation of total sum of squares (SS_T) is given in equation 9. Y_i is the observation in the ith experimental trial. The sum of squares of error (SS_e) is obtained using equation 10.

$$SS_A = \left(\sum_{i=1}^{m_A} \frac{Y_{A_i}^2}{n_{A_i}}\right) - \frac{T^2}{N} \tag{8}$$

$$SS_T = \left(\sum_{i=1}^{N} Y_i^2\right) - \frac{T^2}{N} \tag{9}$$

$$SS_e = SS_T - (SS_A + SS_B + \cdots) \tag{10}$$

MS are calculated by dividing the sum of squares of each factor by its degrees of freedom (DOF). DOF of factor A is calculated as $DOF_A = m_A - 1$. The F value is calculated by in equation 11. The percent contribution (P) of a factor, which measures its relative importance, is computed as shown in equation 12.

$$F_A = \frac{MS_A}{MS_e} \tag{11}$$

$$P_A(\%) = \frac{SS_A - (MS_e \times DOF_A)}{SS_T} \tag{12}$$

6.3.3 Prediction of optimum performance

The response variables are predicted using the following additive factor effects model, given in equation 13. N is the number of total observations, T is the sum of all the observations; and $\overline{A}_i$ and $\overline{B}_j$ are the mean factor effects at levels i and j.

$$Y_m = \frac{T}{N} + \left(\overline{A}_i - \frac{T}{N}\right) + \left(\overline{B}_j - \frac{T}{N}\right) + \ldots \tag{13}$$

6.4 Results and discussion

6.4.1 Preliminary selection of operating parameters

Preliminary tests were performed to screen and determine the ranges of the main operating parameters, namely pH, temperature and dissolved solids content, before performing the main experimental design. The filtration performance (in terms of filtration resistance) and lignin yield were observed while varying a single parameter and keeping the other parameters constant at the following values, precipitation temperature: 75°C, solids content of black liquor: 30%, precipitation pH: 9.6, CO_2 flow rate: 1 L/min, duration of the ageing operation: 60 min, agitation rate during carbonation: 730 RPM and, agitation rate during ageing: 122 RPM.

6.4.1.1 Effect of precipitation pH

Three experimental trials were performed at precipitation pH values of 8.2, 9 and 10, covering the range between minimum feasible pH using CO_2 and highest pH with apparent lignin precipitation. As shown in Figure 6-2, the lignin yield gradually increased with decreasing precipitation pH, having values of 73% at pH 8.2 and 43% at pH 10. The filtration resistance had a minimum around pH 9 and it increased as pH either increased or decreased. The particle sizes of precipitated lignin were 11.0, 37.9 and 22.8 μm at pH values 8.2, 9.0, 10.0, respectively.

The apparent pK_a value of a lignin molecule increases with molecular weight and hence the high molecular weight fractions values precipitate at high pH values. As pH decreases, the low molecular weight fractions with low apparent pK_a values start to precipitate. As a consequence, the lignin yield increases with decreasing pH. The lower molecular weight fractions have a lesser number of active sites than higher molecular weight fraction of to adsorb other lignin colloids and clusters and as a result, to grow in size (Norgren et al., 2002; Sri et al., 1989; Zhu, 2013). Also, they have higher surface charges due to lower pK_a values, which reduces aggregation. This can possibly explain the small particle sizes at pH value of 8.2. However, the particle size at pH 9 was higher than the size at pH 10. This could be related to the concentration of lignin particles at pH 10, which is low, resulting in less particle-particle collisions and aggregation.

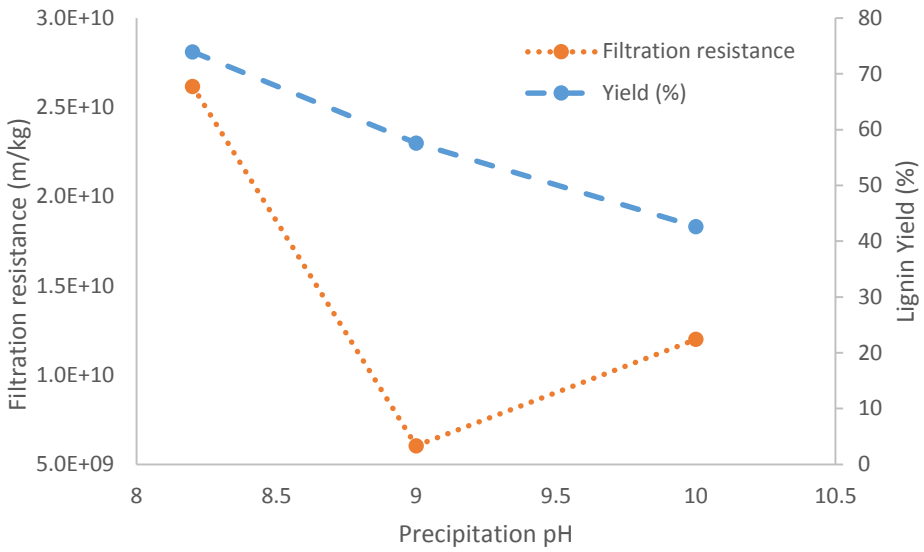

Figure 6-2: Variation of filtration resistance and lignin yield with precipitation pH

6.4.1.2 Effect of temperature

Three experimental trials were performed at temperatures of 70, 75 and 80°C. As shown in Figure 6-3, the filtration resistance reached its minimum and the yield reached its maximum at precipitation temperature of 75°C, making optimum in terms of both response parameters. The particles size of precipitated lignin were 30.6, 60.2 and 121.5 µm at temperatures of 70, 75 and 80°C, respectively.

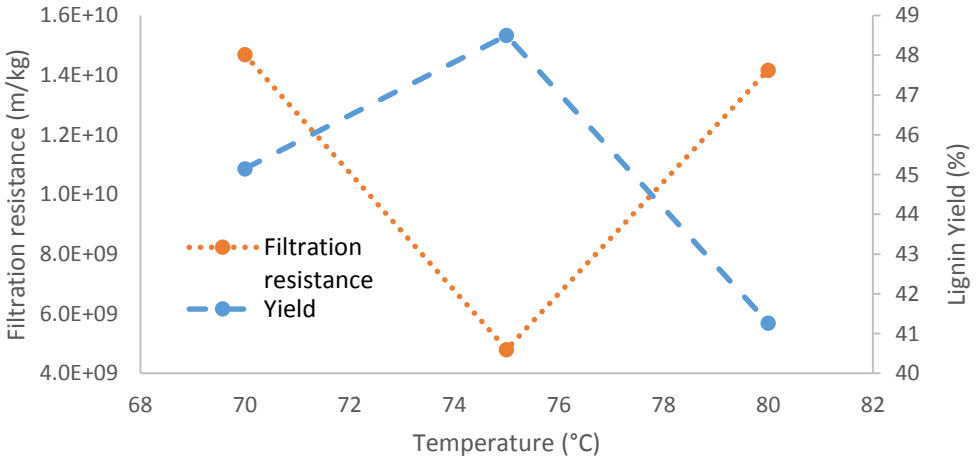

Figure 6-3: Variation of the filtration resistance and lignin yield with precipitation temperature

Lignin becomes more soluble at higher temperatures, leading to reduced yields (Evstigneev, 2011; Theliander, 2010; Zhu et al., 2014) and this way explain the observed decrease of the yield from 48 to 41% for temperatures ranging 75 to 80°C. As more thermal energy is provided to the system at higher temperature, the electrostatic repulsion forces increase, increasing the electrical double layer thickness and hence the solubility (Lee et al., 2012). However, the apparent pK_a value of lignin molecules increases with increasing temperature (Norgren & Lindstrom, 2000a, 2000b). Therefore, at high temperatures, lignin start to precipitate at higher pH values due to reduced surface charges. The reduced surface charges on lignin molecules promote aggregation, possibly explaining the large lignin particle sizes at higher temperatures.

Despite a large increase in particle size, the filtration resistance was higher at 80°C. We observed the presence of gel like lignin in some parts of the cake at 80°C, which hindering filtration. This is due to glass transition of some lignin fractions to liquid state at higher temperatures and it has been reported in the literature to occur at temperature ranges 80-85°C and higher (Loutfi et al., 1991).

The yield increase observed when the temperature rises from 75 to 80°C could be due to the increase of particle size, since larger particles are retained on the filter cloth. For the black liquor used in this work, the temperature of 75°C is suitable as the operating precipitation temperature and deviation from this value adversely impact the process in terms of both yield and filtration.

6.4.1.3 Effect of solids content

Three experimental trials were performed at black liquor solids contents of 30, 35 and 40%. Figure 6-4 shows the variation of filtration resistance and lignin yield with solids content. The lignin yield increased with increasing solids content. The ionic strength of black liquor increases with increasing solids content, resulting in a compressed electrical double layer (Norgren et al., 2001). This decreases the solubility of the lignin and increases the yield (Theliander, 2010).

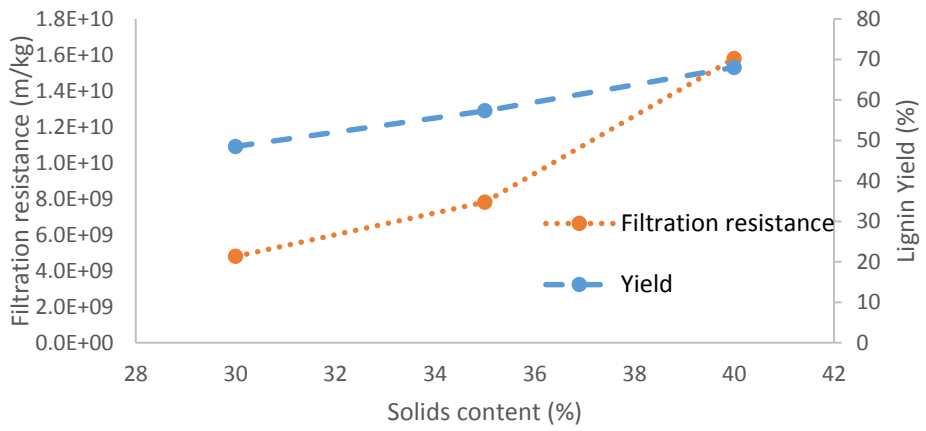

Figure 6-4: Variation of filtration resistance and yield with black liquor solids content (%)

The particles size of precipitated lignin were 60.2, 54.8 and 39.2 µm at solid contents of 30, 35 and 40%, respectively. Generation of fine particles at high solids contents that have been reported in the literature, is consistent with this result (Loutfi et al., 1991). Particle sedimentation at the bottom of the stirred tank was observed during the ageing operation (agitated at 122 RPM) at 40% solids content, suggesting insufficient fluid flow generated by the impeller to suspend all the solid particles. The insufficient solids suspension could cause smaller particle size and sharp increase in the filtration resistance at solids content 35 - 40%. Also, the increasing concentration of black liquor components such as soaps and hemicelluloses with increasing solids content, which have been reported to adversely affect the lignin filtration (Ohman et al., 2007b; Wallmo, Theliander, et al., 2009), can increase the filtration resistance.

Using more concentrated black liquor is advantageous, despite the increase in filtration resistance, because of the increase in lignin yield and the reduction of the required volume of black liquor. Thus, solid contents up to 37% and faster agitation rates were considered in the experimental design to provide sufficient particle suspension.

6.4.2 Design of experiments

Traditional approach to perform experiments involves the change of one parameter at a time while holding the other parameters constant. Although this approach can be used to screen and determine the range of operating parameters, it can often fail to identify the optimum process conditions and can lead to incorrect conclusions. Furthermore, this approach results in large number of experimental trials. The Taguchi OA DOE method, where all the parameters are varied

simultaneously in a balanced manner, were used in this investigation to overcome such problems and to rapidly identify the optimal range of operating parameters.

Based on the results of the preliminary experimental trials, the black liquor solids content, precipitation pH, ageing residence time and ageing agitation rate were chosen as input parameters (factors) for the study. The residence time of the ageing operation was included in the study to determine its impact and eventually to reduce the size of the ageing vessel. An L_9 orthogonal array was used to determine the effects of each factor at three factor levels. Table 6-3 shows the selected parameters and their levels. A minimum number of nine experiments have to be performed for the L_9 design.

Table 6-3: The parameters (factors) and their levels

Parameter	Levels
Black liquor solids content (%)	30, 33.5, 37
pH	9.4, 9.6, 9.7
Ageing residence time (min)	15, 30, 60
Agitation rate (RPM)	72, 122, 154

The main purpose of the acid precipitation process is the production of low ash lignin. This can be achieved by maximizing the filtration performance of the process. In this study, the filtration performance was characterized by the filtration resistance of the lignin cake and the ash content of the washed cake. Although the main criteria is high filtration performance, the costs associated with the process must be minimized. The lignin yield and the chosen input parameters including solid content, precipitation pH and ageing residence time can affect the capital and operating costs of the process. Therefore, the lignin yield was also chosen as a response parameter. The solids content determines the volume of the black liquor that has to be treated by the process, the precipitation pH determines the CO_2 demand and the ageing residence time determines the size of the ageing vessel.

6.4.3 Lignin Yield Optimization

The lignin yields generated in the experiment trials are presented in Table 6-4. It varied from 48.1 to 66.6% and it seems to increase with decreasing precipitation pH and increasing black liquor solids content. The S/N ratio plots shown in Figure 6-5 illustrate the effects of each investigated

parameter on the lignin yield. The larger-is-better optimization option (discussed in section 6.3.1) was chosen in generating S/N ratio plots for yield because it is desirable to have a higher yield. Each graph shows the relative variation of the signal (response variable) to the noise (variance) for each investigated factor. The peak points of the plots represent the level of a factor which generates the highest yield, hence the optimal conditions for maximizing the lignin yield.

Table 6-4: Experimental results for lignin yield

Trial no.	Solid content (%)	pH	Ageing time	Agitation rate (RPM)	Mean lignin yield (%)
1	30	9.8	60	72	50.8
2	30	9.6	30	122	50.5
3	30	9.4	15	154	50.7
4	33.5	9.8	30	154	48.1
5	33.5	9.6	15	72	51.8
6	33.5	9.4	60	122	59.3
7	37	9.8	15	122	50.9
8	37	9.6	60	154	58.0
9	37	9.4	30	72	66.6

The overall mean S/N ratio was 34.6 for the lignin yield. The variation around the mean was found to be highest for the precipitation pH. The black liquor solid content also showed large variations around the overall mean S/N ratio. The ageing time and agitation rate produced lower variations of the yield, but not small enough to be negligible. The optimum conditions that maximize lignin yield were chosen at the highest values of the mean S/N ratios. The largest lignin yield was obtained at solids content (37%), pH (9.4), ageing residence time (60 min) and agitation rate (72 RPM).

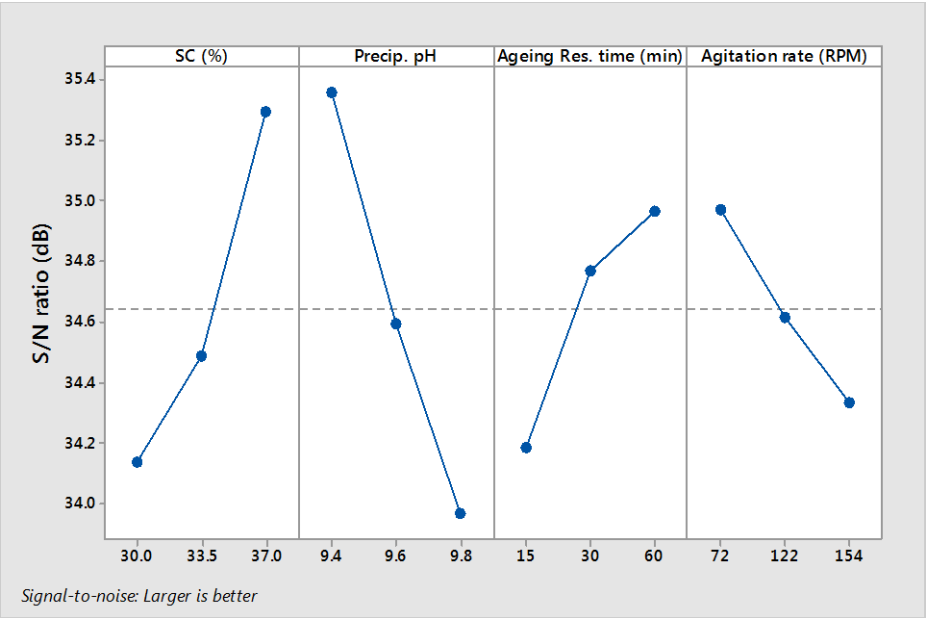

Figure 6-5: Main effect plots for S/N ratios of lignin yield: (a) Black liquor solids content (%), (b) Precipitation pH, (c) Ageing residence time (min), (d) Agitation rate (RPM)

6.4.4 Filtration Performance Optimization

The filtration performance of the process was evaluated using the specific filtration resistance of the lignin cake and ash content of the washed lignin cake as performance indicators. The values observed for filtration performance during the experimental program are shown in Table 6-5. The filtration resistance varied from 4.99 E+09 to 1.31 E+10 m/kg while the ash content varied from 0.2 to 8.2 %. Lignin cakes with lower filtration resistance seem to have a lower ash content according to the Table 6-5Table 6-5.

Table 6-5: Experimental results for filtration resistance and ash content of lignin cake

Trial no.	Solids (%)	pH	Ageing time	Agitation rate (RPM)	Filtration resistance (m/kg)	Ash content (%)
1	30	9.8	60	72	6.45E+09	1.2
2	30	9.6	30	122	7.50E+09	1.0
3	30	9.4	15	154	7.71E+09	1.6
4	33.5	9.8	30	154	1.03E+10	4.6
5	33.5	9.6	15	72	1.07E+10	3.0
6	33.5	9.4	60	122	4.99E+09	0.2
7	37	9.8	15	122	1.28E+10	7.2
8	37	9.6	60	154	1.04E+10	1.6
9	37	9.4	30	72	1.31E+10	8.2

Figure 6-6 shows the S/N ratio plots for filtration resistance and ash content of the washed lignin cake for black liquor solids content, precipitation pH, ageing residence time and agitation rate. The optimization criteria of smaller-is-better was used for both filtration resistance and ash content in order to maximize the filtration performance. The computed mean S/N ratios were -198.8 and -6.0 for filtration resistance and ash content, respectively. All the factors had large variations around the mean S/N ratio values, suggesting their important influences on filtration performance. The S/N plots for filtration resistance and ash content showed similar trends with minor exceptions in the magnitude and pattern. This indicates that lignin cakes with low filtration resistance have better washability which result in low ash content. The optimum conditions for lowest filtration resistance and ash content were at solids content (30%), precipitation pH (9.4), ageing residence time (60 min) and agitation rate (122 RPM).

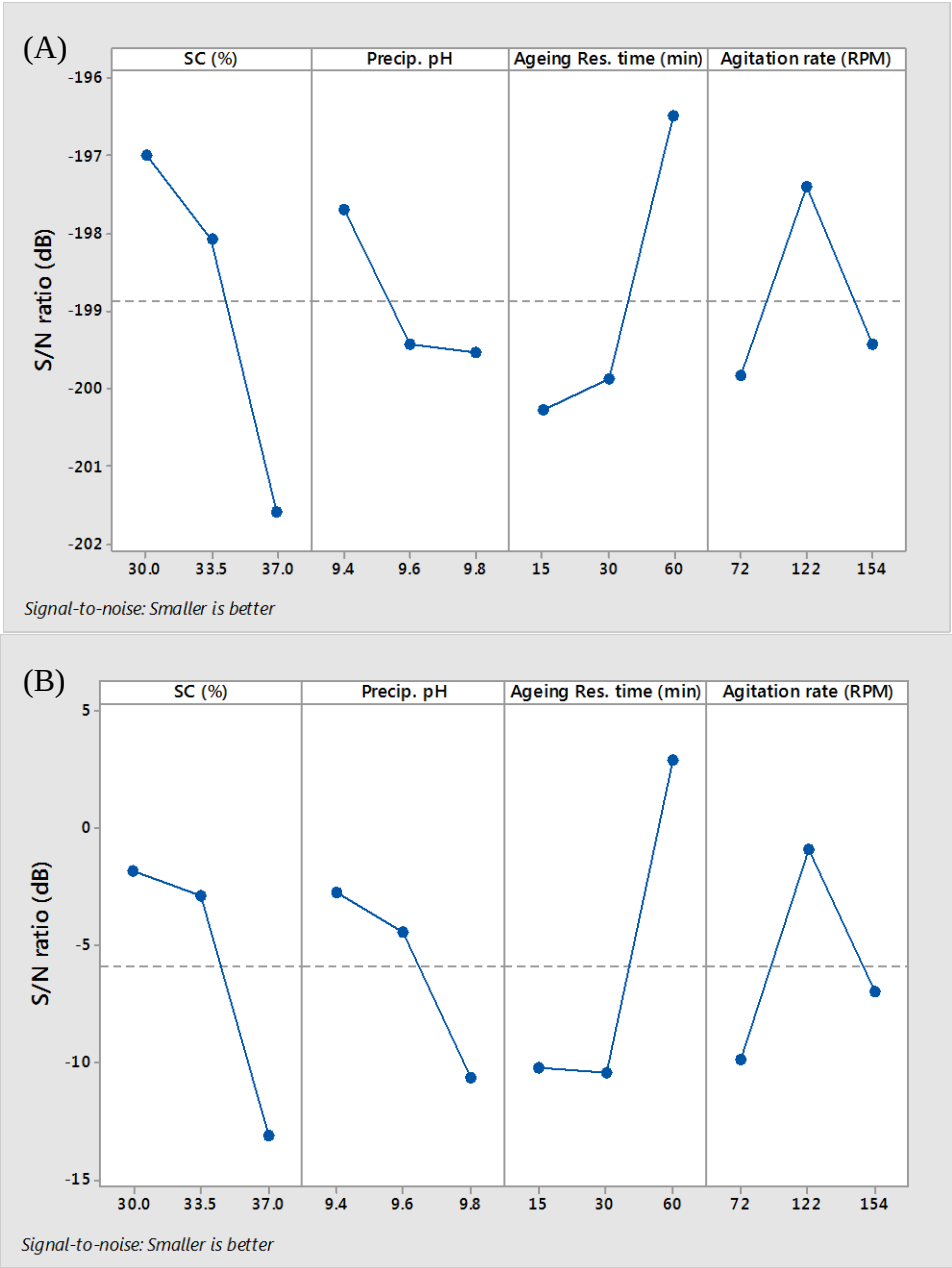

Figure 6-6: Main effect plots for S/N ratios of (A) lignin cake filtration resistance and (B) ash content of washed cake for (a) Black liquor solids content (%), (b) Precipitation pH, (c) Ageing residence time (min), (d) Agitation rate (RPM)

6.4.5 ANOVA Results

An ANOVA was carried out to estimate the significance and the relative importance of the each factor. As Taguchi OA design does not include replicate tests, a factor with lowest sum of squares

(SS) were included (pooled) in the error term in order to perform the ANOVA computation. The F value, which was calculated as the ratio of the mean sum of squares of factor effect and within group variation of the system, was utilized to assess the significance of the factors. The significance can be assessed by comparing the F value to a critical F value ($F_{critical}$), which can be found in F value tables in most statistical experimental design books (Roy, 2001). In this work, the factors and error had two degrees of freedom. The corresponding $F_{critical,2,2}$ value was 9.55 for 95% confidence interval. The significance test, however, does not indicate the magnitude of the contribution of each factor in generating an effect. A percent contribution (P), which provides an indication of the magnitude of each factor, was used to assess the relative importance of each factor.

The ANOVA results for the lignin yield is shown in the Table 6-6Table 6-6. The agitation rate, which had the lowest SS and hence the lowest influence, was included in the error term for the analysis. None of the computed F-values were higher than the $F_{critical}$ value of 9.55, suggesting none of the factors were significant compared to the error term. In other words, all the investigated factors must be taken into consideration in yield optimization. The factor percent contributions were highest for precipitation pH and solids content at 33.8% and 22.5%, respectively, indicating they have highest influence on the yield.

Table 6-6: Results of ANOVA for lignin yield

Factor	**DOF**	**SS**	**MS**	**F-Value**	**P (%)**
Solids content (%)	2	91.2	45.6	3.3	22.5
pH	2	123.2	61.6	4.5	33.8
Ageing time	2	41.9	20.9	1.5	5.1
Agitation rate (RPM)	2	27.3	-	pooled	-
Error	2	27.3	13.7		38.5
Total	8	283.7			100.0

Table 6-7 and Table 6-8Table 6-8 show the ANOVA for the filtration resistance of the lignin cake and ash content of the washed cake. In the filtration resistance ANOVA computation, the precipitation pH, which had lowest SS, was included in the error term. The solids content was statistically significant with high percent contribution of 50.3% for filtration resistance. The percent contribution of the ageing time was also relatively high at 25.6%. In the ANOVA computation of the ash content, the agitation rate was included in the error term. None of the considered factor were significant. The solids content had the highest percent contribution at 39.2% for ash content. Therefore, when considering overall filtration performance, the significance of none of the parameters was could be anticipated.

Table 6-7: Results of ANOVA for filtration resistance of lignin cake

Factor	**DOF**	**SS**	**MS**	**F-Value**	**P (%)**
Solids content (%)	2	3.93E+19	1.96E+19	11.3	50.3
pH	2	3.46E+18	-	pooled	-
Ageing time	2	2.17E+19	1.08E+19	6.3	25.6
Agitation rate (RPM)	2	6.84E+18	3.42E+18	2.0	4.7
Error	2	3.46E+18	1.73E+18		19.4
Total	8	7.12E+19			100.0

Table 6-8: Results of ANOVA for ash content of washed lignin cake

Factor	**DOF**	**SS**	**MS**	**F-Value**	**P (%)**
Solids content (%)	2	30.4	15.2	6.73	39.2
pH	2	9.1	4.6	2.02	7.0
Ageing time	2	22.1	11.0	4.88	26.5
Agitation rate (RPM)	2	4.5	-	pooled	-
Error	2	4.5	2.3		27.3
Total	8	66.2			100.0

6.4.6 Selection of Overall Optimum Operating Conditions

The main purpose of the acid precipitation process is to produce lignin with low ash content, and this can be achieved by optimizing the filtration performance of the process. The identified optimal operating conditions were: solids content (30%), precipitation pH (9.4), ageing residence time (60 min) and agitation rate (122 RPM) as discussed in the section 6.4.4. Although, the process produces low ash lignin at these conditions, the lignin yield and levels of operating conditions are important parameters, which affect the capital and operating costs of the lignin plant.

Although, increase of black liquor solids content increases the yield, this affects negatively the filtration performance as shown in S/N ratio plots for filtration resistance and ash content (Figure 6-6). The solid content had high percent contributions (P) on all the response parameters (lignin yield, filtration resistance and ash content). This suggests that it has a large influence on the overall process performance and hence should be carefully manipulated in the optimization efforts.

The precipitation pH can be identified as a more flexible parameter in process optimization. It can be readily used to control the lignin yield and it has a relatively low influence on the filtration performance as indicated by lower percent contributions on both filtration resistance and ash

content. It is optimal to operate the process at low pH value (9.4) in terms of lignin yield and filtration performance, but it may increase the CO_2 demand and size of the acidification vessel.

Despite having a low percentage contribution on the lignin yield, the ageing residence time had higher contributions on filtration resistance and ash content. Both, yield and filtration performance found to be highest at 60 min. It is therefore recommended to operate the process at this condition. However, higher residence time implies larger vessels. The process could operate at lower residence times for applications that do not require high purity lignin.

The agitation rate had larger effect on filtration performance than on lignin yield. Therefore, operating at optimum condition for filtration performance (122 RPM) can be suggested. During the experimental program, we observed the sedimentation of lignin particles in the bottom of the mixing vessel for experimental trials with higher yield (at solid content of 37%) and lower agitation rate (72 RPM). This may be caused by due to insufficient hydrodynamic flow to keep particles in suspension and as a consequence reduce the filtration performance of the precipitated lignin. Even though, higher agitation rates can keep the particles in suspension, high shear generated by faster agitation could break-up the particles, and affecting the filtration adversely. Therefore, better hydrodynamic systems, which provides sufficient hydrodynamic flow with low shear rates, must be considered for acid precipitation processes operating with higher solids contents and yields.

6.4.7 Result Validation

The optimal conditions for filtration performance (solids content: 30%, precipitation pH: 9.4, ageing residence time: 60 min and agitation rate: 122 RPM) was verified by performing a confirmation trial. The observed values for lignin yield, filtration resistance and ash content were 56.4%, 3.53E+09 m/kg and 0.09%, respectively, while the additive main factor effects model, given in Eq. 13, predicted 56.0%, 3.53E+09 m/kg and -1.14. Except from ash content, the observed and predicted results for the lignin yield and filtration resistance were in good agreement for optimal conditions. The additive model equation was clearly not adequate in predicting the ash content, hence require different modeling approaches considering interaction effects.

The validation experimental trials confirmed that ash content of lignin can be kept very low (0.09-0.2%) for solid content range of 30-33.5% while maintaining the remaining parameters at the optimal values for filtration performance (pH: 9.4, ageing time: 60 min and agitation rate: 122

RPM). If higher ash content is acceptable (~1-2%), it is possible to operate the process at solids content as high as 37%, as verified by trial 8, and this in turn reduce the production costs of lignin. Better hydrodynamic design, however, should be considered when operating at higher solids contents. Also, it is possible to reduce the ageing residence time, decreasing the ageing vessel size for production of 1 to 2% ash content lignin.

6.4.8 The Acid Precipitation Process and Pulp Mill Interaction

The lignin precipitation process is integrated in the liquor cycle of the Kraft pulping mill. It receives a stream of black liquor diverted from the multiple effect evaporator train, which concentrate black liquor. After lignin separation, the acidified lignin lean black liquor is recycled back to the evaporator section. Black liquor stream for lignin precipitation can be extracted between 2nd and 3rd effects of the multiple effects evaporator train, where the solids content is usually in the range of 30 to 35%. In an operating Kraft pulping mill, there are operating disturbances, time and seasonal changes in the operating conditions, which can change the properties of the black liquor including solids content, inorganic salt content and lignin content.

The solids content had a large influence on lignin yield and filtration performance. Therefore, variations in the black liquor solids content can produce significant variations in a lignin precipitation process performance including yield and filtration performance. If they are not monitored and controlled, variations in yield can increase or decrease the amount of extracted lignin, affecting the calorific value of the black liquor. Also, variations in filtration performance can lower the quality of the produced lignin and create bottlenecks in the filtration and washing equipment. Therefore, further investigation is suggested. This should include controllability studies and determination of robust operating points, less sensitive to variations in black liquor properties.

6.5 Conclusion

The influence of process parameters on the filtration performance and yield of the acid precipitation process were analyzed using a oxidized softwood black liquor. The values of operating parameters, namely solids content, precipitation pH, ageing residence time and agitation rate, that achieved highest yield and filtration performance (minimum filtration resistance and ash content) were determined using Taguchi method. The following main conclusions can be drawn.

- According to the ANOVA analysis results, the solids content and ageing residence time had the largest influences on filtration performance, while precipitation pH and solids content had largest influences on lignin yield. However, the statistical significance of the investigated parameters on both filtration performance and lignin yield was not justified, indicating that all the studied parameters must be considered when optimizing the process for yield and filtration performance.

- Through the S/N ratio analysis, the optimal parameters for filtration performance have been determined at solid content: 30%, precipitation pH: 9.4, ageing residence time: 60 min and agitation rate: 122 RPM, while optimal parameters for lignin yield were at solid content: 37%, precipitation pH: 9.4, ageing residence time: 60 min and agitation rate: 72 RPM. A confirmation test was performed to validate the prediction of optimal parameters for filtration performance producing lignin having 0.09% ash content, with of 3.53 E+09 m/kg filtration resistance and 56.4% yield.

- The solid content was identified as the most critical parameter in optimization efforts as it had large and opposite influences on filtration performance and yield. The operating range of solids content for the investigated black liquor was determined as 30-33.5% which produced lignin with 0.09 to 0.2% ash content and yield up to 59.3% while keeping the other parameters at their optimal values for highest filtration performance.

- The precipitation pH had a large influence on yield but a low influence on filtration performance, making it a relatively flexible parameter to adjust and control the lignin yield. Higher ageing residence times (60 min) were required to produce low ash lignin as indicated by the S/N ratio and the ANOVA analysis. The agitation rate had a lower influence compared to the other parameters but its significance was not negligible. The filtration resistance was optimal at 122 RPM. Poor filtration performances were observed if agitation rate was either higher or lower than optimal value, which could be due particle sedimentation at tank bottom at slower speeds and particle shearing at faster speeds.

- If a lignin product with higher ash content (1-2%) is acceptable for its intended use, the operating conditions can be altered to achieve lower production costs. The solid content can be increased so that lignin yield is increased and the treated black liquor volume

decreased. The ageing residence time can be decreased, resulting in smaller vessel size. Consideration of better hydrodynamic mixing systems is recommended when increasing the operating solid content.

6.6 Acknowledgements

This work was financially supported by the BiofuelNet Canada, a network of centers of excellence and Natural Science and Engineering Research Council of Canada. We are also grateful to the pulping mill which provided the black liquor.

Chapter 7 FEASIBILITY AND ECONOMICS OF USING LIME KILN FLUE GASES FOR PRECIPITATION OF LIGNIN FROM BLACK LIQUOR

7.1 Introduction

Integrated forest biorefineries offer opportunities to increase the competitiveness and profitability of pulp and paper mills. Lignin, which is currently burnt in the Kraft pulp mill recovery boiler, can be recovered and converted into a broad spectrum of bio-based products using integrated biorefinery processes. Extraction of lignin can also be used to debottleneck an overloaded recovery boiler thus allowing mills to increase pulp production. Acid precipitation is one of the most promising method for lignin extraction. In this process, part of the black liquor is diverted from the evaporators and treated with CO_2 to precipitate the lignin. The precipitated lignin is washed with H_2SO_4 and water to remove impurities. Lignin lean black liquor after filtration and wash filtrates are returned to the recovery cycle of the mill (Kouisni et al., 2011; Loutfi et al., 1991).

The cost of CO_2 has been reported as one of the largest operating cost of the lignin precipitation plant and therefore the use of internally supplied CO_2 from flue gases has been suggested as a measure of improving the economics of the process (Loutfi et al., 1991; Olsson et al., 2006; Tomani et al., 2011). Benali et al. (2014) analyzed CO_2 capture from flue gases using monoethanolamine (MEA) and concluded that the operating costs were prohibitive, therefore CO_2 capture by chemical absorption cannot be considered as a viable option. The annualized capital costs varied from 4,980 – 1,531,000 $/a without considering the flue gas cleaning and temperature reduction equipment costs. The higher capital and operating costs of carbon capture and storage has been one of the factors that hinders its application in power plants. The production cost increase of electricity has been estimated to be 42-66% for power plants with post combustion carbon capture (Rubin, Chen, & Rao, 2007).

Wallmo, Richards, et al. (2009) conducted lignin precipitation studies with 99.7%, 50%, 15% CO_2 concentrations and observed that the rate of pH reduction decreases with decreasing CO_2 concentration. When 99.7% CO_2 was used, it took around 25 min to reach pH 9 while it took around 60 min to reach pH 9 when 50% CO_2 was used. The precipitated lignin had filtration resistances ranging from 1E+10 to 3E+10 m/kg.

The two main CO_2 producers in the Kraft mill are the recovery boiler and the lime kiln. Lime kiln flue gases has a higher CO_2 concentration due to its calcination reaction (Stevens et al., 1989). The direct use of lime kiln flue gases for acidification eliminates the use of expensive carbon capture technologies, it could therefore be an interesting option to improve the economics of precipitation and to reduce greenhouse gas emissions of integrated lignin biorefinery plants.

However, there are only few studies on the effects of dilute CO_2 on the acidification kinetics and on the filtration and washing. To our knowledge, the economic attractiveness of such internal CO_2 usage proposals have not been performed. In this work, we have investigated the feasibility of using lime kiln flue gases in the acid precipitation process, using several types of softwood black liquor. The process proposals were simulated in Aspen Plus® and the economic feasibility have been evaluated.

7.2 Experimental Section

7.2.1 Experimental setup

The same experimental setup described in Chapter 6 was used in this work. A gas mixture of 25% CO_2 and 75% N_2 (by volume) was used for black liquor acidification.

7.2.1.1 Experimental Procedure

The same experimental procedure as in Chapter 6 was followed in the experiments. It is briefly described here. Black liquor of ~48% dissolved solids was received from the partner Kraft mills. It was diluted to 30% and pre-filtered to remove any suspended solids such as fibers, dregs and soap; 1.3 liters of black liquor was added to the vessel and the mixer was started. The black liquor sample was heated up to the 75°C. 3 mL of Antifoam B emulsion (Sigma-Aldrich) was added to the black liquor to minimize foaming. When the black liquor temperature was 75°C, the pH measurement was started and gas bubbling for acidification of the black liquor was initiated. A CO_2 flow rate of 3 L/min was utilized throughout the acidification. The agitation speed was then set to the 730 RPM. The pH was measured periodically throughout the acidification using a MetroHM Unitrode combination glass pH electrode. The CO_2 bubbling was stopped when the pH reached the range of 9.9-10.0 (measured at room temperature). The agitation was continued using the same impeller for 1 hour at 122 RPM speed and the temperature was maintained at the same

value as during the acidification. The slurry was cooled to ~55°C and filtered using Buchner filtration funnel. The cake was washed by pouring 800 mL of 0.4 H_2SO_4 on the top of the cake followed by 200 mL of water. A sample of unwashed lignin cake was extracted for particle size analysis.

7.2.2 Analytical Procedures

The same analytical procedures as in Chapter 6 was used to characterize black liquors.

7.2.3 Black Liquor Properties

Four softwood black liquors have been used in the investigation. Liquor A and D were oxidized black liquors. The characterization of each liquor is given in Table 7-1. The same black liquors has been used in the investigation presented in Chapter 5.

Table 7-1: The properties of the investigated black liquor.

Properties / **Liquor**	**A**	**B**	**C**	**D**
Total solids (%)	30	30	30	30
UV lignin (% total solids)	38.9	41.8	38.5	38.3
Klason lignin (% total solids)	32.6	32.5	30.1	30.2
Acid soluble lignin (% total solids)	4.5	7.5	5.4	5.3
Inorganics or ash (% total solids)	40.1	27.3	28.2	28.3
Organics (% total solids)	59.9	72.7	71.8	71.7
Na (% total solids)	18.8	18.3	22.7	22.5
Residual alkali (g/L)	8.0	3.4	17.1	18.1
Sulfide content (g/L)	1.72	7.5	19.3	1.2
pH at room temperature	12.6	12.9	13.3	13.4
Dynamic viscosity (mPas)	7	8	9	9

7.2.4 Experimental Results

During the preliminary tests of black liquor acidification, significant foaming was observed. This has to be expected as inert N_2 gas bubbles escaping from black liquor creates foam. The foaming was largely reduced using Antifoam emulsion, however, it could not be completely eliminated.

The acidification of black liquors using dilute CO_2 took around 50-70 min depending on the residual alkali content of the liquor. Acidification time of liquors A and B was about 50 min, while liquor C and D took about 70 min to reach pH 10. When pure CO_2 was used, liquors A and B took 12-15 min for acidification while liquor C and D had around 20 min acidification time.

Table 7-2 shows the filtration performance and yield obtained from the experiments. The precipitated lignin in this study showed relatively higher filtration resistances than lignin precipitated using pure CO_2, as presented in Chapter 5 and Chapter 6. Lignin precipitated from liquor A and D could be washed by pouring acid directly on top of the cake. Lignin cakes from liquor B and C plugged completely with the acid addition. The cakes from liquor A and D had acceptable ash contents and lignin production rates. The particle size measurements revealed that lignin from liquor A and D had larger particles sizes (30-40 μm) than lignin obtained from liquor B and C (10-20 μm). However, these particle sizes were much smaller than those of lignin precipitated by pure CO_2 at optimal conditions.

Table 7-2: The results of the experiments using different black liquors.

Liquor	**Specific filtration resistance (m/kg)**	**Yield (%)**	**Washing time (min)**	**Ash content (%)**	**Lignin production rate (kg/m^2.h)**
A	8.58E+09	59.1	1.2	0.22	185.2
B	2.33 E+09	40.8	-	-	-
C	9.99E+10	37.3	-	-	-
D	1.02 E+10	38.3	1.6	0.57	151.6

The smaller particle sizes could be due to continuous particle restructuring during the longer acidification operation, in which the shear rates are higher. The precipitated lignin particles at the

end of the acidification operation can, therefore, be more stable, having achieved final structures, hindering further particle growth during the ageing operation. The fact that, the precipitated lignin from oxidized black liquors (A and D) had larger particles, could be due to increased aggregation ability of oxidized lignin. It might be possible to improve filtration using low shear during the acidification operation, but, this is not practical as higher agitation rates are required for good gas dispersion. Use of other mass transfer devices such as packed columns could be a possibility, however, foaming, fouling, lignin precipitation and sticking on mass transfer surfaces would be operationally challenging.

In conclusion, it was feasible to use lime kiln flue gases to precipitate lignin without significant difficulties in filtration and direct displacement washing, when oxidized liquor is used. If un-oxidized liquor is used, re-slurry washing has to be considered, as the generated cakes were difficult to wash directly. In the latter case, the filtration and washing equipment would be larger due to higher filtration resistance.

7.3 Economic Evaluation

7.3.1 Process Flowsheets and Simulation

Two process flowsheet variations were considered in the analysis. They both produce 70 t/d of lignin.

1. Process 1: The process uses externally purchased pure CO_2 for the black liquor acidification.
2. Process 2: CO_2 for the black liquor acidification is supplied by the lime kiln flue gases. The process includes pre-treatment of flue gases and post-treatment of acidification reactor exhaust to remove sulphur gases. The process flowsheet is given in Figure 7-1.

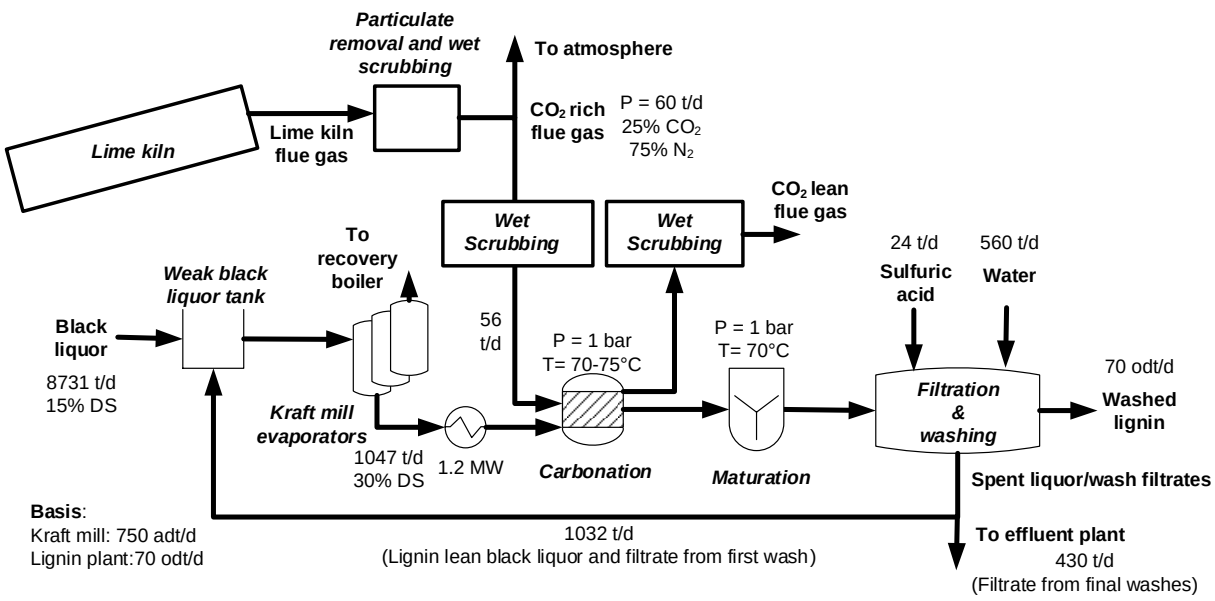

Figure 7-1 : Acid precipitation process flowsheet with lime kiln flue gas CO_2 supply

The processes were simulated using Aspen Plus® flowsheet simulator. The acid precipitation process was defined by the parameters given in Table 7-3. The electrolyte modeling approach proposed in 4.3.3 was used in the simulations. The additional pre-treatment included wet scrubbing to remove all the contaminants from the gases. All the operations after acidification including filtration and washing have been assumed to be unchanged in order to simplify the cost estimations, even though somewhat reduced filtration performances were observed in the experimental work.

Table 7-3 : Parameters of lignin precipitation process.

Parameter	**Value**
Process lignin yield (%)	60
CO_2 demand (t/t lignin)	0.25
H_2SO_4 demand (t/t lignin)	0.34
Water demand (t/t lignin)	8
NaOH demand (t/t/ lignin)	0.1

7.3.2 Economic Analysis

Preliminary cost estimation methods and literature published cost data with scaling factors and cost indices have been used for installed equipment cost estimates (Gooding, 2012; Wilson, 1971). Table 7-4 summarizes the economic analysis of the two processes. The fixed capital investment for each process was estimated without considering the indirect costs. The investment cost difference between two processes arise from the size of the acidification reactors and scrubbers required for the gas cleaning. The difference in acidification kinetics have been incorporated to estimate of the size of the acidification reactors.

Table 7-4 : Economic analysis for two processes.

Cost component	**Process 1 (M$)**	**Process 2 (M$)**
Acidification reactors	1.4	3.3
Scrubbers (Gas cleaning)	0	0.6
Other equipment (Filter press, storage tanks, pumps, heat exchangers)	7.2	7.2
Contingency at 40%	3.5	4.5
Total capital investment	12.1	15.5
CO_2 cost	1.9	0
Other operating costs (Chemicals and steam)	4.9	4.9
Total operating cost	6.7	4.9
Revenue from lignin sales	18.6	18.6
Net profit after 30% tax	8.3	9.6

The reduction of recovery boiler steam production was assumed to be compensated by burning more natural gas in the power boilers. The following purchase prices were used in the analysis; CO_2: 300 $/t, H_2SO_4: 150 $/t, NaOH: 500 $/t, natural gas: 3 $/GJ. The difference in the operating cost of two processes is due to internal CO_2 supply in the process 2. The total operating cost were

272 and 197 $/t of lignin for process 1 and process 2, respectively. The estimated payback time were 1.5 and 1.6 years for process 1 and 2, respectively. This indicates that the use of lime kiln flue gases for acidification were not economically attractive compared to the use of externally purchased high purity CO_2 for the considered set of process parameters.

The benefit gained from the CO_2 cost saving was not sufficient to justify the additional invested capital in process 2, particularly in the acidification reactors. The payback period of process 1 increases with increasing CO_2 price and demand, as given in Figure 7-2. To exceed the payback time of process 2, the CO_2 price and demand have to be higher than ~465 $/t and ~0.4 t/t lignin, respectively. Therefore, the CO_2 price, demand or both have to be much higher than currently reported values for process designs with lime kiln flue gas utilization, to be economically attractive. The scale of the lignin precipitation processes, which are usually 50-100 t/d, may also contribute to the economic unattractiveness of the mass integration with the receptor mill, due to lower economies of scale. The internal CO_2 supply might be a possibility with much larger scale lignin processes.

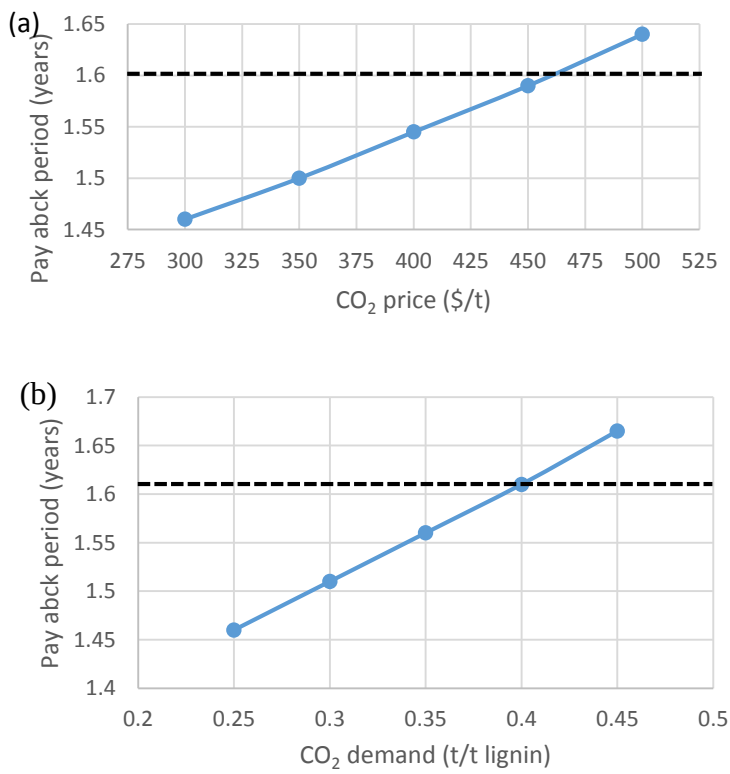

Figure 7-2 : The sensitivity of the payback period of the process 1 to the (a) CO_2 price (b) CO_2 demand

Decreasing the size of the acidification vessel by using efficient mass transfer devices is another possibility for improving the economic attractiveness of the process. However, capital and operational costs and operational disturbances due to foaming and fouling have to be carefully considered. Also, the kinetics of pure CO_2 usage could be benefited from improved mass transfer devices, further reducing the capital costs of process 1. Despite the economic indicators, the process 2 clearly reduces the greenhouse gas emissions from the Kraft mill, making it more environmentally attractive. Incentives for environmental performance could improve its profitability.

7.4 Conclusion

The lignin precipitation experiments were performed using dilute CO_2 with a composition corresponding to lime kiln flue gas. The study showed that it was feasible to use lime kiln flue gases without a large impact on the lignin filtration performance, when oxidized black liquor was used. This makes it possible to use direct displacement washing after filtration. However, the filtration resistance was much higher for non-oxidized black liquor and direct displacement washing was not feasible.

The process simulation and economic analysis revealed that the use of flue gases was less economically attractive than the use of externally purchased CO_2. The elimination of CO_2 purchase cost reduced the operating costs, however, the higher capital costs for gas cleaning and larger acidification reactors increased the payback period. The CO_2 price and demand have to be higher than ~465 $/t and ~0.4 t/t lignin, respectively, for the use of flue gases to be profitable.

Chapter 8 GENERAL DISCUSSION

The development and integration of lignin biorefineries in Kraft pulping mills have been discussed in this thesis. Article 1 and 2 concentrate on the implementation and integration while article 3 and 4 focus on the acid precipitation process development. Chapter 7 considers both integration and development aspects. In the following discussion, the main findings, limitations and connections between different sections of the thesis have been examined, in a general manner.

8.1 Process Implementation and Integration

8.1.1 Energy Impacts and Mitigation

The lignin precipitation process does not require a major heating duty. The incoming black liquor must be cooled to ~75°C before precipitation occur; temperature reduction is about 20°C. In some cases, further cooling of the lignin slurry was required before filtration to improve the filterability. The optimal slurry temperature was about 60°C for the black liquors investigated in this thesis. However, these cooling duties were relatively small (0.03 MW/t lignin) hence they do not have a major impact on the total energy demand of the Kraft mill.

Despite the absence of major heating or cooling duties in the acid precipitation process, the recovery boiler steam production decreased with lignin extraction. The steam demand of multiple effect evaporator train increased mainly due to recycle of wash filtrates. This creates extra energy demands in terms of energy deficits in the Kraft pulping mill, when a lignin extraction plant is implemented. The reduction of high pressure steam production in the recovery boiler reduces the power production of the mill, as discussed in article 1. The least capital intensive way to address the power and steam deficit is to increase the steam production of the biomass or power boilers of the mill. Part of the produced lignin, biomass or natural gas can be combusted, depending on the availability of power boilers with additional capacities.

In article 1, it has been shown that power and steam deficits generated by lignin removal can be addressed by energy optimization with pinch analysis, for a representative Canadian softwood Kraft pulping mill. Addressing power deficit, however, requires installation of condensing turbines in order to generate power from medium and low pressure steam. Technologies such as biomass gasification with integrated gasification combined cycle (IGCC) with higher energy efficiency,

could be potential options for addressing lignin extraction energy demands. An economic analysis for the proposed options in the article 1 have not been performed.

For the Canadian Kraft pulping mill studied in article 2, a steam saving potential up to 37 % have been identified at 0.32 M$/MW average heat exchanger cost in a previous study (Keshthkar, 2013). The saved steam can be used to compensate low and medium pressure steam demands brought forth by lignin precipitation, without considerable capital investments. However, addressing the reduced power production requires further capital costs to change the steam turbine configuration. Such implementations with steam saving projects and upgraded steam turbine configuration were not profitable when compared with increased high pressure steam production in power boilers at current natural gas prices of ~3 $/GJ.

8.1.2 Lignin Extraction Ratio and Pulp Production Increase

Estimating the lignin extraction ratio is crucial for the implementation of lignin precipitation processes in Kraft pulping mills. It determines the size of the lignin plant as well as the possible pulp production increase. The recovery boiler is the most affected equipment by the lignin extraction in the Kraft mill. The energy content of black liquor, measured by the heating value, reduces with lignin extraction as it becomes more diluted with inorganics. If it becomes too low, the safe and efficient operation of the recovery boiler is compromised. Several recovery boiler specific parameters can be used to estimate this impact. In this work, it has been estimated by means of a simple parameter, the minimum acceptable higher heating value (HHV) of the black liquor for a given recovery boiler. The minimum acceptable HHV of black liquor that guarantees the efficient operation of the recovery boiler has been reported to be about 12.5 MJ/kg (Perin-Levasseur, Z. et al., 2011).

The ultimate and proximate analyses can be used to estimate the HHV of black liquor, however, the accuracy of the estimates depends on the quality and the quantity of the available experimental data. In the absence of such data, a linear interpolation approach has been used in this work, as discussed in article 2. A linear differential equation based on total energy content has been proposed to estimate the deviations of HHV from a reference value.

A lignin extraction of 15% was estimated for the studied Canadian softwood Kraft pulping mill, considering a minimum HHV of 12.3 MJ/kg. The recovery boiler steam production was reduced

by 13%. The decrease in recovery boiler energy production will allow increasing pulp production, if the mill is limited by the recovery boiler thermal capacity. The pulp production could be increased by 14.9% for the studied Kraft mill. It should be noted that these value are specific to the mill and hence they may not be directly transferrable to the other mills.

The lignin extraction ratio is largely dependent on the black liquor composition, particularly on the lignin content. The investigated mill had 35% lignin (o.d. basis) in the black liquor, which provides a feasible 15% lignin extraction. If the lignin content is lower, such as in hardwood pulping mills, the lignin extraction ratio would be higher. Lignin extraction ratios around 30% have been reported from the mills with low lignin black liquor (Hamaguchi & Vakkilainen, 2010). On the other hand, if the lignin content is higher (around 42%), lignin extraction ratios about 10% would be feasible. The lignin extraction extents discussed in this work are the most economical because it can be implemented without major upgrades to the recovery boiler. Lignin extraction up to 50% is feasible as reported by Valimaki et al. (2010) to maintain a minimum adiabatic temperature (T_{ad}) and a hearth heat release rate (HHRR) for a operational recovery boiler. However, major upgrades will be required to operate the recovey boiler at 50% lignin extraction. The lignin extraction ratios reported in this thesis can hence be taken as most conservative values.

8.1.3 Process Modelling and Liquor Cycle Chemical Balance

The largest impacts of acid precipitation of lignin are on the Kraft mill energy balance, however the effects on the chemical balance cannot be neglected. The chemical balance, usually expressed in terms of Na and S, is mainly affected mainly by the higher percentage of bound Na (~12% wt.) in the precipitated lignin. Removal of bound Na requires further lowering of the pH, which can be done by H_2SO_4 washing. At lower pH values, the surface charges of lignin are completely neutralized by protonation, thus removing bound Na ions. The wash filtrates produced in acid washing operations contain the bound Na, however, mixed with S coming from sulfate ions. Recycling the wash filtrates is a way to recover the Na, but it can also add extra S to the liquor cycle. If additional S is introduced, it has to be removed from the process by a purge. A recovery boiler electrostatic precipitator dust (ESP) purge can be used for this pupose in order to maintain desired sulfidity level for Kraft mill operation. However, it also removes Na, which is then has to be compensated by make-up NaOH or Na_2CO_3.

In the article 2, simulation models have been developed to estimate the pH and composition variations in the black liquor and to compute the Na/S balances of the liquor cycle. The Aspen Plus® electrolyte model has been used to estimate the pH and composition variations. The black liquor ionic equilibrium involves not only the inorganic components but also organic components such as lignin phenolic and carboxyl groups. The pH variation of the model including only the inorganic components showed large deviations from experimental data for pH values below 11. The prediction of the pH variation was significantly improved by adding an ionic component to represent the typical composition and acidity of phenolic groups of lignin (3.4 mmol/g of lignin and pK_a value of 10), for the validated pH range of 7-13. This showed that the electrolyte equilibrium approach can be successfully applied for modeling black liquor pH variation.

However, the pK_a values of lignin can vary broadly (pK_a: 6.2-11.3) depending on its structure, functional groups and molecular weight. This requires the model to be validated for a different black liquor application. Also, the model was validated only for the pH 7 to 13 range. The estimation of lower pH values may require dividing lignin into several sub-groups based on their molecular weight and pK_a values to provide better distribution of lignin acidity. Further development of the model can be suggested, extending it into the areas of prediction of the protonation and bound Na removal and lignin aggregation. These efforts, however, require large sets of experimental data in terms of molecular weights and pK_a values for model structure development and validation.

A mass balance model, which was implemented in MS Excel™, has been developed for the estimation of Na/S balances of the liquor cycle. Balancing of Na and S was performed according to several implementation scenarios involving wash filtrate recycle and black liquor pH re-adjustment, based on the constraints of different Kraft pulping mills. The analysis revealed that scenarios involving complete disposal or excessive recycle of wash filtrates increased the make-up NaOH demand, which was about 0.2 t/t of lignin. The mill studied had an external S requirement of 5.3 kg/adt, which was fulfilled by the addition of make-up salt cake ($Na_3H(SO_4)_2$). Therefore, the mill had room to accommodate the additional S that comes with wash filtrates by reducing the salt cake input. This was feasible because $Na_3H(SO_4)_2$ has lower Na/S ratio than Na_2SO_4. Therefore, recycling wash filtrates recovered more Na than adding $Na_3H(SO_4)_2$. Hence, it was feasible to reduce the make-up NaOH demand down to 0.14 t/t of lignin by recycling 5 t/t of lignin wash filtrates without re-alkalizing the black liquor. If the wash filtrate recycle increases further,

the make-up NaOH demand also increases as extra S has to be removed by ESP purge, thus removing more Na. The additionally recycled water increased the evaporator steam demand. It is important to note that the Na/S balance strategy have to be considered case by case. It is highly dependent on the current balance of the Na and S in the mill.

The efficiency of the washing step, defined as the percentage of chemicals removed by adding a certain quantity of acid, can depend on the cake properties as well as the type of the washing operation (Re-slurry or displacement washing). If more acid is consumed for washing, the amount of S in the wash filtrates will be higher, negatively affecting Na/S balance. The sensitivity of the NaOH demand to various washing conditions was investigated by the changing the washing step efficiency. It was feasible to reduce the make-up NaOH demand down to 0.1 t/t of lignin by improving the washing efficiency.

Most Kraft pulping mills are also limited by the recovery operations other than the recovery boiler. The Kraft pulping mill investigated had a bottleneck at the lime kiln, which only allowed a production increase up to 10%. The recycling strategies changed the chemical loads to recausticizing and lime kiln sections and the water load to the evaporators. Therefore, the recycling strategy has to be balanced in order to minimize the chemical losses, loads to recovery operations and to maximize the pulp production increase. The constraints of the Kraft mill such as the need to re-alkalize the black liquor should also be taken into account when choosing the best strategy for adjusting the chemical balances.

8.1.4 Internal Supply of Chemicals

The feasibility and economics of using lime kiln flue gases as acidification medium have been discussed in Chapter 7. It was shown that it is feasible to obtain easily filterable and washable lignin using dilute CO_2 such as lime kiln flue gases in laboratory experiments, when oxidized liquor was used. However, the acidification kinetics were slower and foaming problems were encountered. An economic analysis was performed, considering additional gas cleaning and larger acidification vessels to accommodate flue gases. The extra capital investment needed for flue gas acidification did not bring enough returns in terms of CO_2 cost savings. The CO_2 price and demand had to be higher than ~465 $/t and ~0.4 t/t lignin, respectively, for the process to be more economically attractive than external CO_2 purchase. More efficient mass transfer devices such as

packed columns could be interesting options, however, related costs and operational difficulties such as foaming have to be considered.

The opportunities for internal supply of H_2SO_4 were qualitatively discussed, in the article 2. The chemical balance strategies reduce the use of salt cake in the liquor cycle, which is a byproduct of ClO_2 generator. This readily available salt cake can be purified into H_2SO_4 and Na_2SO_4 or H_2SO_4 and NaOH using commercially available technologies. However, the amount of available salt cake was lower than was needed by the lignin washing operation, for the mill investigated. If more byproduct salt cake is available, the installation of purification technologies can become interesting. However, the lower price of H_2SO_4 compared to the other chemicals used in acid precipitation process (CO_2 and NaOH) does not justify higher capital investment on purification technologies.

8.2 Process Development

Filtration and washing of precipitated lignin have been found to be difficult due to higher filtration resistances, slower washing rates and dissolution of lignin during washing. The filtration and washing equipment have been reported to be the most capital intensive in a lignin precipitation plant, making up to 30% of the total equipment cost. Therefore, there are incentives to optimize the acid precipitation process, particularly the filtration and washing operations. In article 3, the effects of mixing hydrodynamics during lignin precipitation has been presented as means of improving lignin filtration. In article 4, a systematic optimization of process parameters to achieve higher yield and filtration performance is presented.

8.2.1 Effects of Mixing Hydrodynamics

The hydrodynamic conditions during initial aggregation and growth of colloidal particles affect the size and shape of the final particle structures. In article 3, the turbulent shear rate and hydrodynamic flow pattern were varied during lignin coagulation and floc growth. The turbulent shear rate was varied applying different mixing power levels during acidification and ageing steps while the flow pattern was varied using two different impeller systems; Maxblend^{TM} (MB) and Pitched Blade Turbine (PBT). The particle and filtration properties were characterized.

The lignin flocs, generated at the end of the acidification step, were made of primary lignin particles with 1-2 μm size and fractal dimension D_f=2.15-2.65. These sizes and shapes did show a dependency on the hydrodynamic conditions. They were consistent with the properties of lignin particles (1-2 μm size and fractal dimension D_f=1.9-2.45) that were aggregated by Brownian motion, as reported in the literature (Norgren et al., 2002). Therefore, the hydrodynamic conditions had a negligible effect on the size or shape of the primary lignin particles.

As primary particles aggregated to form larger flocs, the effects of hydrodynamic conditions became important. As flocs get larger, their size become increasingly comparable with the size of turbulent fluctuations (length scale), exposing the flocs to shear forces. Under shear, the weak flocs tend to break and re-aggregate. This interplay of breakage and aggregation determines the final particle size and shape. The lignin flocs generated at high shear acidification were small and compact while low shear acidification produced large but loose flocs.

Both compact and loose flocs aggregated into much larger flocs, when the turbulent shear level was reduced by decreasing the mixing power level during the ageing step. The final floc size was mostly dependent on the shear level, having largest particle sizes at lowest shear rates. However, the initial floc properties had a large impact on the size and the structure of the final flocs. The effect of the impeller type in the aggregation of compact initial flocs into larger flocs was negligible. These flocs had narrow distributions and SEM images showed compact and large final flocs.

Despite negligible effect of the impeller type on growth of compact flocs, the impeller flow pattern showed an impact on the aggregation of loose flocs into larger flocs. Moreover, the size distribution of loose flocs were wide and had a fraction of fine particles. Loose flocs can generally be considered to have lower strength due to fewer links between primary particles. Therefore, high shear in the impeller zone can break-up these loose bonds, creating fine particles and wide size distributions As a result, the MB impeller, which created relatively lower shear, minimized the breakage of loose flocs and provided better aggregation of loose flocs.

The filtration performance of the compact and large flocs were clearly higher than loose and small flocs. The filtration performance of loose flocs increased with increasing size, but remained below the performance of the compact flocs. Differences in the lignin yield were also observed according to lignin floc size and compactness. The lignin production rate at the filter varied from 86 to 244

kg/h.m^2 for the investigated hydrodynamic power levels. Differences of this magnitude can lead to large reductions on filter areas, resulting in large improvements in the filtration and washing equipment sizes.

The results of this investigation were confirmed when three other black liquor samples from different origins were used. As expected, large differences in particle sizes and filtration properties were observed for varying hydrodynamic conditions. Higher turbulent shear levels during acidification and lower levels during ageing produced best filtration performances. However, differences according to the black liquor type was also observed. The oxidized black liquor samples with lower sulfide content provided higher lignin filtration rates. The variation of filtration performance according to black liquor composition was, however, not investigated in this study and it is recommended that it is done in future studies.

8.2.2 Systematic Parameter Optimization

The lignin yield and filtration resistance of the acid precipitation process have been reported to be affected by number of operating parameters. Easily filterable lignin can be obtained only in a narrow range of conditions. In article 4, the operating parameters of the acid precipitation process were optimized to achieve higher filtration performance and yield. The Taguchi experimental design approach was used to investigate namely, black liquor solids content, precipitation pH, ageing residence time and ageing agitation rate.

According to the statistical analysis, the solids content and ageing residence time had large influences on filtration performance while precipitation pH and solids content had large influences on lignin yield. The black liquor solids content have been identified as the most critical parameter as it had large and opposite influences on filtration performance and yield. The filtration performance was higher at lower solids content but the lignin yield was lower. The operating range of solids content that provided good filtration performance with sufficient yield was 30-33.5%.

Both filtration performance and yield were higher at lower pH values. However, operating at lower pH values may increase the CO_2 demand. The sensitivity of the filtration performance to the precipitation pH was low, which made it a flexible parameter to adjust lignin yield. Higher ageing residence times close to 60 minutes provided good filtration performance and yield.

Among the agitation rates studied during ageing operation, a rate of 122 RPM provided highest filtration performance, while a higher or lower rate deteriorated it. This observation is somewhat different than the conclusion in article 3, where lowest agitation rate during ageing step provided highest filtration performance. However, the operating black liquor solids content was 30% for the study presented in article 3, while it varied from 30 to 37% for the study in article 4. At higher solids content about 37%, lignin sedimentation at the bottom of the tank was observed. This is due to insufficient hydrodynamic flows provided by the impeller and it can avoided by using better hydrodynamic systems such as MB impeller described in article 3.

Chapter 9 CONCLUSION AND RECOMMENDATIONS

9.1 Conclusion

The main objective of this thesis has been achieved. Novel understanding, models and guidelines were developed for the design and integration of acid precipitation based biorefineries in Kraft pulping mills to improve the cost effectiveness and environmental efficiency. The scope of the project was limited to extraction and purification of lignin.

Process integration opportunities to supply lignin biorefineries with the required energy and chemicals exist in Canadian Kraft pulping mills. It was shown that it is feasible to address the demands of lignin biorefinery using internal heat and chemical recovery. The environmental performance could be improved and reduction of greenhouse gas emissions could be achieved.

However, the economics of such lignin biorefineries with energy and chemical integration may not be favorable under current circumstances. The low and medium pressure steam demands generated by lignin biorefinery can be compensated with low cost steam saving projects. Addressing the power deficits, however, require modifications in the steam turbine configuration, which could be expensive. The CO_2 and H_2SO_4 in the mill are at lower quality than required by the lignin biorefinery, thus requiring additional equipment and purification processes to accommodate them in the biorefinery. Given that lignin biorefineries are relatively small in scale, the energy and chemical prices has to be higher than current levels, for such integrated process solutions to be economically attractive, in the absence of incentives for the environmental performance.

Emphasis should be laid on the proper implementation of lignin biorefinery within the Kraft mill so that disruptions on the liquor cycle mass and energy balances be minimal and the highest lignin extraction ratio and pulp production increase are achieved. Minimizing the disruption of the liquor cycle Na/S balance by using an appropriate wash filtrate recycle strategy is critical in reducing NaOH make-up demand. The recycle strategy also affected the processing loads to other chemical recovery operations, which would require the balancing of impacts to achieve optimal implantation in terms of NaOH demand and pulp production increase. The affected operations are evaporator train, recausticizing and lime kiln.

Potentials for process optimization exist during the process development phase, which could lead to better economics. The analysis of the process revealed that the properties of precipitated lignin

can be controlled by manipulation of hydrodynamics of the process, facilitating better filtration and washing. Considerable reductions of filtration equipment size was possible using hydrodynamic optimization. Similarly, systematic investigation of operating parameters made it possible to identify the most important parameters that affect the process performance. The optimization of those parameters by considering the trade-offs between lignin purity and cost of production should be considered to improve overall benefits.

9.2 Original Contributions

The main original contributions are summarized below.

- Impact of lignin extraction on the steam and power balance of a representative Canadian Kraft pulping mill have been established.
- A simulation models for evaluation of implementation of lignin biorefinery were developed. It included a validated electrolyte equilibrium model based on inorganic and organic components in the black liquor for predicting pH and composition variations during black liquor acidification and a mass and energy balance model incorporating Na/S balances of the liquor cycle.
- Guidelines for optimal implementation of lignin biorefineries in Kraft pulping mills in terms of energy, chemicals, lignin extraction ratio and pulp production increase have been developed.
- Effects of mixing hydrodynamics during initial aggregation, growth and breakage of lignin have been identified and it was used to improve the filtration step.
- The most critical parameters that affect yield and filtration performance have been identified and optimized.

9.3 Recommendations

This work left many topics open, which are recommended for future research.

9.3.1 Integrated Forest Biorefineries (IFBR)

This work focused on the implementation of lignin biorefineries in Kraft pulping mills. Impacts on the Kraft pulping mill and process integration opportunities were indetified. For higher economic and environmental performance, the impacts on the Kraft process must be minimized. The process integration opportunities were promising in reducing external energy and chemical requirement of the process, however, the proposals were not economically attractive at current energy and chemical prices and for the scale of feasible lignin biorefineries.

Considering the implementation of several biorefinery technologies in the Kraft pulping mill could lead to IFBR configurations with higher degree of process integration and cost effectiveness. Increasing the number of implemented biorefinery technologies allow large number of such IFBR configurations to be considered. There could be opportunities in counter balancing the impacts of one biorefinery technologies with another biorefinery technology. For example, the energy deficits crated by lignin extraction may be balanced by hemicellulose or cellulose biorefiney technology which produce organic waste that can be recycled into black liquor. Similarly, the Na/S balance could be addressed by a biorefiney process that uses Na based chemicals, which require recycling.

This would generate opportunities to utilize waste chemical purification technologies more effectively. For example, a lignin biorefinery with acid washing and a hemicellulose biorefinery with acid-hydrolysis would require sulfuric acid. Installation of ClO_2 generator waste purification technologies could be justified by an increased demand of sulfuric acid. Also, a waste stream from one biorefiney can be used as an input in another. As example, CO_2 generated in gasification based biorefinery could be used in acid precipitation based lignin biorefinery.

Moreover, the consideration of multiple biorefinery options would produce more opportunities for energy integration. Having multiple biorefinery options producing a wide array of products could help to decrease the risk and improve the scale of a complete IFBR complex, providing better economies of scale.

9.3.2 Process Modelling of the Lignin Biorefinery

An electrolyte equilibrium model for black liquor acidification was proposed and validated in this work. This model offers further opportunities in improving process modeling of the lignin biorefinery.

Modelling of lignin aggregation, which requires taking into account, charge neutralization of lignin molecules, ionic strength of the solution and temperature, would facilitate the prediction of lignin yield of the acid precipitation process. The currently proposed electrolyte equilibrium approach could facilitate the development of a thermodynamic framework for such a model. The model structure development could be semi-empirical and require validation from large number of experimental data.

The development of lignin aggregation model will require measuring the properties of lignin such as molecular weight, functional groups and pKa values. The model structure has to be determined according to the behavior and patterns identified using experimental data. The model validation and parameter identification will be required for different black liquor types.

9.3.3 Lignin Floc Strength Measurement and Improvement

In this thesis, the lignin floc strength was discussed in relation to its compactness. More compact flocs were assumed to be stronger according to explanations in the published literature. However, the characterization of the strength of lignin flocs could provide better understanding of the properties of lignin flocs that produce efficient lignin filtration and washing.

Macroscopic and microscopic techniques can be used in floc strength measurement. The macroscopic methods include impeller agitation and ultrasonic mixing, which provide relative measurements of floc strength, depending on the final size of the flocs and the amount of energy supplied to the system. However, results from different methods and materials are not directly comparable as the strength is given as a relative quantity. The microscopic techniques, which include micromechanics and micromanipulation, measure the forces required to break the flocs and hence provide absolute strength values. These techniques require development of rigorous experimental procedures to perform the measurements with sufficient accuracy.

By developing such techniques, the absolute floc strength values for lignin precipitated at different operating conditions using different black liquor can be obtained. It would help to understand the

main parameters that affect floc strength, providing better control on lignin aggregation and on the properties of precipitated lignin.

9.3.4 Novel Precipitation Reactor Proposals

In the acid precipitation process, the acidification and ageing operations are usually performed in batch mode, resulting in large reactor and vessel sizes. This leads to higher investment costs. Process intensification measures can be used to reduce reactor size, making lignin biorefinery process more economically attractive.

As shown in this thesis, the level of turbulence plays an important role in lignin aggregation, growth and breakage. The precipitated particle size and shape can be controlled using the turbulent shear level. These concepts can be extended to designing novel intensified reactor types, which offer hydrodynamic control and continuous operation. For example, the hydrodynamic cavitation reactors, which create high intensity turbulence due to throttling effect, can be used to create the higher turbulence levels required during the initial aggregation of lignin to create compact lignin flocs.

9.3.5 Control and Stabilization of the Acid Precipitation Process

As found in this work, the black liquor solids content had a large influence on the lignin yield and filtration. The varying solids content affects the concentration of black liquor components, resulting in variations in the process performance as well. Apart from variations of black liquor composition due to operation disturbances, there are timely and seasonal changes in the operating conditions, which can change the composition of the black liquor including solids content, inorganic salt content and lignin content in an operational Kraft pulping mill. If not monitored and controlled, these variations can cause significant deviations of the process performance. The variations in yield can increase or decrease the amount of extracted lignin, affecting the calorific value of the black liquor. The variations in filtration performance can lower the quality of the lignin produced and create bottlenecks in the filtration and washing equipment. Therefore, further investigation of this aspect is recommended.

This investigation could be started by defining the variations of black liquor composition in an operating Kraft pulping mill. Mill information systems and mass balance models, which were

developed in this work, could be used to estimate the black liquor composition. Once the variations are defined, similar black liquor compositions can be extracted from the mill or model solutions can be prepared. Experimental design approaches, including response surface designs or Taguchi robust designs, can be used to model the process responses according to composition variations. The response surface models can be used in designing advanced control strategies to ensure stable operation of the process. The Taguchi robust design can be used to select process operating conditions that have lowest sensitivities to black liquor composition.

9.3.6 Control of Lignin Properties

Value added lignin applications require a lignin feedstock to have certain chemical and physical properties. These properties, which include molecular weight and polydispersity, ash content, lignin content, volatiles content and structure and functional groups of lignin molecules, are highly dependent on the intended use of lignin. Therefore, future lignin biorefinery development efforts should focus on tailoring the properties of extracted lignin to the end use.

This work deals with extraction deals with extraction and primary treatment of lignin. Further work can be done on controlling the lignin properties during extraction stage. The variation of lignin properties with different process operating conditions should be investigated and ways to precipitate lignin, with similar properties required by the intended use, should be studied. For example, the molecular weight of lignin can be controlled using precipitation pH.

The definition of required lignin properties would be best performed in collaboration with groups who develop lignin value added products. The characterization of lignin properties and molecular structure, however, requires advanced analytical techniques, which is in the area of organic chemistry. Development of such techniques would require related expertise or collaboration with research groups focusing on lignin properties characterization.

BIBLIOGRAPHY

Abdelwahab, N. A., & Nassar, M. A. (2011). Preparation, optimisation and characterisation of lignin phenol formaldehyde resin as wood adhesive. *Pigment and Resin Technology, 40*(3), 169-174. doi: 10.1108/03699421111130432

Ajao, O. (2014). *Development of hemicellulose Biorefineries for integration into Kraft pulping mills.* (Ecole Polytechnique de Montreal, Montreal, Canada).

Alen, R., Patja, P., & Sjöström, E. (1979). Carbon dioxide precipitation of lignin from pine kraft black liquor. *Tappi, 62*(11), 108-110.

Andersson, P. (2014). *A dynamic Na/S balance of a kraft pulp mill.* (Karlstad University).

Argyropoulos, D. S., Sun, Y., & Palu, E. (2002). Isolation of residual kraft lignin in high yield and purity. *Journal of Pulp and Paper Science, 28*(2), 50-54.

Axelsson, E., Olsson, M. R., & Berntsson, T. (2006). Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade. *Nordic Pulp and Paper Research Journal, 21*(4), 485-492.

Baker, F. (2011, March 22-24, 2011). *Utilization of sustainable resources for materials for production of carbon fiber structural and energy efficiency applications.* Paper presented at Nordic Wood Biorefinery Conference, Stockholm, Sweden.

Benali, M., Périn-Levasseur, Z., Savulescu, L., Kouisni, L., Jemaa, N., Kudra, T., & Paleologou, M. (2014). Implementation of lignin-based biorefinery into a Canadian softwood kraft pulp mill: Optimal resources integration and economic viability assessment. *Biomass and Bioenergy, 67*(0), 473-482.

Bhattacharjee, S., Datta, S., & Bhattacharjee, C. (2006). Performance study during ultrafiltration of Kraft black liquor using rotating disk membrane module. *Journal of Cleaner Production, 14*(5), 497-504.

Biermann, C. J. (1996). *Handbook of pulping and papermaking* (2nd Ed ed. Vol. 2): Academic press.

Blackwell, B., & Lincoln, D. (1998). Sodium/sulphur/chlorine balance demonstrated low liquor losses at a kraft mill. *Pulp and Paper Canada, 99*(1), 74-78.

Bo, X., Gao, B., Peng, N., Wang, Y., Yue, Q., & Zhao, Y. (2012). Effect of dosing sequence and solution pH on floc properties of the compound bioflocculant–aluminum sulfate dual-coagulant in kaolin–humic acid solution treatment. *Bioresource Technology, 113*(0), 89-96.

Bozell, J., Holladay, J., Johnson, D., & White, J. (2007). Top value added Chemicals from Biomass.Volume II–Results of Screening for Potential Candidates from Biorefinery Lignin, US Department of energy, report PnnL-983. In P. N. N. Laboratory (Ed.), *http://www1.eere.energy.gov/bioenergy/pdfs/pnnl-16983.pdf*.

Brown, T., Gilsenan, R., Singbeil, D., & Paleologou, M. (2011). *Bio-energy and Bio-chemicals Synthesis Report*. FPInnovations.

Chien-Wei Chen, M. (2014). *Commercial viability analysis of lignin based carbon fibre.* (Simon Fraser University).

Cloutier, J. N., Azarniouch, M. K., & Callender, D. (1993). Electrolysis of weak black liquor Part I: Laboratory study. *Journal of Pulp and Paper Science, 19*(No.6), J244-J248. doi: 10.1007/bf00260690

Cloutier, J. N., Azarniouch, M. K., & Callender, D. (1994). Electrolysis of weak black liquor Part III: Continuous operation test and system design considerations. *Pulp & Paper Canada, 95*(5), T210-T214. doi: 10.1007/bf00260690

Cloutier, J. N., Azarniouch, M. K., & Callender, D. (1995). Electrolysis of weak black liquor Part II: Effect of process parameters on the energy efficiency of the electrolytic cell. *Journal of Applied Electrochemistry, 25*(5), 472-478. doi: 10.1007/bf00260690

Cloutier, J. N., & Beaudoin, L. (2014, 8-13 June, 2014). *New source of caustic for Kraft mills from the electrolysis of sodium sulphate - preliminary economics.* Paper presented at International Chemical Recovery Conference, Tampere, Finland.

Dahlin, P. (2015). *Na/S balances at Skoghall mill 2015: Balances after reconstruction of the fiber line.* (Master, Karlstad University).

Danielson, B., & Simonson, R. (1998). Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood. *Journal of Adhesion Science and Technology, 12*(9), 923-939. doi: 10.1163/156856198X00542

Davy, M., Uloth, V., & Cloutier, J. (1998). Economic evaluation of black liquor treatment processes for incremental kraft pulp production: A comparison of two processes at Paprican. *Pulp & Paper Canada, 99*(2), 35-39.

Diffo, C. (2013). Lignin Biorefinery Technology and Markets. Retrieved from http://www.reseauvco.ca/fileadmin/vco/documents/Webinairs/PowerPoint_Presentation.pdf

Dong, D., Fricke, A. L., Moudgil, B., & Johnson, H. (1996). Electrokinetic study of kraft lignin. *Tappi journal, 79*(7), 191-197.

Duarte, G., Ramarao, B., Amidon, T., & Ferreira, P. (2011). Effect of hot water extraction on hardwood kraft pulp fibers (Acer saccharum, sugar maple). *Industrial and Engineering Chemistry Research, 50*(17), 9949-9959. doi: 10.1021/ie200639u

Evstigneev, E. (2011). Factors affecting lignin solubility. *Russian Journal of Applied Chemistry, 84*(6), 1040-1045. doi: 10.1134/S1070427211060243

Farag, S., & Chaouki, J. (2015). Economics evaluation for on-site pyrolysis of kraft lignin to value-added chemicals. *Bioresource Technology, 175* 254-261. Retrieved from http://www.sciencedirect.com/science/article/pii/S0960852414015284

Frank, E., Steudle, L., Ingildeev, D., Sporl, J., & Buchmeiser, M. (2014). Carbon fibers: Precursor systems, processing, structure, and properties. *Angewandte Chemie - International Edition, 53*(21), 5262-5298. doi: 10.1002/anie.201306129

Fredrik, O., & Theliander, H. (2007). Filtration properties of lignin precipitated from black liquor. *Tappi Journal, 6*(7), 3-9.

Gellerstedt, G., & Henriksson, G. (2008). Chapter 9 - Lignins: Major Sources, Structure and Properties. In M. N. B. Gandini (Ed.) *Monomers, Polymers and Composites from Renewable Resources* (pp. 201-224). Amsterdam: Elsevier.

Gindl-Altmutter, W., Fürst, C., Mahendran, A., Obersriebnig, M., Emsenhuber, G., Kluge, M., . . . Liebner, F. (2015). Electrically conductive kraft lignin-based carbon filler for polymers. *Carbon, 89*(0), 161-168.

Gooding, C. (2012). *Comparison of the LignoBoost™ and SLRP™ Lignin Recovery Processes.* Paper presented at TAPPI International Bioenergy & Bioproducts Conference, Savannah, United States.

Guan, J., Waite, T., & Amal, R. (1998). Rapid Structure Characterization of Bacterial Aggregates. *Environmental Science & Technology, 32*(23), 3735-3742. doi: 10.1021/es980387u

Hamaguchi, M., & Vakkilainen, E. (2010, 12-15 October). *The influence of lignin removal on the energy balance of future pulp mills.* Paper presented at XXI TECNICELPA Conference and Exhibition, Lisbon, Portugal.

He, Z., He, L., Yang, J., & Lu, Q. (2013). Removal and recovery of Au(III) from aqueous solution using a low-cost lignin-based biosorbent. *Industrial and Engineering Chemistry Research, 52*(11), 4103-4108. doi: 10.1021/ie303410g

Helander, M., Sevastyanova, O., Chowdhury, S., Lange, H., Zhang, L., Wedin, H., . . . Lindström, M. (2013). *Evaluation of Physico-Chemical Properties and Prediction of Spinning Parameters for High-Quality Lignins Produced by Ultra-Filtration of Industrial Kraft Pulping Liquor.* Paper presented at 17th International Symposium on Wood, Fiber and Pulping Chemistry (SWFPC), Vancouver, British Columbia, Canada.

Helmerius, J., von Walter, J., Rova, U., Berglund, K., & Hodge, D. (2010). Impact of hemicellulose pre-extraction for bioconversion on birch Kraft pulp properties. *Bioresource Technology, 101*(15), 5996-6005. doi: 10.1016/j.biortech.2010.03.029

Hidalgo-Millán, A., Zenit, R., Palacios, C., Yatomi, R., Horiguchi, H., Tanguy, P. A., & Ascanio, G. (2012). On the hydrodynamics characterization of the straight Maxblend® impeller with Newtonian fluids. *Chemical Engineering Research and Design, 90*(9), 1117-1128.

Holmqvist, A., Wallberg, O., & Jonsson, A. (2005). Ultrafiltration of kraft black liquor from two Swedish pulp mills. *Chemical Engineering Research and Design, 83*(8 A), 994-999. doi: 10.1205/cherd.04204

Howell, J., & Thring, R. (2000). Hardwood lignin recovery using generator waste acid. Statistical analysis and simulation. *Industrial & engineering chemistry research, 39*(7), 2534-2540.

Ibaseta, N., & Biscans, B. (2010). Fractal dimension of fumed silica: Comparison of light scattering and electron microscope methods. *Powder Technology, 203*(2), 206-210.

Jarvis, P., Jefferson, B., Gregory, J., & Parsons, S. A. (2005). A review of floc strength and breakage. *Water Research, 39*(14), 3121-3137.

Jarvis, P., Jefferson, B., & Parsons, S. (2005). Breakage, Regrowth, and Fractal Nature of Natural Organic Matter Flocs. *Environmental Science & Technology, 39*(7), 2307-2314. doi: 10.1021/es048854x

Jin, W., Tolba, R., Wen, J., Li, K., & Chen, A. (2013). Efficient extraction of lignin from black liquor via a novel membrane-assisted electrochemical approach. *Electrochimica Acta, 107*(0), 611-618.

Joensson, A., Nordin, A., & Wallberg, O. (2008). Concentration and purification of lignin in hardwood kraft pulping liquor by ultrafiltration and nanofiltration. *Chemical Engineering Research and Design, 86*(11), 1271-1280.

Joensson, A., & Wallberg, O. (2009). Cost estimates of kraft lignin recovery by ultrafiltration. *Desalination, 237*(1-3), 254-267.

Kamal, W. (2011). *Analysis of Energy Systems and Performance Improvement of a Kraft Pulping Mill.* (École Polytechnique de Montréal).

Kamm, B., Gruber, P., & Kamm, M. (2006). *Biorefineries - Industrial Processes and Products - Volume 2* (Vol. 1). Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.

Kannangara, M., Marinova, M., Fradette, L., & Paris, J. (2012). *Lignin recovery by acid precipitation in a kraft mill: An energy perspective.* Paper presented, 740 rue Notre-Dame ouest, Bureau 810, Montreal, Quebec, H3C 3X6, Canada (Vol. 2, pp. 28-32).

Keshthkar, J. (2013). *Steam and water combined analysis, integration and efficiency enhancement in Kraft pulping mills.* (Ecole Polytechnique Montreal).

Kim, H., Hill, M. K., & Fricke, A. L. (1987). Preparation of kraft lignin from black liquor. *Tappi journal (USA).*

Kouisni, L., Fang, Y., Paleologou, M., Ahvazi, B., Hawari, J., Zhang, Y., & Wang, X. M. (2011). Kraft lignin recovery and its use in the preparation of lignin-based formaldehyde resins for plywood. *Cellulose Chemistry and Technology, 45*(7-8), 515-520.

Kouisni, L., Holt-Hindle, P., Maki, K., & Paleologou, M. (2012). The lignoforce system: A new process for the production of high-quality lignin from black liquor. *J-FOR: The Journal of Science and Technology for Forest Products and Processes, 2* 6-10.

Kresta, S. (1998). Turbulence in stirred tanks: Anisotropic, approximate, and applied. *The Canadian Journal of Chemical Engineering, 76*(3), 563-576. doi: 10.1002/cjce.5450760329

Laaksometsä, C., Axelsson, E., Berntsson, T., & Lundström, A. (2009). Energy savings combined with lignin extraction for production increase: case study at a eucalyptus mill in Portugal. *Clean Technologies and Environmental Policy, 11*(1), 77-82.

Lake, M., & Blackburn, J. (2014). SLRP(TM)-An Innovative lignin-recovery technology. *Cellulose Chemistry and Technology, 48*(9-10), 799-804.

Lee, R., Stack, K., Richardson, D., Lewis, T., & Garnier, G. (2012). Effect of shear, temperature and pH on the dynamics of salt induced coagulation of wood resin colloids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 396*(0), 106-114.

Lin, M. Y., Lindsay, H. M., Weitz, D. A., Ball, R. C., Klein, R., & Meakin, P. (1989). Universality in colloid aggregation. *Nature, 339*(6223), 360-362.

Lockhart, J. (2008). *Precipitator dust purification for Kraft mill chloride reduction.* Paper presented at Black liquor recvoery boiler advisory committe Conference, Atlanta, United States.

Loutfi, H., Blackwell, B., & Uloth, V. (1991). Lignin recovery from kraft black liquor: preliminary process design. *Tappi Journal, 74*(1), 203-210.

Lundberg, V., Axelsson, E., Mahmoudkhani, M., & Berntsson, T. (2012). Process integration of near-neutral hemicellulose extraction in a Scandinavian kraft pulp mill – Consequences for the steam and Na/S balances. *Applied Thermal Engineering, 43*(0), 42-50.

Luo, J., Genco, J., Cole, B., & Fort, R. (2011). Lignin recovered from the near-neutral hemicellulose extraction process as a precursor for carbon fiber. *BioResources, 6*(4), 4566-4593.

Maciel, A. V., Job, A. E., Mussel, W. N., & Pasa, V. M. D. (2012). Pyrolysis and auto-gasification of black liquor in presence of ZnO: An integrated process for Zn/ZnO nanostructure production and bioenergy generation. *Biomass and Bioenergy, 46*(0), 538-545.

Mao, H., Genco, J., Heiningen, A., Zou, H., Luo, J., & Pendse, H. (2008). *Technical economic evualation of a northern hardwood biorefinery using the "near-neutral" hemicellulose pre-extraction process.* Paper presented at Engineering, Pulping and Environmental Conference 2008, TAPPI, August 24, 2008 - August 27, 2008, Portland, OR, United states (Vol. 3, pp. 2088-2139).

Mao, H., Genco, J. M., Yoon, S. H., van Heiningen, A., & Pendse, H. (2008). *Technical economic evaluation of a hardwood biorefinery using the "near-neutral" hemicellulose pre-extraction process.* Paper presented, 25650 North Lewis Way, Stevenson Ranch, CA 9138-1439, United States (Vol. 2, pp. 177-185). doi: 10.1166/jbmb.2008.309

Marinova, M., Mateos-Espejel, E., Jemaa, N., & Paris, J. (2009). Addressing the increased energy demand of a Kraft mill biorefinery: The hemicellulose extraction case. *Chemical Engineering Research and Design, 87*(9), 1269-1275.

Mateos-Espejel, E., Radiotis, T., & Jemaa, N. (2013). Implications of converting a kraft pulp mill to a dissolving pulp operation with a hemicellulose extraction stage. *Tappi Journal, 12*(2), 29-38.

Moosavifar, A., Sedin, M., & Theliander, H. (2009). Changes in viscosity and boiling point elevation of black liquor when a fraction of lignin is removed - Consequences in the evaporation stage. *Appita Journal, 62*(5), 383-390.

Moosavifar, A., Sedin, P., & Theliander, H. (2006). Viscosity and boiling point elevation of black liquor: Consequences when lignin is extracted from the black liquor. *Nordic Pulp and Paper Research Journal, 21*(2), 180-187.

Natural-Resources-Canada. (2006). *Benchmarking energy use in Canadian pulp and paper mills*. Ottawa: Natural Resources Canada.

Natural-Resources-Canada. (2015). Canadian Forest Industry: Statistical data. Retrieved from http://cfs.nrcan.gc.ca/statsprofile

NORAM-Engineering. (2015). Generator Acid Purification (GAP™) - Reducing Chemical Make-up Costs. Retrieved from http://www.noram-eng.com/docs/groups/pulp-paper/Generator%20Acid%20Purification%20%28GAP%29.pdf

Norgren, M., & Edlund, H. (2014). Lignin: Recent advances and emerging applications. *Current Opinion in Colloid & Interface Science, 19*(5), 409-416.

Norgren, M., Edlund, H., & Wågberg, L. (2002). Aggregation of lignin derivatives under alkaline conditions. Kinetics and aggregate structure. *Langmuir, 18*(7), 2859-2865.

Norgren, M., Edlund, H., Wågberg, L., Lindström, B., & Annergren, G. (2001). Aggregation of kraft lignin derivatives under conditions relevant to the process, part I: phase behaviour. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 194*(1–3), 85-96.

Norgren, M., & Lindstrom, B. (2000a). Dissociation of phenolic groups in kraft lignin at elevated temperatures. *Holzforschung, 54*(5), 519-527. doi: 10.1515/HF.2000.088

Norgren, M., & Lindstrom, B. (2000b). Physico-chemical characterization of a fractionated kraft lignin. *Holzforschung, 54*(5), 528-534. doi: 10.1515/HF.2000.089

Ohman, F., & Theliander, H. (2006). Washing lignin precipitated from kraft black liquor. *Paperi ja Puu, 88*(5), 287-292.

Ohman, F., & Theliander, H. (2007). Fitration properties of lignin precipitated from black liquor. *Tappi Journal, 6*(7), 3-9.

Ohman, F., Wallmo, H., & Theliander, H. (2007a). A novel method for washing lignin precipitated from kraft black liquor - Laboratory trials. *Nordic Pulp and Paper Research Journal, 22*(1), 9-16.

Ohman, F., Wallmo, H., & Theliander, H. (2007b). Precipitation and filtration of lignin from black liquor of different origin. *Nordic Pulp and Paper Research Journal, 22*(2), 188-193.

Olsson, M. R., Axelsson, E., & Berntsson, T. (2006). Exporting lignin or power from heat-integrated kraft pulp mills: A techno-economic comparison using model mills. *Nordic Pulp and Paper Research Journal*.

Paul, E. L., Atiemo-Obeng, V., & Kresta, S. (2003). *Handbook of Industrial Mixing: Science and Practice*: Wiley.

Perin-Levasseur, Z., Benali, M., & Paris, J. (2010). *Lignin Extraction Technology Integrated in a Kraft Pulp Mill : Implementation Strategy.* Paper presented at 3rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Lausanne, Switzerland.

Perin-Levasseur, Z., Savulescu, L., & Benali, M. (2011). Lignin production path assessment: Energy, water, and chemical integration perspective. *J-FOR, 1*(3), 25-30.

Preto, F., Zhang, X., & Wang, J. (2008). Gasification behavior of carbon residue in bed solids of black liquor gasifier. *Experimental Thermal and Fluid Science, 32*(7), 1421-1428.

Radiotis, T., Sullivan, J., MacLeod, M., Syed, S., & O'Hagan, T. (2007). *Improved methods for measuring residual effective alkali in kraft black liquors part 2: Comparison of titration methods.* Paper presented at Engineering, Pulping and Environmental Conference 2007,

TAPPI, October 21, 2007 - October 24, 2007, Jacksonville, FL, United states (Vol. 4, pp. 2388-2436).

Ragnar, M., Lindgren, C., & Nilvebrant, N. (2000). pKa-values of guaiacyl and syringyl phenols related to lignin. *Journal of wood chemistry and technology, 20*(3), 277-305.

Rofouieeraghi, P. (2012). *Biomass gasification integrated into a reference Canadian Kraft mill.* (École Polytechnique de Montréal).

Rose, M. (2013). Catalysis for the Conversion of Biomass and its Derivatives. (Max Planck Research Library for the History and Development of Knowledge.) Edited by Malte Behrens and Abhaya K. Datye. *Angewandte Chemie International Edition, 52*(37), 9613-9613. doi: 10.1002/anie.201305619

Roy, R. (2001). *Design of experiments using the Taguchi approach*: Wiley-Interscience.

Rubin, E., Chen, C., & Rao, A. (2007). Cost and performance of fossil fuel power plants with CO2 capture and storage. *Energy Policy, 35*(9), 4444-4454.

Saake, B., & Lehnen, R. (2000). Lignin. In *Ullmann's Encyclopedia of Industrial Chemistry*: Wiley-VCH Verlag GmbH & Co. KGaA.

Saito, T., Perkins, J., Jackson, D., Trammel, N., Hunt, M., & Naskar, A. (2013). Development of lignin-based polyurethane thermoplastics. *RSC Advances, 3*(44), 21832-21840. doi: 10.1039/c3ra44794d

Saturnino, D. (2012). *Modeling of Kraft Mill Chemical Balance.* (University of Toronto).

Savulescu, L., Kim, J., & Smith, R. (2005). Studies on simultaneous energy and water minimisation—Part I: Systems with no water re-use. *Chemical engineering science, 60*(12), 3279-3290. doi: 10.1016/j.ces.2004.12.037

Silva, E., Zabkova, M., Araújo, J., Cateto, C., Barreiro, M., Belgacem, M., & Rodrigues, A. (2009). An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chemical Engineering Research and Design, 87*(9), 1276-1292.

Smolarski, N. (2012). *High-Value Opportunities for Lignin: Unlocking its Potential*. Frost & Sullivan.

Smook, G. (1992a). Chemical recovery. In *Handbook for pulp and paper technologists* (Third Edition ed.). Vancouver: Angus Wilde Publications.

Smook, G. (1992b). *Handbook for pulp and paper technologists* (Third Edition ed.). Vancouver: Angus Wilde Publications.

Smook, G. (1992c). Kraft pulping. In *Handbook for pulp and paper technologists* (Third Edition ed.). Vancouver: Angus Wilde Publications.

Smook, G. (1992d). Overview of pulping methodology. In *Handbook for pulp and paper technologists* (Third Edition ed.). Vancouver: Angus Wilde Publications.

Snowdon, M., Mohanty, A., & Misra, M. (2014). A Study of Carbonized Lignin as an Alternative to Carbon Black. *ACS Sustainable Chemistry & Engineering, 2*(5), 1257-1263. doi: 10.1021/sc500086v

Spicer, P., Keller, W., & Pratsinis, S. (1996). The Effect of Impeller Type on Floc Size and Structure during Shear-Induced Flocculation. *Journal of Colloid and Interface Science, 184*(1), 112-122.

Spicer, P., Pratsinis, S., Raper, J., Amal, R., Bushell, G., & Meesters, G. (1998). Effect of shear schedule on particle size, density, and structure during flocculation in stirred tanks. *Powder Technology, 97*(1), 26-34.

Sri, R., Yasar, L., & Douglas, L. (1989). Association of Kraft Lignin in Aqueous Solution. In *Lignin* (Vol. 397, pp. 144-154): American Chemical Society.

St. Pierre, J., Duran, L., & van Heiningen, A. (2015). Fast pyrolysis of muconic acid and formic acid salt mixtures. *Journal of Analytical and Applied Pyrolysis, 113*(0), 591-598.

Statistics-Canada. (2013). The Great U.S. Recession and Canadian Forest Products. Retrieved from http://www.statcan.gc.ca/pub/11-626-x/11-626-x2013028-eng.htm

Stevens, F., Grace, T., & Leopold, B. (1989). *Alkaline pulping: Pulp and paper manufacture*: Technical Section, Canadian Pulp and Paper Association.

Stewart, D. (2008). Lignin as a base material for materials applications: Chemistry, application and economics. *Industrial Crops and Products, 27*(2), 202-207.

Theliander, H. (2010). *The lignoboost process: Solubility of lignin.* Paper presented at International Chemical Recovery Conference, Williamsburg, VA, United states (Vol. 2, pp. 33-42).

Theliander, H., Ohman, F., Axegard, P., & Tomani, P. (2005). *Novel process for separation of lignin from kraft black liquor.* Paper presented, Cincinnati, OH, United states (pp. 9535-9535).

Tomani, P. (2010). The lignoboost process. *Cellulose Chemistry and Technology, 44*(1-3), 53-58.

Tomani, P. (2013). Update on LignoBoost lignin and Applications. Retrieved from http://www.spci.se/shared/files/Per_Tomani_SPCI_2013_UT.pdf

Tomani, P., Axegard, P., Berglin, N., Lovell, A., & Nordgren, D. (2011, May 9-12, 2011). *Integration of lignin removal into kraft pulp mill and use of lignin as biofuel.* Paper presented at 5th International colloquium on Eucalyptus Pulp, Porte Seguro, Bahia, Brazil.

Tomlinson, G., & Tomlinson, G. (1948). *Canada Patent No. Canada Patent No. 448.476*.

Tran, H. (2008, 7-10 Januray, 2008). *The Kraft Recovery Process.* Paper presented at Tappi Kraft Recovey Short Course, St. Petersburg, Florida, United States.

Uloth, V., & Wearing, J. (1989a). Kraft Lignin Recovery: Acid Precipitation Versus Ultrafiltration, Part II: Technology and Economics. *Pulp and Paper Canada, 90*(10), 357-360.

Uloth, V., & Wearing, J. (1989b). Kraft lignin recovery: acid precipitation versus ultrafiltration. I: Laboratory test results. *Pulp & Paper Canada, 90*(9), 67-71.

Vakkilainen, E. (2000). Estimation of elemental composition from proximate analysis of black liquor. *Paperi ja Puu/Paper and Timber, 82*(7), 450-454.

Vakkilainen, E., & Valimaki, E. (2009). *Effect of lignin separation to black liquor and recovery boiler operation.* Paper presented, Memphis, TN, United states (Vol. 3, pp. 1515-1556).

Valimaki, E., Niemi, P., & Haaga, K. (2010). *A case study on the effects of lignin recovery on recovery boiler operation.* Paper presented at TAPPI/PAPTAC International Chemical Recovery Conference, Williamsburg, VA, United states (Vol. 2, pp. 148-159).

Van Heiningen, A. (2006). Converting a kraft pulp mill into an integrated forest biorefinery. *Pulp and Paper Canada, 107*(6), 38-43.

VanCaeseele, S. (2014). LIGNOFORCE Lignin Recovery from the Kraft Pulping Process. Retrieved from http://www.canbio.ca/upload/documents/van-12-presentations/van-caeseele-shane.pdf

Wallberg, O., & Joensson, A. (2006). Separation of lignin in kraft cooking liquor from a continuous digester by ultrafiltration at temperatures above 100Â°C. *Desalination, 195*(1-3), 187-200.

Wallberg, O., Jonsson, A., & Wimmerstedt, R. (2003). Fractionation and concentration of kraft black liquor lignin with ultrafiltration. *Desalination, 154*(2), 187-199. doi: 10.1016/S0011-9164(03)80019-X

Wallmo, H., Richards, T., & Theliander, H. (2007). Lignin precipitation from kraft black liquors: kinetics and carbon dioxide absorption. *Paperi ja puu, 89*(7-8), 436-442.

Wallmo, H., Richards, T., & Theliander, H. (2009). An investigation of process parameters during lignin precipitation from kraft black liquors: A step towards an optimised precipitation operation. *Nordic Pulp and Paper Research Journal, 24*(2), 158-164.

Wallmo, H., Theliander, H., Jonsson, A. S., Wallberg, O., & Lindgren, K. (2009). The influence of hemicelluloses during the precipitation of lignin in kraft black liquor. *Nordic Pulp and Paper Research Journal, 24*(2), 165-171.

Wienhaus, O., Bernaczyk, H., & Pecina, H. (1990). Research into the precipitation of lignin from sulfate black liquors, particularly by carbon dioxide. *Das Papier, 44*(11), 563-569.

Wilson, G. (1971). Capital investment for chemical plant. *British Chemical Engineering and Process Technology, 16*(10), 931-&.

Wising, U., Algehed, J., Berntsson, T., & Delin, L. (2006). Consequences of lignin precipitation in the pulp and paper industry.

Wooley, R., & Putsche, V. (1996). *Development of an ASPEN PLUS Physical Property Database for Biofuels Components*. Golden,CO,: National Renewable Energy Laboratory.

Xu, Q., Gao, Y., Qin, M., Wu, K., Fu, Y., & Zhao, J. (2013). Nanocrystalline cellulose from aspen kraft pulp and its application in deinked pulp. *International Journal of Biological Macromolecules, 60*(0), 241-247.

Xu, W., & Gao, B. (2012). Effect of shear conditions on floc properties and membrane fouling in coagulation/ultrafiltration hybrid process—The significance of Alb species. *Journal of Membrane Science, 415–416*(0), 153-160.

Yang, L., & Ragauskas, A. (2012). Kraft Lignin-based Rigid Polyurethane Foam. *Journal of Wood Chemistry and Technology, 32*(3), 210-224. doi: 10.1080/02773813.2011.652795

Zhao, L., & Luo, X. (2010). *Fractional isolation and purification of lignin from Pulping Black Liquor*. Paper presented, Piscataway, NJ, USA (pp. 4 pp.). doi: 10.1109/icbbe.2010.5517631

Zhou, M., Qiu, X., Yang, D., Lou, H., & Ouyang, X. (2007). High-performance dispersant of coal–water slurry synthesized from wheat straw alkali lignin. *Fuel Processing Technology, 88*(4), 375-382.

Zhu, W. (2013). *Equilibrium of Lignin Precipitation.* (Chalmers University of Technology, Gothenburg, Sweden).

Zhu, W., & Theliander, H. (2015). Precipitation of lignin from softwood black liquor: An investigation of the equilibrium and molecular properties of lignin. *BioResources, 10*(1), 1696-1714.

Zhu, W., Westman, G., & Theliander, H. (2014). Investigation and characterization of lignin precipitation in the lignoboost process. *Journal of Wood Chemistry and Technology, 34*(2), 77-97. doi: 10.1080/02773813.2013.838267