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TECHNO-ECONOMIC ANALYSIS AND SUPPLY CHAIN DESIGN FOR A FOREST BIOREFINERY TO PRODUCE VALUE-ADDED BIO-BASED PRODUCTS FROM LIGNIN

by

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A doctoral thesis submitted
in partial fulfillment of the requirements for the
degree of Doctor of Philosophy (Forest Sciences)

Faculty of Natural Resources Management
Lakehead University
March 2019

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ABSTRACT

Techno-economic Analysis and Supply Chain Design for a Forest Biorefinery to Produce Value-added Bio-based Products from Lignin

Dessbesell, L. 2019. Techno-economic Analysis and Supply Chain Design for a Forest Biorefinery to Produce Value-added Bio-based Products from Lignin

Keywords: biorefinery, techno-economic analysis, kraft lignin, depolymerized kraft lignin, biophenol, biopolyol, plant capacity, monte carlo simulation, supply chain, cost minimization, biomass, black liquor surplus, value-added bio-based products

By far, several commercial projects for production of lignin-based chemicals started operations around the world. For instance, the LignoBoost process was installed by Domtar in 2013 in the United States, and in 2015 by Stora Enso in Finland. Lather, in 2016, the LignoForce system came into operation at West Fraser in Canada. These commercial initiatives show that lignin has proven its potential as an alternative to petroleum, to reduce emissions and generate a new stream of revenue in the forestry sector. Lignin deems to be a suitable feedstock for energy generation or value-added bioproducts as substitutes to petroleum-based products. However, lignin's characteristics (specifically large molecular weights and low reactivity) limit its direct use as chemicals to substitute petroleum-derived chemicals.

More than 30 years of research towards lignin modification have shown that depolymerization is one of the promising routes to achieve its high-value applications in chemicals. A novel depolymerization process using low-pressure and low-temperature has been developed by Dr. Xu's group – from the laboratory-scale production of depolymerized lignin (DL) to value-added applications of DL for bio-based materials (patent pending). In this process, kraft lignin (KL) is depolymerized using sodium hydroxide as catalyst and ethylene glycol as solvent. The depolymerized kraft lignin (DKL) products have suitable characteristics, such as high hydroxyl a moderately low weight-average molecular weight, for synthesis of biopolymers. The DKL can substitute up to 75% phenol in the manufacture of phenol-formaldehyde resins (PF) and up to 50% in the formulation of polyurethane (PU) foams. The next logical step is to assess the feasibility of this technology. Therefore, the general purpose of this research is to develop a techno-economic analysis and a supply chain (SC) design to identify the most promising technical and economic aspects of commercial production and long-term feasibility of bio-based value-added chemicals and materials from KL.

To this end, firstly the process was scaled up to a pilot scale (~ 4,000 t/y of DKL), and its use as bio-polyols or bio-phenols were assessed in terms of recovery, capital investment, selling price, and feedstock cost. Our initial findings show that production of bio-polyols from KL is slightly more expensive than bio-phenol; however, polyols have a higher market price that compensates the extra cost, resulting in the DKL-to-polyols strategy being initially more attractive than that of DKL-to-phenol. Since the capital expenses tend to decrease as plant size increases, scaling up is crucial to the success of production of bio-based chemicals from lignin. Therefore, our second task focused on the capacity design of a KL biorefinery for the production of bio-phenols. Canada alone has a

KL surplus of ~1.06 million tonnes per year generated by the kraft pulp mills. In this context, several DKL production capacities were designed and its economic feasibility evaluated. The total fixed manufacturing costs varied from ~63 to 154 US$/t for 120,000 to 10,000 t/y KL processing capacities. All scenarios are feasible; however, small capacity results in more extended payback periods (PBP), and KL capacities above 40,000 t/y lead to ~3-year PBPs and high NPVs (above US$35M). Uncertainties in price, feedstock costs, KL supply, capital costs, and demand have a significant impact on the implementation and successful lunching of the biorefining technology for bioproducts. In our first two tasks, the uncertainties in bioproducts prices, feedstock costs and capital costs were addressed through probability analysis using historical data. Nevertheless, competitive advantages are tied to well-designed supply chain (SC) strategies.

Hence, the third task examines a SC design for KL-based phenols and polyols in North America. A SC cost minimization model was applied to several demand scenarios (20% to 50% demand) for a case study for the Canadian kraft pulp industry. At 30% polyols and phenols demand the model indicates eight biorefinery locations resulting in a DKL minimum selling price varying from 1,602 to 1,137 US$/t, small to larger capacities, respectively. This variation is due to fixed costs being higher for smaller plant sizes. The variable cost reduction from transport cost minimization did not compensate installing small DKL plants in the case study. To the best of our knowledge, this is the first in-depth study on the analysis for DKL-based bioproducts production. As future work, introducing capacity flexibility into the model and looking into the effect of mill-specific information and market requirements on the SC design should be investigated in order to make lignin-derived bioproducts a part of the forest industry value chain.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

LIST OF TABLES

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

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DEDICATION

This work is dedicated to my family!
Odete, Jair, Cristiane, Alexandre e Fábris

CHAPTER 1 – General introduction and thesis objectives

1.1 Introduction

The petrochemical industry relies on petroleum that is refined to produce fuels and platform chemicals - precursors of a variety of products, such as, solvents, plastics and paint. The worldwide concerns about crude oil dependence, depletion and the associated environmental emissions have intensified the efforts to discover renewable alternatives to petroleum-based products [1].

One of the efforts is to use lignocellulosic biomass, the most abundant renewable resource on the earth, to replace or substitute petroleum-based chemicals, fuels and materials. Bio-chemicals, also called green chemicals, can be called replacements – with identical chemical structure as the product being replaced; or, substitutes – with different chemical structure and similar or improved functionality [2].

Lignocellulosic resources are primarily constituted of cellulose (40-50%), hemicellulose (25-30%), and lignin (20-30%) [3]. "Lignin is a complex three-dimensional biopolymer of aromatic alcohols" [4]. The primary source of technical lignin is the pulp and paper industry [5]. The global production of lignin is over 70 million t/year, of which 95% is burned in recovery boilers for steam and power generation. Only about 5% of lignin (mainly in the form of lignosulphonate) is utilized for the production of value-added bio-based products, such as dispersants, adhesives and surfactants [6].

Modern kraft pulp mills burn "black liquor" (stream containing kraft lignin (KL)) to recover the pulping chemicals while generating energy. The recovery boiler's capacity limitation allows the removal of a portion of the KL, which could be used in the production of value-added chemicals [7]. Up to 25% of KL could be removed, depending on the black liquor heating value, without significant impact on the recovery boiler operation. For instance, in the scenario of a typical kraft mill (assuming ~10% KL removal for a 1,000 t/day kraft pulp mill) it represents up to 50 t/day of KL, which is associated with up to 50 t/day of added pulp production in the mill [8].

Research on bio-based chemicals and materials from lignin has been successfully achieved in the laboratory and pilot scale, but it is still struggling to gain commercial scale importance and interest of market users [1]. For instance, in 2007, an extensive study by the National Renewable Energy Laboratory (NREL) and the Pacific Northwest National Laboratory (PNNL) [9] reported potentially feasible products from lignin, such as carbon fibre, modified polymers, resins and adhesives as a potential investment in a medium-term future. Moreover, bio-based chemicals are expected to grow significantly and increase their share in overall chemical production to an estimated 9% by 2020 [10], while some of this growth could be attributed to lignin-based chemicals.

Some studies can be found on the process simulation, technical design, economic and environmental assessment of lignocellulosic biorefineries. Examples of economic and technical analysis studies include: fermentation-based sugar conversion biorefinery [11]; bio-oil gasification and fast pyrolysis biorefinery [12]; various biorefinery concepts [13]; and, organosolv biorefinery [14-16]. Examples of technical, economic and environmental analysis studies include a high-octane gasoline biorefinery [17] and a beech wood-based biorefinery [18]. Such studies demonstrate the great variability of feedstock and products of prospective biorefineries; however, the majority of the studies by far focus on bioenergy and biofuels.

A potentially high-volume and high-value application of lignin is its use as substitute for phenol in phenol-formaldehyde (PF) resins. Because phenol is made from petroleum-based feedstock (specifically from benzene via the cumene process), whose price has increased substantially over the last few years [8]. In addition to bio-phenols, bio-based polyols are expected to increase their participation in the global polyols market, as companies are investing in research and development to produce bio-polyols at a commercial scale [19]. Polyurethane (PU) prepared using polyols is one of the most widely consumed polymer products globally. Polyol products comprise polyether polyols and polyester polyols. Commercially available PU products include; for example, flexible foam, rigid foam, coatings, adhesives and sealants [20].

Experts in the field believe that lignin's time has arrived; they stress that several pulp mills around the world are investing in lignin extraction, there is a large scientific body of knowledge on lignin valorization, and that oil prices are unlikely to reach extreme low values [21]. All these factors are helping the recent pull on lignin commercial production. However, the investment is still small and not enough to decrease the gap between public and private investment (as illustrated in Figure 1.1).

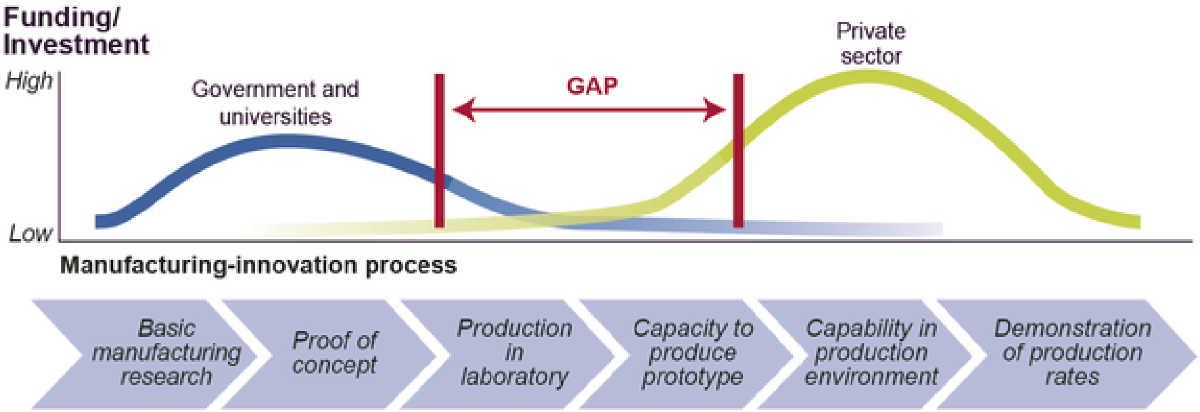

Figure 1.1. Funding and investment gap in the manufacturing innovation process [22].

The knowledge gathered at the laboratory level can provide the basis for pilot scale estimates. Pilot capital and operating costs estimates for biorefineries tend to be lower than real costs [23]. Therefore, sensitivity analysis is necessary to understand the risks and show investors representative forecasts. It is also well accepted that the capital and operating costs of a process substantially decrease when increasing its scale to commercial scale [23,24]. Although being more expensive, the pilot scale is necessary to provide volumes that can be tested in the customers' or partners' production line, and also to further optimize the process previously developed in controlled laboratory conditions. More than 15 small-scale lignin production pilots are operating in North America, mostly with patented technologies originated from many years of laboratory research; still, they struggle to move towards commercial production.

Lignosulfonates, for instance, have a proven developed range of applications that provide a stable commercial production level; this has not yet been developed for KL [25]. This is partially because of limitations of KL use without modification after recovery from black liquor, and lack of studies on the techno-economics, scaling up and supply chain of KL-based chemicals. Technology feasibility investigation at the early-stage can provide crucial insights moving from laboratory to pilot, and from pilot to commercial scales.

1.2 Research objectives

A novel depolymerization process using low-pressure and low-temperature has been developed by Dr. Xu's group – from the laboratory-scale production of depolymerized lignin (DL) to value-added applications of DL for bio-based materials (patent pending). In this process, KL is depolymerized using sodium hydroxide as catalyst and ethylene glycol as solvent. The depolymerized kraft lignin (DKL) products have suitable characteristics, such as high hydroxyl a moderately low weight-average molecular weight, for synthesis biopolymers. The DKL can substitute up to 75% phenol in the manufacture of phenol-formaldehyde resins (PF) and up to 50% in the formulation of polyurethane (PU) foams.

The general purpose of this thesis work was to develop techno-economic analysis and supply chain (SC) design methods for a forest biorefinery based on the novel low-temperature/pressure depolymerization process developed by Dr. Xu's group in order to achieve economic and commercial production of bio-based phenols/polyols from KL and its long-term feasibility. The specific objectives of this Ph.D. project were to:

1. Review the literature on potential products and markets for bio-based value-added materials and chemicals from lignin, investigate forest biomass SC literature revising methods applied, and determine the scope of the studies.
2. Conduct a technical-economic analysis of the forest biorefinery to estimate the overall costs of bio-polyols produced from KL.
    - Develop a conceptual process design to estimate fixed and variable costs for production of bio-polyols from KL;
    - Evaluate the feasibility of the production of bio-polyols from KL, compared to petroleum-based polyols.
    - Perform a sensitivity and risk analysis to identify the most sensitive parameters to the feasibility.
3. Conduct a technical-economic analysis to estimate the overall costs for production of bio-phenols from KL by the forest biorefinery.
    - Develop a conceptual process design to estimate fixed and variable costs for production of bio-phenols from KL;

- Evaluate the feasibility of the production of bio-phenols from KL, compared to petroleum-based phenols.
- Perform a sensitive and risk analysis to identify the most sensitive parameters to the feasibility.

4. Develop an SC network design for a forest biorefinery to produce bio-based PF/PU polymers from KL.

- Review the literature and gather market information on phenol and polyols.
- Conduct a case study considering the KL supply availability in the Canadian kraft pulp industry.
- Identify the SC configuration including location, markets to be supplied, capacity and KL supply that minimizes the production and transportation costs of lignin-based phenols and polyols.
- Perform a scenario analysis to investigate the effects of changes in demand to the overall minimum selling price of lignin-based chemicals for PF/PU polymers.

1.3 Thesis outline

This is a manuscript-based thesis, including five peer-reviewed papers published or to-be-published. In each chapter the format of tables, figures and references and English language style, might differ slightly as per varying publication requirements for the journals. Efforts have been made to integrate the chapters into one coherent thesis with caution not to change the content of each paper.

1. Chapter 2 – Dessbesell, L., Leitch, M., Pulkki, R., Xu, C. (Charles). 2019. Lignin supply, market and applications overview, submitted to Renewable and Sustainable Energy Review for publication.

2. Chapter 3 – Dessbesell, L., Yuan, Z., Hamilton, S., Leitch, M., Pulkki, R., Xu, C. (Charles). 2018. Bio-based polymers production in a kraft lignin biorefinery: techno-economic assessment. Biofuels, Bioproducts and Biorefining 12, 239–250. doi.org/10.1002/bbb.1834
3. Chapter 4 – Dessbesell, L., Yuan, Z., Leitch, M., Paleologou, M., Pulkki, R., Xu, C. (Charles). 2018. Capacity Design of a Kraft Lignin Biorefinery for Production of Biophenol via a Proprietary Low-Temperature/Low-Pressure Lignin Depolymerization Process. ACS Sustainable Chemistry & Engineering 6, 9293–9303. doi.org/10.1021/acssuschemeng.8b01582
4. Chapter 5 – Dessbesell, L., Xu, C. (Charles), Pulkki, R., Leitch, M., Mahmood, N., 2016. Forest biomass supply chain optimization for a biorefinery aiming to produce high-value bio-based materials and chemicals from lignin and forestry residues: a review of literature. Canadian Journal of Forest Research 277–288. doi.org/10.1139/cjfr-2016-0336
5. Chapter 6 – Dessbesell, L., Paleologou, M., Pulkki, R., Xu, C. (Charles). 2018. Towards commercial lignin-based polymers: supply chain cost minimization. J-FOR. (accepted paper).

Each article as listed above is linked to the thesis's specific objectives. Figure 1.2 shows the motivation and link between the chapters. Objective 1 was achieved in chapters 2 and 5. These chapters present an extensive review and analysis that provide background information and identify the knowledge gap of the target research. Chapter 2 demonstrates the potential markets of lignin-based phenols and polyols and the challenges that prevent its commercialization. In Chapter 5, the screening of lignocellulosic biomass SC studies shows the lack of studies on bio-based chemicals and materials from lignin.

Objectives 2 and 3 are covered in chapters 3 and 4. Chapter 3 presents an initial design and cost analysis for production of bio-based phenols and polyols from KL via the forest biorefinery based on the forest biorefinery based on the novel low-temperature/pressure depolymerization process developed by Dr. Xu's group. Data from many years of process optimization from our research team were used to estimate the costs, mass and energy balances inputs to a pilot scale process. Commercial suppliers were contacted to estimate the single equipment costs and bulk feedstock costs. This initial design was then assessed economically, and a sensitivity analysis was conducted followed by a risk evaluation performed to identify the critical parameters affecting the feasibility and the likelihood of a successful investment. Chapter 3 demonstrated the need for further investigation of scaling up the KL-based phenols production. In chapter 4 several capacities were investigated, and uncertainty analysis was performed for the selected technically and economically feasible commercial capacity.

Objective 4 was accomplished by the study presented in chapter 6. In chapter 6, several demand scenarios of phenols and polyols in North America were considered. The SC cost minimization model showed the impact of the fixed and transportation costs on the unit cost of KL-based phenols/polyols in a case study of Canadian Kraft pulp mills. Demonstrating the importance of SC strategic design insights in the early stage of biorefinery strategy assessment. Finally, chapter 7 provides general conclusions of the thesis and recommendations on future work towards lignin valorization for bioproducts and SC.

All the chapters were proposed, researched, developed and written by Dessbesell L. Chapter 1 and 7 were developed and written by Dessbesell L. and have been revised by the Ph.D. committee members, Pulkki R., Xu C., Leitch M. Chapter 2 and 5 were proposed, researched, developed and written by Dessbesell L. In chapters 3 and 4, Dessbesell L. gathered the cost data, developed the research design, performed the economic analyses, ran the recovery, capacity and sensitivity scenarios, developed the monte carlo simulation, processed and interpreted the results, and wrote and submitted the papers. In chapter 6, Dessbesell L. gathered the data, designed and wrote the model, prepared and presented the information, interpreted the results, wrote and submitted the manuscript. Additionally, the coauthors in each article have revised and contributed with valuable advice on the analysis and interpretation of results for all papers.

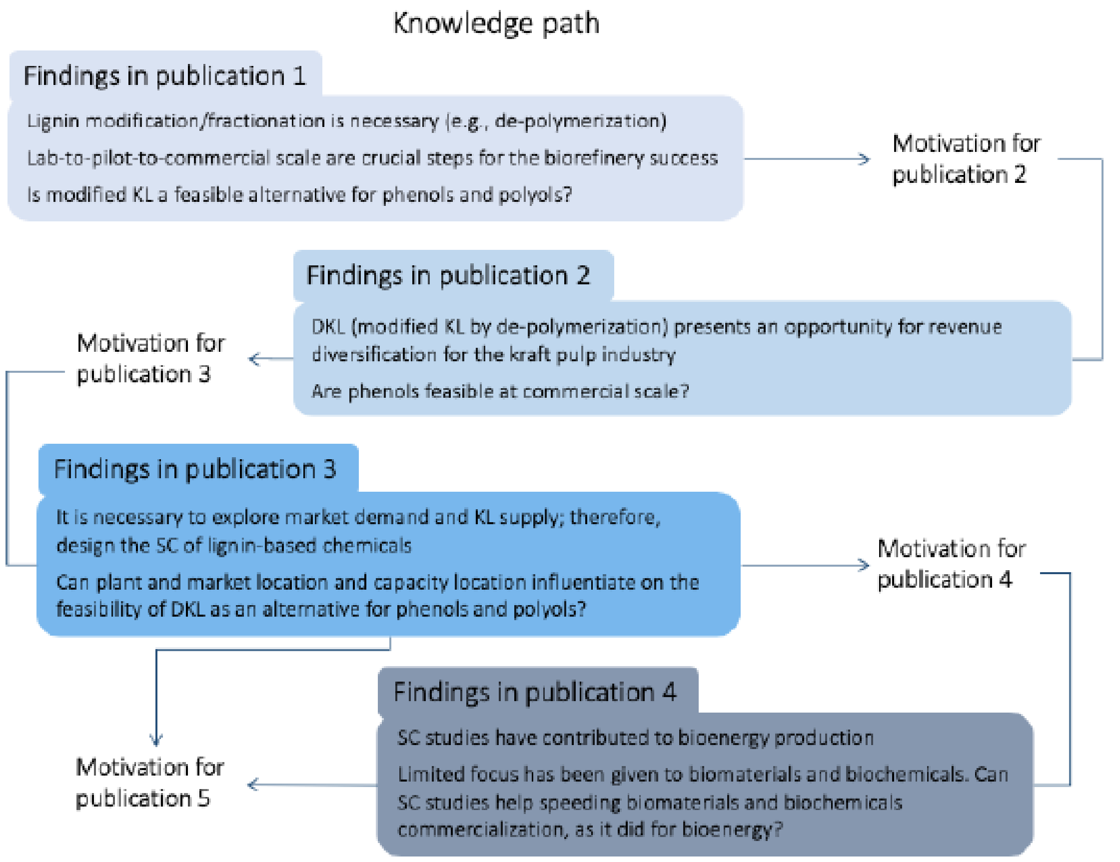

Figure 1.2. Questions connecting and motivating each publication presented in the thesis.

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CHAPTER 2 – Lignin supply, market and applications overview

ABSTRACT

Lignin is an abundant renewable feedstock for bio-based chemicals materials and energy. As the biorefinery concept grows, companies are looking into extracting the highest possible value out of biomass; hence, looking into uses of lignin for bio-based chemicals and materials in addition to bioenergy. Technical lignin is a side-product of biomass conversion processes, such as ethanol production and pulping. Lignin precipitated from pulp liquors can be directly used to substitute petroleum-based polymers partially, or undergo modifications aiming for production of bio-based polymers at higher substitution ratios and superior properties. Numerous studies have addressed lignin extraction, conversion and applications; however, a limited focus has been given to the supply and market of technical lignin. This paper presents and discusses supply and capacity of technical lignin, and price and demand of current and future potential applications of lignin. Among all types of technical lignin, lignosulfonates have a well-established market dominated by two companies. Kraft lignin (KL) supply is growing; its production increased by 150% from 2014 to 2018. Carbon fibre is a promising application in the long-term, as its demand is expected to increase, and lignin-based carbon fibers could present unique characteristics compared with those derived from other carbon fibre's precursors. The most demonstrated application for KL is for the production of bio-based phenol formaldehyde (PF) resins. Production of bio-based polyurethane (PU) foams is another favorable application. For both applications (e.g., lignin-based PF/PU), lignin modification, producing more uniform and reactive bio-chemicals, would allow a more extensive market penetration. However, extra processing results in additional costs. Thus, modification technologies should aim for using low-cost catalysts and solvents and running at low pressure and temperature. Lastly, more research efforts should be directed to feasibility investigation, scaling up, and market and supply chain analyses of forest biorefinery for the production of lignin and lignin-derived bioproducts by modification.

Keywords: lignin market, lignosulfonates, kraft lignin, biopolymer, biorefinery, biophenols, biopolyols.

2.1 Introduction

Petroleum polymers are used in a wide range of products being essential in people's daily life [1]. In fact, a major portion of the revenue (~42%) of petroleum refineries comes from chemicals, plastics and materials compared to only ~4% of volume [2]. Natural polymers, also called biopolymers, such as cellulose are also present in many everyday products such as papers. Cellulose is the most abundant biopolymer, followed by lignin [3]. Lignin is predominantly present in woody biomass, representing around one third of the solid matter in wood, depending on the species [4,5]. For several decades, efforts have been made to use lignin as a petroleum substitute for chemicals and materials.

The most abundant source of technical lignin is the chemical pulping, and around 90% of the pulp production comes from the kraft process [6]. This method generates lignin in the form of "black liquor". Black liquor is traditionally directed to a recovery boiler to recycle chemicals and generate energy [7]. Several pulp mills in North America have increased pulp production, hence generating more lignin and in most cases exceeding the calorific capacity of their recovery boilers. Since to increase the recovery boiler size is extremely expensive, a viable alternative is to precipitate lignin out of black liquor, hence reducing the calorific load going into the recovery boiler [8]. The world production of dissolved lignin from chemical pulping is estimated at 70 million tonnes per year (Mt/y) [7]. After securing the kraft mill energy demand, the amount of kraft lignin (KL) available for precipitation, prior to entering the boiler, ranges from 5 to 20% [9,10], corresponding to about 3.5 to 14 Mt/y of KL; while many authors have suggested an average volume of 8 Mt/y [7,11].

The most commercially explored type of lignin is lignosulfonate, a by-product from the sulfite pulp process. Lignosulfonates have a consolidated market as dispersants, release control, resins and binders [12]. Its market size is approximately 1.1 Mt/y in 2016 [13], with a forecasted compound annual growth rate (CAGR) of ~3%, for 2017 - 2025 [14]. Lignosulfonates producers are looking into new applications targeting other value-added chemicals and materials. Meanwhile, the kraft pulping industry is also keen on investing on valorization of KL for bio-based chemicals and materials. More efficient and less costly KL extraction technologies have been developed, thus opening up new possibilities of revenue generation from the KL stream.

North America and Europe are leading in lab-scale research, pilot and commercial scale KL processing initiatives. Yet, a big gap exists between the KL producers and the consumers, which slows down KL market development. New lignin applications need to be tested and improved to meet market specifications and become commercially viable [15]. A lignin market pull is expected between 2023 and 2028 [16]. With more KL being extracted, partnerships will be established resulting in increased KL demand for manufacture of bio-substitutes to petroleum-based chemicals. Signs of this movement can be observed, where, the academia, potential producers and consumers are working in multidisciplinary teams for ambitious projects on cost-competitive and high-value applications of lignin [17–19]. This should speed up the launch of lignin-based products [20].

So far, publications have focused on lignin chemistry, characterization, biorefinery research, extraction and modification. Many literature reviews with hundreds of papers on lignin are available [4,7,21–28]. These publications bring extensive valuable information, but they contain limited info, usually with a few paragraphs or figures, on the market of lignin and lignin-based products. However, as the move towards commercialization of lignin-based biorefineries starts, more information is needed regarding the market, main producers and potential users of lignin-based products. The purpose of this chapter is to provide a critical review on both research advances and market overview of lignin-based bioproducts, innovatively focusing on the supply, demand, capacity of lignin-based bioproducts and trends of potential lignin applications.

2.2 Methods

To retrieve peer reviewed papers a set of keywords, such as lignin, lignin applications, lignocellulosic biomass, biorefinery, lignosulfonates, organosolv lignin, hydrolysis lignin, and a combination of the keywords were introduced to the search engine of Web of Science. First, literature review papers were selected to analyze the coverage on the lignin sources and types, characteristics, conversion technologies, and potential applications. It was identified that there are a lack of publications converging supply and market detailed information on lignin applications. To address the problem, additional relevant sources were consulted besides peer-reviewed papers, as summarized below:

- Annual reports and websites of pulping, biorefineries and chemical companies.
- Articles from magazines, such as Canadian Biomass, BiofuelsDigest, Paper Advance, Independent Chemical Information Service (ICIS) Business Online.
- Market consulting companies report summaries: ICIS, Business Wire, Research and Markets, etc.
- Reports of research groups and agencies, such as International Energy Agency (IEA), and the US Department of Energy's Bioenergy Technologies Office (BETO). A survey on lignin was submitted to North American companies and research groups by BETO, and the survey responses are available to the public [29].
- The Resource Information Systems Inc. (RISI) report "The lignin: technology, applications and markets: special market analysis study [13].
- Patent information came from the World Intellectual Property Organization (WIPO), using the keyword "lignin" in the front page considering all offices and

all languages, obtaining 17,889 results that were then processed in categories, such as country, year and applicants.

Throughout the text for simplification, please read B: billion(s), M: million(s), k: thousand(s), t: tonne(s), and y: year. All price and cost values are in US$ (United States of America) dollars.

2.3 Lignin sources

Lignin is present naturally in lignocellulosic plants accounting for approximately 300 Bt with a CAGR of 7% [30]. Of this immense amount, approximately 50 to 70 Mt/y is currently produced as technical lignin, mostly in the pulp/paper industry, of which around 2-5% is used for chemicals and materials [4,5]. Technical lignin can be defined as a form of lignin isolated after a series of biomass processing. The types of technical lignin vary largely in terms of molecular weight and structure, which essentially determine the routes for lignin valorization and applications [31]. Detailed information on technical lignin production, properties, and analysis are available in literature [11,32]. A summarized overview of technical lignin types is provided below.

- Lignosulfonates are a by-product from sulfite pulping [33]. They are the most commercially explored type of technical lignin; accounting for more than 90% of the total lignin on the market [34]. It is widely used as industrial dispersants and concrete additives [35].
- KL is produced in the kraft pulping process in the form of a by-product called black liquor. The black liquor is mainly utilized in recovery boilers for heat and power generation, and to recycle pulping chemicals [36]. KL accounts for ~85% of the total

technical lignins availability [37], however, only around 2.5% is currently extracted for commercialization.

- Soda lignin is produced from the soda pulping process, which is mainly applied for biomass from annual crops and, to a certain extent, for hardwoods [4].
- Hydrolysis lignin is produced in cellulosic ethanol plants as a by-product of the enzymatic hydrolysis process that separates lignin from cellulose and hemicellulose [31,38].
- Organosolv lignin is also produced from the pulping process that employs organic solvents to separate lignin from cellulose; it generates a low-sulfur and low molecular weight lignin [4].

LignoBoost and LignoForce processes are the two major commercial technologies for extracting lignin from spent liquors. The LignoBoost process was developed by Chalmers University of Technology and Innventia in Sweden. Now the technology is sold and installed by Valmet. The LignoForce process was developed by FPInnovations and NORAM Engineering, both from Canada. Another system, SLRP - sequential liquid lignin recovery process and purification, developed by Lignin Enterprises LLC and Clemson University in the US is seeking partners for a demo scale [11].

The LignoBoost technology is based on acidification of black liquor after filtration [39]. The LignoForce process developed by FPInnovations employs an extra oxidation step to convert sulfur compounds and facilitate the filtration process [40]. According to FPInnovations, the lignin extracted from kraft pulp mills black liquor using LignoForce process is priced at about 600 $/t [9], however, this price might fluctuate dramatically as more lignin becomes available and new applications are identified. More details on technical lignin recovery can be found in Vishtal and Kraslawski [4].

2.4 Overview of lignin-related patents and research

Thousands of scientific papers have been published covering lignin applications, characteristics and conversions aiming value-added products. Several review papers have summarized the published findings. Among the most general papers on lignin, one can suggest the following: lignin types, modification and conversion [21]; lignin profiling and screening [1]; lignin derivatives and applications [20].

Another fact demonstrating the interest in lignin is the number of patents involving its production, modification and application. Since 2008, 17,889 patents were registered in WIPO. China and the US are leading in patents, followed by the applications under the Patent Cooperation Treaty (PCT), also called international applications. For instance, several patents from FPInnovations were filed for PCT. The European Patent Office covers European countries, including Germany and United Kingdom, as listed in the graph (Figure 2.1 (a)). This graph also presents patents from Germany and United Kingdom that are not included under the European Patent Office category. As shown in the image, Canada, Japan and United Kingdom have around a thousand patents each (Figure 2.1 (a)).

The number of patents has increased over the years, the peak so far was in 2017 (Figure 2.1 (b)), led by The API Intellectual Property Holdings, Llc, Shell Oil Company and Westvaco (Figure 2.1 (c)). Among the top applicants there are many pulp companies demonstrating strong interest of the sector in adding value to the lignin stream. The API Intellectual Property Holdings, Llc is a US patent law firm focused in food, materials chemistry and biotechnology. Shell Oil Company's takes the second place in number of patents on processing cellulosic biomass, extraction and applications of lignin (Figure 2.1 (c)).

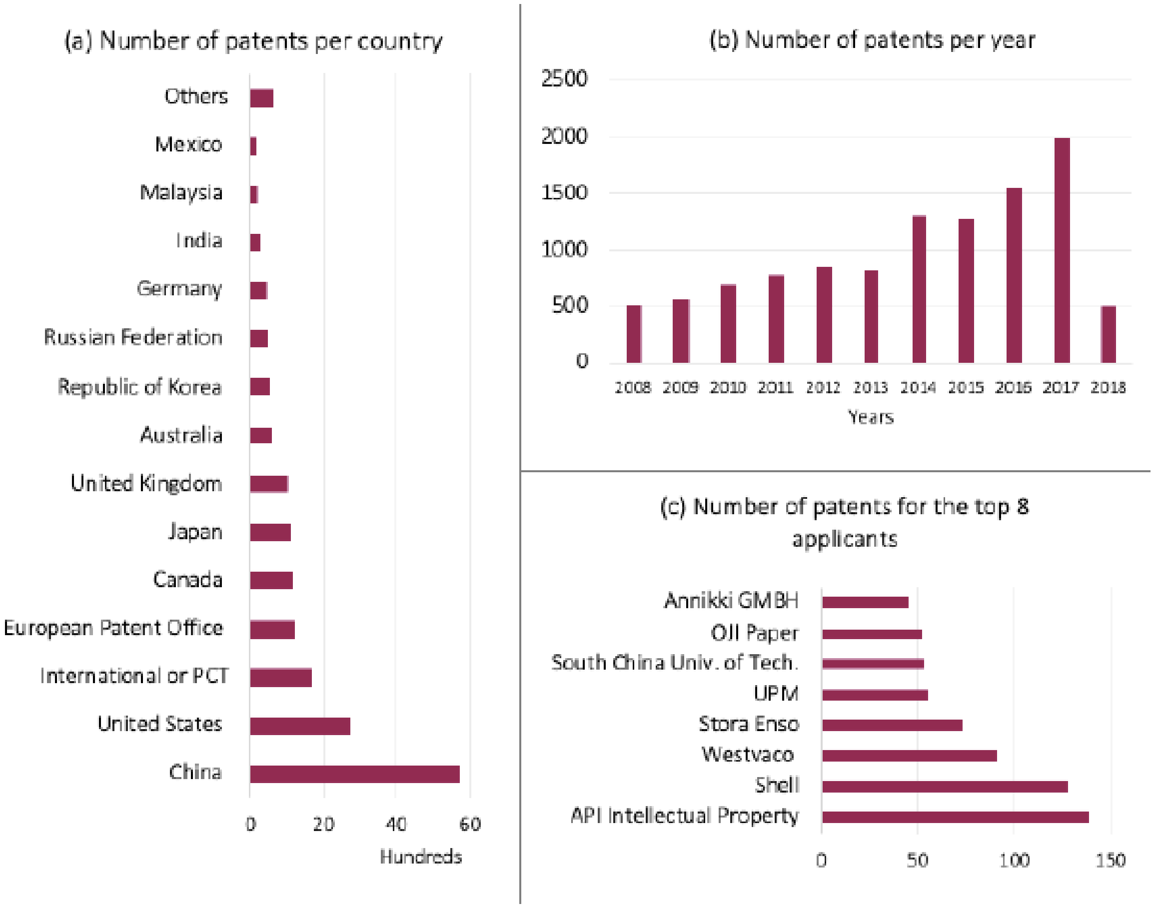

Figure 2.1. Summary of lignin-related patents from 2008 to October 2018 obtained at WIPO.

2.5 Lignin production and supply

The world's commercial production of technical lignin is totaled at about 1.65 Mt/y, among which lignosulfonates dominate almost 80% of the market (Figure 2.2). The lignosulfonates market is consolidated, and its primary applications are surfactants, bonding agent for pelletization, dispersant in ceramics and concrete admixture [41]. The world's market for lignosulfonate is forecasted to grow at 1% CAGR [42].

The annual global KL production was estimated at 60,000 t [30] in 2011, 75,000 in 2015, and our study identified a current production capacity of 265,000 t/y. Six KL commercial producers contribute to the 16% as shown in Figure 2.2, within them, Aditya Birla Domsjö in Sweeden, Stora Enso in Finland, and Ingevity in the US are the larger producers. Among all types of technical lignin, KL production is growing at a faster rate. Comparing the results with the forecasted values shown in Table 2.1, KL has already achieved the forecast production for year 2025; however, it is far from reaching the optimistic forecast scenario for 2025 suggested in the study of Miller et al. [13].

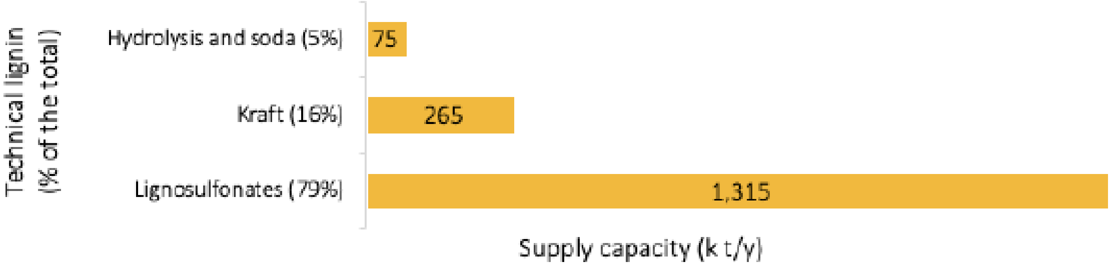

Figure 2.2. Commercial production of technical lignins, base year 2018.

Table 2.1. Lignosulfonate and KL commercial production in 2015 and the forecasts [13].

	Production in 2015 (kt)	Forecast for 2020 (kt)	Forecast for 2025 (kt)	Optimistic Forecast for 2025 (kt)	Potential (kt)
Lignosulfonate	1,100	1,400	1,550	2,000	3,000
Kraft lignin	75	200	250	2,500	78,000

KL is largely available at kraft pulp and paper mills and its extraction methods are becoming more efficient, as they have now been optimized at commercial scale. Additionally, in terms of applications, the industry sees the opportunity of shifting from low-price applications, such as for energy generation (e.g., \$70 and \$150 per t) [31], to high-value ones such as for chemicals and materials (e.g., phenols ~\$1300 t) [43]. Still, challenges, like petroleum price fluctuation, KL characteristics, and currently-low substitution ratios, are slowing down the KL market growth.

Production of organosolv, soda and hydrolysis lignins is still small. Soda lignin is produced by GreenValue in India, and hydrolysis lignin (HL) by Ibicon in Denmark. In 2017, an investment was announced in Thunder Bay for HL production on a pilot scale (100 t/y) using the FPInnovations TMP-Bio technology to provide information to de-risk scale-up and boost the HL product-driven research [44]. Organosolv is not yet produced at a commercial scale, as most of the initiatives are still at a laboratory or pilot scale [29].

Our study identified 22 companies commercially producing lignin (at an amount above 5,000 t/y). As shown in Figure 2.3, Borregaard LignoTech remains the main producer of technical lignin, followed by Tembec, which recently became part of Rayonier Advanced Materials. Two companies in Russia (OAO Kondopoga and Vyborgskaya Cellulose) come in the third place, although specific amounts of lignosulfonates produced in these two companies were unable to be identified.

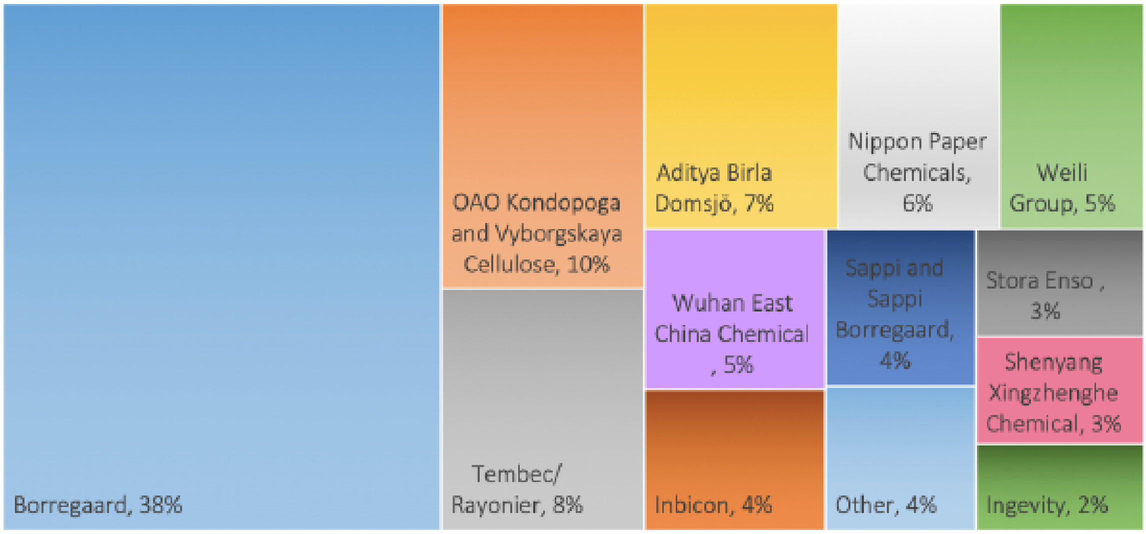

Figure 2.3. Distribution of commercial producers of lignins, base year 2017.

The current lignin production capacity per country is driven by the countries that have lignosulfonates plants (Figure 2.4). In the US, for instance, Borregaard LignoTech in a partnership with Rayonier Advanced Materials Inc. recently started operation of a 100,000 t/y lignosulfonate plant in Florida. China has six lignosulfonates producers, which together puts the country to be the second lignin supplier. The third largest supplier country is South Africa, accommodating Sappi and Borregaard lignosulfonate plants, followed by Norway with a Borregaard plant.

Data from Russia were difficult to confirm for 2017, while there is one source of data [13] revealing that the country had 160,000 t/y of lignosulfonates in 2015 produced by the companies OAO Kondopoga and Vyborgskaya Cellulose. Japan comes next due to Nippon Paper Chemicals production capacity of 100,000 t/y of lignosulfonates. Canada comes in seventh, with a total capacity of 90,000 t/y, attributed to West Fraser's capacity of 10,000 t/y KL, and the Rayonier's capacity of 80,000 t/y lignosulfonates. Other countries, such as Finland, France, Germany, Denmark and Spain, have lignin production capacity ranging from 50,000 to 70,000 t/y. In Brazil, Suzano SA will start operations in 2019 of the country's first KL lignin production plant, with a capacity of 20,000 t/y.

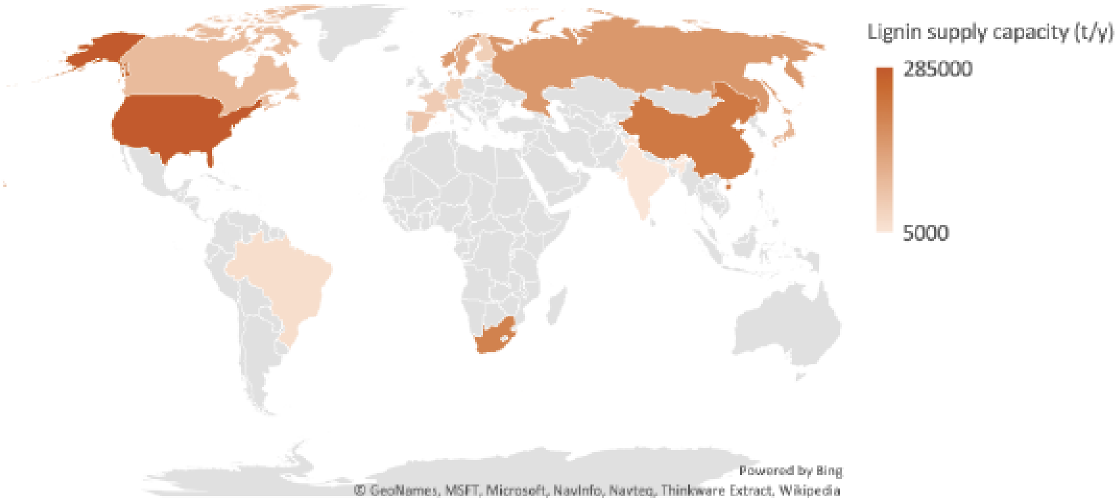

Figure 2.4. The current lignin production capacity per country, base year 2017-2018.

2.6 Potential applications of lignin

A lignin profiling study identified the following best applications based on technical lignin characteristics: softwood KL (MeadWestvaco Indulin AT) replacing phenol in the synthesis of phenol formaldehyde (PF) resins; lignosulfonate (Tembec Arbo SO1) replacing polyols in polyurethane (PU) foams; and, organosolv lignin (Aldrich, hardwood) in the manufacture of carbon fibre [1]. More applications generally described in other studies are listed and described in Table 2.2.

Table 2.2. Purity and potential applications of various technical lignins [22,30,45].

Technical lignin	Purity	Potential products
Lignosulfonates	Medium	Additives in bitumen, vanillin, feedstock for refinery
Kraft lignin	Medium-high	Additives, biofuel, BTX, activated carbon, phenolic resins, carbon fibres, phenol
Organosolv	High	Activated carbon, phenolic resins, carbon fibres, vanillin, phenol derivatives
High-grade lignin	Very high	Carbon fibres, vanillin, phenol derivatives

Figure 2.5 displayed market price vs. market size for technical lignins and their potential lignin applications. The bubbles in the graph represent the market size for each potential lignin application and each technical lignin. The size is based on the average market volume times the average market value (center of the bubble). The percentage shows the share of each item with regards to the total market size of all products represented in the graph. Three lignin potential application categories can be distinguished in Figure 2.5: high-volume low-value e.g., bioenergy; low-volume high-value e.g., carbon fibres; and intermediate-volume intermediate-value e.g. phenol. The square in Figure 2.5 shows an area called “sweet spot”, which corresponds to the

products with moderate market price and volume where applications of technical lignin would potentially bring higher returns [46,47].

The potential global production of lignin from kraft pulping could theoretically substitute up to 2% of the world's principal petrochemicals production [11]. In terms of volume, BTX (benzene, toluene and xylene), bitumen and phenol are the largest potential markets for lignin (Table 2.3). However, the market prices of BTX and bitumen are low, thus a less attractive application for KL, organosolv and high-grade lignin, but would be suitable for lignosulfonates (Figure 2.5). In fact, the uses of lignin in 2015 were directly linked to lignosulfonates' applications for vanillin, additives and dispersants (Table 2.3).

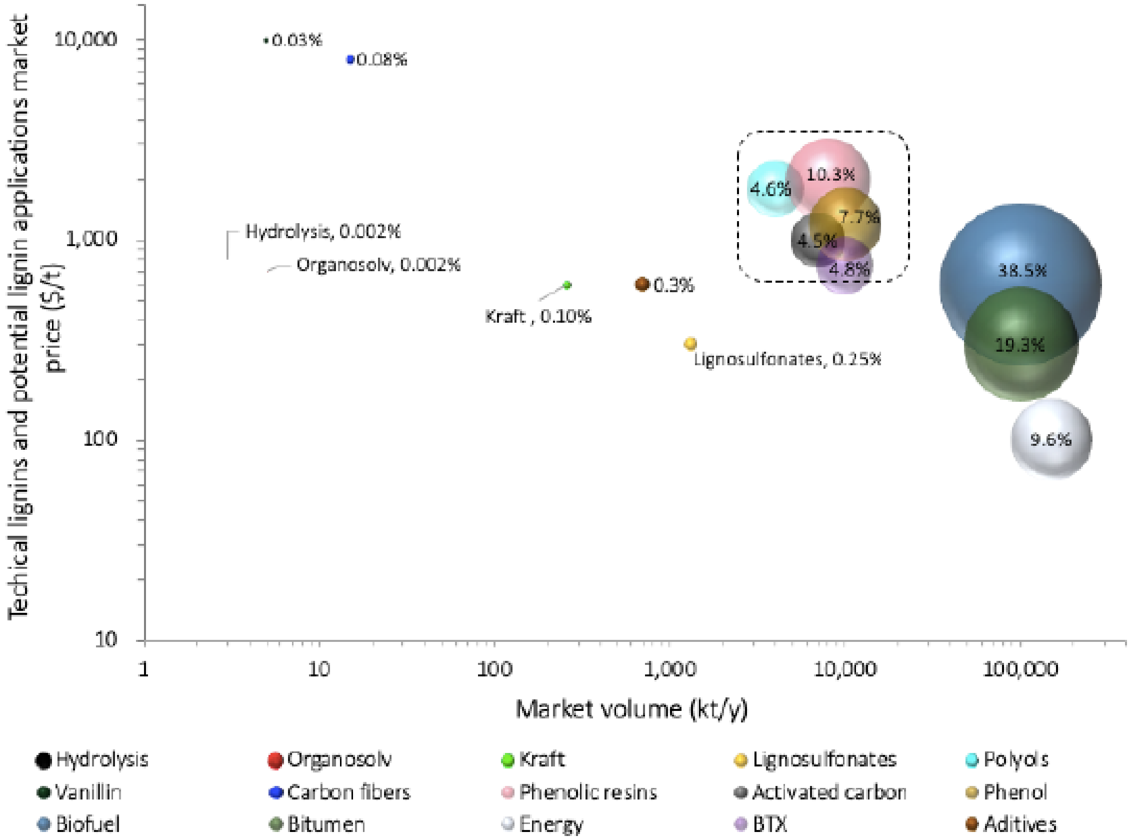

Figure 2.5. Technical lignins and potential lignin applications: market price vs. market volume and size. Drawn by the author with information gathered from literature [13,30,45,48–51]. Note: Both axes are plotted in logarithmic scale base 10 to cover the large range of values. Also, thermoplastics were not included in the figure to allow a readable scale, however we included thermoplastics information in the paragraphs that the figure.

Table 2.3. Global current and potential production of lignin by applications, base year 2015 [13].

Applications	Current production (kt)	Potential production (kt)
Vanillin	30	200
Phenolic resins/phenolic derivatives	35	1,000
Carbon fibre	0	25
Activated carbon	0	400
Polyols[1]	0	3,000
Phenol	5	5,000
BTX	0	20,000
Additives in bitumen, asphalt	5	10,000
Cement/Concrete additives	500	4,000
Miscellaneous dispersants and binders	400	2,000

[1] Information not available in reference [13]; therefore, estimates were based on [52] considering 30% of the demand.

The aromatic nature of lignin brings many possibilities; hence, other value-added opportunities are receiving attention. For instance, VTT (Technical Research Centre of Finland) – the world's fourth largest research funding group [17], is testing KL modification to produce thermoplastic lignin composites and compounds (e.g., plasticization of lignin, polymer blends and fibre reinforced composites) [53] using commodity thermoplastic precursors (e.g., polypropylene, polyethylene and polyvinyl chloride) at a price of ~1,700 $/t [54]. The thermoplastic overall demand was estimated to be 280 M t/y in 2017 [55].

In terms of fields of applications, lignin valorization can be separated into three major categories: lignin-to-energy; lignin as a macromolecule; and lignin-to-chemicals [56,57]. The route towards value-added applications, such as aromatic chemicals, requires modification steps, as exemplified in Figure 2.6 with the pathway developed by Valmet for lignin extracted by the LignoBoost process. Many properties of lignin, such as odour [40], colour [58], reactivity [59], strength and thermal stability [60] need to be improved to meet the market standards.

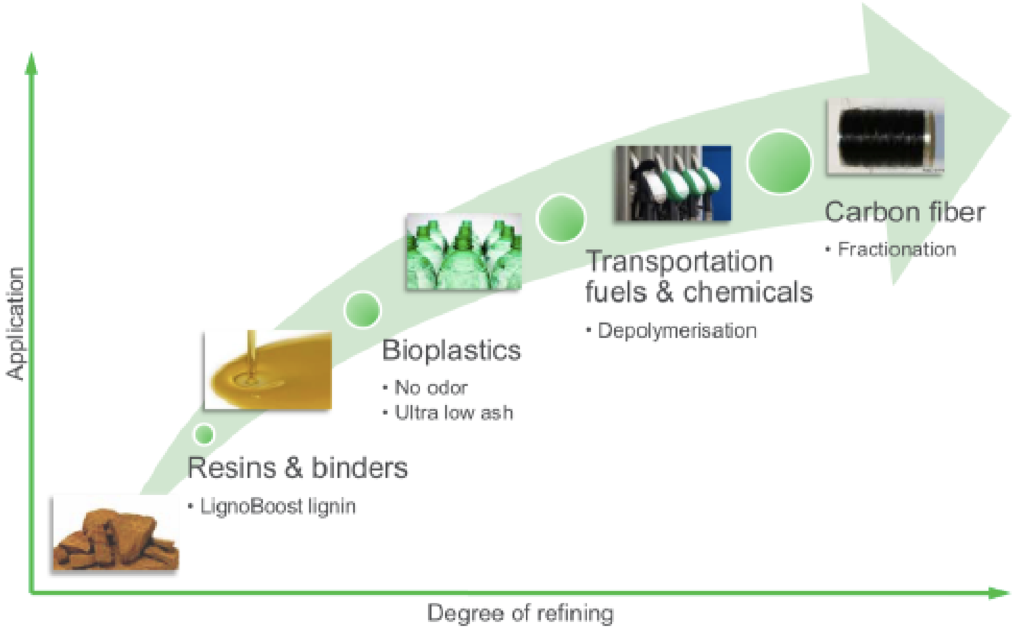

Figure 2.6. Matching lignin with value-added applications [12].

Our work focuses on the market opportunities for lignin products, more specifically KL; hence, we don't cover lignin modification and fractionation methods. Several publications can be suggested to the readers regarding lignin improvement strategies for different purposes: hydrogels and nanocomposites [61], polymers, blends and composites [37], aromatic compounds [48], phenols, polyols, and epoxy resins [38,59,62,63], liquid fuels and hydrogen [21], and various other potential applications [20,45,56]. Also, Sun et al. [64] have published a very comprehensive literature review on lignin modification approaches and applications.

Lignin characteristics vary extensively among technical lignin type [8]. It also changes within the same technical lignin; for instance, KL varies according to the separation technology, wood species and pulp mill running processes. Therefore, in the next section, we start narrowing down this study, focusing first on potential products from KL, then specifically on utilizing softwood KL as a substitute for phenols and polyols.

2.7 Phenols and polyols from kraft lignin

The similarities of lignin with phenols resulted in extensive research on lignin as a substitute to phenol [65,66]. Among the technical lignins, KL is most commonly used due to its relatively low cost and high reactivity; therefore, showing extreme potential for resins and adhesives, especially PF resins. However, direct substitution of phenol with lignin - after extracted from black liquor either by LignoBoost or LignoForce methods, is limited in the percentage substitution. Therefore, modification is needed to improve KL characteristics according to the target product. Table 2.4 lists several examples of KL modification methods and their targeted products.

Table 2.4. KL modification methods and their targeted products.

Kraft lignin-based products	Modification	References
Polyols	Depolymerization	[38,67]
Phenol	Depolymerization	[67–72]
Phenol and polyols	Phenolation	[73,74]
Epoxy resins	Depolymerization	[75–77]
Carbon fibre	Propargylation	[78,79]
Dispersants	Carboxymethylation	[80,81]

Reactivity of KL for formaldehyde can be enhanced by phenolation, which consists of using an acid to break lignin in the presence of phenol [73]. Zhang et al. developed a low-cost process that uses low amounts of sulfuric acid, no solvent and low temperatures (~100 °C) that allowed up to 40% phenol replacement with KL in the formulation of commercial standard phenol formaldehyde resins and adhesives and 10% in phenolic foams [74]. Thermochemical conversion of lignin targeting aromatics were extensively discussed in previous papers [66,82]. The first challenge is to obtain a bio-phenol displaying characteristics that allow the maximum level of phenol substitution in PF resins. The complex structure of KL results in a lower reactivity than petroleum-based phenol; on the other hand, the polyphenolic macromolecule structure of the KL presents more steric hindrance than petroleum phenols [83]. The goal is not to compromise the resin attributes complying with the standards of product quality and production.

The extent of modification applied to the original KL can strongly change the percentage of substitution of phenol by bio-phenol in the products manufacture [68]. For instance, for KL without modification the substitution optimistically is 30 wt.% (weight percent) in the synthesis of phenolic resins for plywood [71]. By depolymerization, the most studied approach for modification of lignin for biophenol [84], phenols with lower molecular weights (Mw) and higher hydroxyl non-aliphatic phenolic groups, were achieved, allowing higher replacement ratios in the synthesis of PF resins [85].

Some examples of biophenol performance when replacing petroleum-based phenols are provided as follows. Substitution of petroleum phenol in phenolic resol resins synthesis resulted in resins with comparable or even improved dry and wet bonding strength than the reference commercial PF resin, at substitution levels varying from 25 to 75 wt.%. In terms of curing temperature, the best outcome was obtained at 50 wt.% substitution [64]. Depolymerized kraft lignin (DKL) with various Mw was incorporated at up to 75 wt.% substitution level in the production of PF resin [68]. Incorporating DKL seems to facilitate higher molecular interaction and enhanced entanglement; although, it might likewise increase steric hindrance effects [68]. Danielson and Simonson [71] found that a 50 wt% substitution level of phenol with KL presents the best outcomes with regards to resin viscosity, bonding ability and storage.

One of the main applications of polyols is the manufacture of PU foams, flexible and rigid, which is also an opportunity for lignin. The reaction of a polyol with an isocyanate creates the PU resins and foams [87]. Like for phenols, KL can be directly used as a biopolyol in the production of PU foams. Similar limitations were observed when KL is a substitute for polyol, i.e., crude KL's low reactivity and solubility in the polyol system limits the direct substitution up to 20 wt.% [37,88]. The efforts of using un-modified lignin as a natural polyol were reported by Belgacem and Gandini [89].

Depolymerization and oxypropylation KL modification proved to yield technically higher-quality bio-based polymers enabling higher substitution ratios. DKL produced quality PU rigid foam when substituting polypropylene glycol (PPG400 a petroleum polyol) at 50% wt.% substitution. In the same study, oxypropylated DKL successfully produced PU rigid foams, replacing similarly 50% of the petroleum polyol [90], due to the fact that the oxypropylation process uses around 50 wt.% DKL and 50 wt.% propylene oxide (petroleum based); Although at the same bio-replacement, the advantage of oxypropylation of DKL compared to using DKL without oxypropylation is that the oxypropylation yields a liquid product, which ease the PU foaming process than that with the DKL powder [90]. More details on polyols from lignin are available in previous papers [37,91,92].

2.8 Supply and market for phenols and polyols

Phenol is a chemical intermediate for the production of many other chemicals. It is produced via the cumene oxidation process, using benzene and propene as feedstock

(3:1 molar ratio) to generate cumene which then goes under partial oxidation via the Hock re-arrangement [93]. Acetone is produced as a by-product at a phenol/acetone molar ratio of 1/0.6 [94]. Therefore, the demand for acetone also drives the phenol market. In 2016 the global demand for phenol was ~11.4 Mt [95], with a CAGR of ~4% during 2010-2017 [96]. Table 2.5 lists the primary phenol producers and consumers. The demand varies according to the demand for phenol derivatives (Figure 2.7). Phenol derivatives (e.g. bisphenol and PF resins) are essential ingredients in a broad range of industrial products, e.g., epoxy, polycarbonates, plywood, bakelite, nylon, detergents, herbicides and pharmaceutical drugs [97].

Table 2.5. Main phenol producers and consumers, base year 2015. Updated from [13].

Company name	Primary country	Consumer	Producer
Arclin	US	Yes	Na*
BASF	Germany	Yes	Na
Bayer Polymers Shanghai	China	Yes	Na
Borealis	Finland	Na	Yes
Cepsa Quimica	Spain	Na	Yes
Chang Chun PC	Taiwan	Yes	Yes
Deepak Phenolics	India	Na	Yes
Domo GmbH	Germany	Yes	Na
Dow Chemical	US	Yes	Yes
DSM	Netherlands	Yes	Na
Formosa Chemicals and Fibers	Taiwan	Na	Yes
Georgia Pacific	US	Yes	Na
Haverhill / Altivia	US	Na	Yes
Honeywell	US	Yes	Yes
Ineos	US	Yes	Yes
Jiangshu Haili	China	Na	Yes
Kumbo P&B Chemicals	South Korea	Yes	Yes
LG Chemicals	South Korea	Yes	Yes
Lihuayi Weiyuan	China	Na	Yes
Mitsui Chemicals	Singapore	Yes	Yes
Momentive Specialty Chemicals	US	Yes	Na
Nan Ya Plastics	Taiwan	Yes	Na
Radidi Group	Italy	Yes	Na
SABIC	US	Yes	Yes
Shell	US	Na	Yes
Sinopec	China	Na	Yes
Taiwan Prosperity Chem	Taiwan	Na	Yes
Versalis	Italy	Na	Yes
Zhuhai Shi You	China	Na	Yes

*Na: not applicable

Figure 2.7. Global demand pattern for phenol in 2016 [94,97].

The most important region is the Asia-Pacific, which contributed more than 50% of the global phenol production in 2016. Europe comes in second followed by North America [95]. Country-wise, China has remained the largest market for many years for production and consumption of phenol [98]. Many phenol producers are also consumers (Table 2.5). Ineos represents the world's largest phenol and acetone producer, 4 Mt/y in 2018, with plants in Belgium, Germany and the US [99]. Other prominent players are Mitsui Chemicals, Cepsa Quimica, Kumho P & B Chemicals and LG Chemicals [95].

As presented earlier, lignin-based phenol can readily replace or substitute petroleum-based phenol in the manufacture of PF resins. PF is the most commonly used adhesive in the production of engineered wood products, like plywood, oriented strand board, laminated veneer and fiberboards. Additionally, PF is also applied to other industrial products such as abrasives and insulation [65]. On a global perspective, North America is the largest consumer of wood adhesives, with increasing demand coming from the housing market growth in Canada and the US [100].

Another application, within the sweet spots showed previously (Figure 2.5), is the use of KL as a substitute for polyols. Polyether and polyester are the two main types of polyols which originate in different processes. Polyether is produced via anionic ring addition in the polymerization of ethylene oxide or propylene oxide, and, ethoxylation or propoxylation of a polyhydric alcohol with a catalyst produces polyether polyols [101]. One of the main applications of polyether polyols is in PU. PU resins are the fasted growing portion of the polyols market, which are used in the manufacture of foams (rigid and flexible), elastomers, coatings, adhesives, binders and sealants (Figure 2.8) [102]. As for the end-use industries, the main drivers in the polyol market are construction, automotive, footwear and electronics [101].

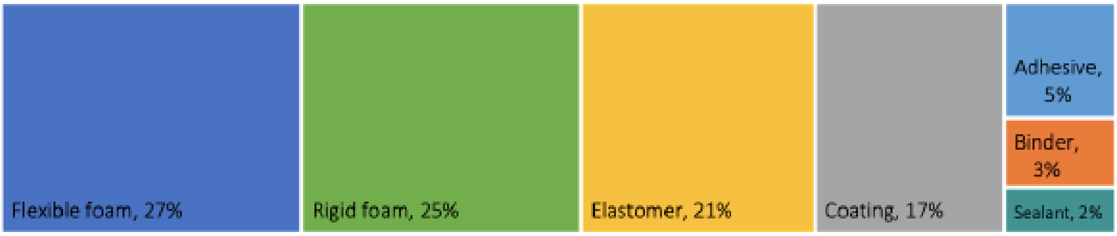

Figure 2.8. Global PU market share by product segment, base year 2014 [103,104].

The anticipated polyol demand in 2018 is 10.4 M t [52], with a CAGR of 8.91% for 2019 [105]. The leading companies in polyether polyol supply are DowDuPont, Covestro, Shell and BASF; together they represent around 50% of the world's total polyol production capacity [106]. A list of the major producers is provided in Table 2.6.

Table 2.6. Principal polyol manufacturers, base year 2017 [107].

Company name	Primary country
BASF (Badische Anilin und Soda Fabrik)	Germany
Cargill[1]	US
DowDuPont[2]	US
Lanxess Aktiengesellschaft	Germany
Mitsui Chemicals	Japan
Shell International	Netherlands
Covestro[3]	US
Stepan Company	US
Repsol	Spain
Lonza Group	Swiss

[1] Main types of polyols produced are erythritol, glycerin, sorbitol, mannitol, isomalt, xylitol and maltitol.
[2] Dow Polyurethanes. [3] Formerly known as Bayer Material Science.

KL-based polyols may compete with Natural Oil Polyols (NOP) that currently represent the majority of the bio-based polyol market. Bio-based PU's are produced from bio-based polyols (substitution ratios of 30-70%) and synthetic isocyanates. The majority of NOPs are produced from soybean, castor and palm oils. The bio-based PU market is expected to grow at 6.5% CAGR. In 2013, construction was the main end-use if bio-based PU, corresponding to 35% of the total bio-PU production [108].

2.9 Future of KL as an alternative to phenols and polyols

Although several mills started to extract KL worldwide, its price is still not openly known. Some estimates suggested a price varying from 260 to 500 $/t [48]. From the LignoForce system, the KL minimum selling price is estimated at 600 $/t [9]. Phenols and polyols price fluctuate substantially, influenced by crude-oil prices and supply, versus demand variations. From June 2014 to June 2017 the average price of phenol in the US was ~1,304 $/t, varying from ~970 to 2,028 $/t in the period. Polyols average price was ~1,931 $/t in 2017. Moreover, the polyol production in North America has been stable, with the demand and supply in balance over recent years [87].

Nevertheless, further processing of KL aiming more reactive lignin-based phenols plays the main role in the feasibility of this bioproduct. Our studies on KL depolymerization for phenols and polyols demonstrate that both applications are feasible at a commercial scale, considering KL as a feedstock priced at 600 $/t and product selling price above 1,300 $/t. The most relevant risks are related to target polymers price variations, demand, chemical recovery limitations and the uncertainty in technology fixed costs [43,109].

2.10 Overall outlook

Several lessons were learned from past commercialization KL initiatives, such as in the early 1940s substantiated by high oil prices [110]. Lignin needs to be competitive and resilient to petroleum price variations. European and North American companies are investing faster towards the biorefinery transformation for lignin valorization [109]. Although, they might face more challenges initially, such as obtaining partnerships with the end-industry and optimizing existing manufacture processes to employ lignin, they will have competitive advantages compared to companies entering the market later [109]: i.e., advantages such as long-term partnerships, a track record of product improvement, and the development of SC unique strategies, etc. As shown previously in this paper, the most promising lignin applications are in low-to-medium-volume markets, which could be satisfied by many lignin producers.

The business of producing large quantities of commodities at low returns is not compatible with biorefinery projects [111]. Therefore, it is necessary to develop a portfolio diversification plan to identify a sustainably feasible set of products. Either by developing a generic level study, without a specified plant, or a specific level considering constraints, business and culture of a particular company or plant [112]. However, it is challenging to methodically measure risks related to a new technology [113].

Phase-based strategies to decrease risks and achieve successful scaling up, implementation and market penetration are proven to be successful. Examples of this strategy can be observed in the West Fraser KL plant in Hinton, Alberta, Canada, seems to be using a phase-based approach as well. They started with a small, yet commercial-scale lignin extraction plant. Initially, they are experimenting, improving, and testing their KL in resins used in their engineered wood product mill. Meanwhile, the company is decreasing risks, building partnerships and identifying the most successful strategy to scale up and diversify their production towards value-added products.

For long-term sustainability of biorefineries, it is critical to consider SC visions and implications. SC design for bioenergy is a well-studied subject; still, little attention is given when it comes to biomaterials and biochemicals [114]. It is indeed difficult to model a SC for products that might not have a market or a specific end use. A great study by Dansereau et al. [115], provides an extensive model for biorefinery portfolio evaluation considering SC performance on decision making. Efforts on minimizing the overall SC cost, while identifying the capacity and potential KL products production locations, targeting phenols and polyols market, were carried by our research group [116]. SC studies can bring valuable information to speed up the lignin market establishment.

Another topic to be considered, as the lignin chemicals market starts to develop, is possible regulations on the label "bio-based products", e.g., the threshold content of bio-based chemicals in the final product. Thus, this subject should be discussed and taken into consideration when companies decide to invest in lignin-based chemicals.

Questions remain, should KL producers sell lignin "as is" after removing it from black liquor? What are the market's expectations regarding KL-based alternatives to petroleum chemicals? What modification approach results in the best cost benefit? These questions should be answered as the lignin market pull continues and long-lasting synergies among the academia, lignin producers and consumers are established.

2.11 Conclusions and knowledge gaps

Lignin opportunities are immense, which have been discussed and studied for decades. The most secure and well-known pathway of lignin utilization is for bioenergy, which is a low-value application, and in the traditional applications of lignosulfonates – a limited market already dominated by a few companies. As KL recovery in pulp mills has more than doubled in the last few years, its use as a phenol substitute is being tested on an industrial scale. Applications bringing direct attention concerning market value and size are polyols, BTX and thermoplastics. Additionally, in the long-term, production of carbon fibre and other specialized materials from lignin is expected to increase as they are of high value products with an expected fast-growing demand.

Lignin modification is necessary to overcome substitution limitations and achieve a stable product with market desired characteristics. Therefore, moving from the laboratory scale to pilot and then to commercial scale for lignin modification, are crucial steps for the success of emerging technologies for lignin valorization. For this to happen, many aspects have to be addressed covering the design specifics of each technology, cost and risk analysis, and SC and market assessments. Regarding a specific mill, additional aspects shall be included: for instance, what value-added applications to target, retrofit or a new plant, becoming end-use producer of lignin-containing materials or a lignin chemicals feedstock supplier.

Bringing together the industry, university research groups, government agencies, potential producers and consumers is critical to speed up lignin valorization. A multidisciplinary task force is needed to understand all aspects of the lignin opportunities, looking into the potential value creation throughout the value chain.

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CHAPTER 3 – Bio-based polymer production in a kraft lignin biorefinery: techno-economic assessment

ABSTRACT

This paper presents a techno-economic and risk analysis of a kraft lignin (KL) biorefinery (3000 tonne of KL·year^{-1} capacity), where KL is depolymerized to produce depolymerized kraft lignin (DKL) as a bio-substitute to polyol and phenol for the production of bio-based polymers (polyurethane and phenolic resins). Three scenarios were examined: (i) DKL as a phenol substitute, (ii) DKL as a polyol substitute, and (iii) oxypropylated depolymerized kraft lignin (Oxy-DKL) a polyol substitute. The Net Present Value was calculated to compare these scenarios. To address the uncertainty risks in feedstock and product price, a sensitivity analysis and a Monte Carlo simulation were performed. Results show that DKL and Oxy-DKL derived from the KL biorefinery are a feasible bio-substitute for petroleum-based polyols with a minimum selling price of 1,440 and 1,623 US\$·t^{-1}, respectively. However, DKL is likely not feasible when replacing phenol (minimum selling price of 1,421 US\$·t^{-1}) due to the current low market price of phenol. The feasibility of the KL biorefinery is highly sensitive to the market prices of the products. Feedstock supply and market demand for lignin-derived biopolyols are still uncertain; therefore, a supply chain design model is necessary for decision-making.

Keywords: biorefinery; kraft lignin, depolymerized kraft lignin; biopolyols; biophenols; techno-economic analysis

3.1 Introduction

In a conventional petrorefinery, around 42% of the revenue comes from 4% of petroleum used that makes chemicals, plastics, and rubbers, while a similar revenue is generated by transportation fuels that consume over 70% of the petroleum used.[1] This suggests that chemicals and materials are much more valuable than fuels. To learn a lesson from the petrorefinery, a biorefinery shall aim at producing high-value bio-based chemicals and materials rather than biofuels. Production of high-value bio-based chemical and material products from forestry and agricultural biomass and residues thus offers an immense opportunity by not only decreasing dependence on oil, but also providing an additional revenue stream to the forestry and agricultural sectors.

Additionally, the forest industry is facing a major challenge to remain profitable due to the decline in newsprint demand and higher fibre costs.[2] This challenge has intensified interest in development of a forest biorefinery for a diversified product portfolio, aiming to transform forest biomass or forestry residues/by-products (such as lignin) into a range of high-value bioproducts.[3]

In this context, techno-economic assessment is crucial for introducing an emerging technology to the market either to provide information for investment decision-making, or to identify if more studies are necessary before implementation. A techno-economic assessment consists of several strictly interrelated phases: evaluating technical feasibility, capital costs, operating costs and revenues, and estimating the profitability using suitable measures of technical and economic profitability.[4]

Several studies can be found in the simulation, technical design, and economic and environmental assessment of lignocellulose biorefineries. Economic and technical analyses have been used to determine the feasibility of various types of biorefinery: fermentation-based sugar conversion biorefinery,[5] bio-oil gasification and fast pyrolysis biorefinery,[6,7] and an organosolv biorefinery.[8–10] Moreover, technical, economic, and environmental analyses have been applied to investigate the feasibility of a high-octane gasoline biorefinery,[11] and a beechwood-based biorefinery.[12] Such studies demonstrated the great variability of feedstock and products for various biorefineries; however, the main focus of those studies has been on the production of bioenergy and biofuels.

Therefore, the objective of this study was to demonstrate techno-economic feasibility of a kraft lignin biorefinery for the production of high-value bio-based chemicals (polyols and phenols) from kraft lignin. The analysis is based on a techno-economic and risk assessment by calculating established economic indicators, such as

Net Present Value (NPV) and using sensitivity analysis and Monte Carlo simulation to incorporate uncertainties in feedstock supply prices and bio-based products selling prices.

3.1.1 Kraft lignin opportunities

The global production of lignin, 'a complex three-dimensional biopolymer of aromatic alcohols',[13] is over 70 Mt·yr^{-1} (M: millions, t: tonnes, International System of Units SI), mainly in the form black liquor produced in kraft pulp mills.[14] It is well known that pulp mills use kraft lignin (KL) for electricity, steam, and inorganic chemicals production. However, in most of the kraft pulp mills in North America, there is a bottleneck in the capacity of recovery boilers because KL production exceeds existing design limits, while increasing the boiler's capacity requires large and unattractive investments.[3] It is more attractive to extract some excess KL from black liquor, and convert kraft lignin into high-value bioproducts, such as biopolyols or biophenols.[15–17]

There are two major commercial technologies for the extraction of kraft lignin from black liquor: the LignoBoost process and the LignoForce process. The LignoBoost process is based on the acidification of black liquor after filtration.[18] The LignoForce process developed by FPInnovations employs an extra oxidation step to convert sulfur compounds and facilitate the filtration process.[19] The West Fraser Timber Company pulp mill, in Hinton, Canada, is constructing a commercial-scale plant to recover lignin with the LignoForce process, the first of its kind in Canada, aiming to extract 30 t·day^{-1} KL for manufacture of lignin-based bioproducts.[20] And, Domtar has been extracting 75 t·day^{-1} KL since 2013, in Plymouth, North Carolina using the LignoBoost process.[21]

KL was studied for producing a variety of bio-based chemicals and materials, such as replacing phenol in the synthesis of phenolic adhesives/resins,[13,21,22,23] and polyol to produce polyurethane foams.[24,25] Globally a large amount of polyols is employed in the manufacture of polyurethane flexible or rigid foams, via reactions of polyols with an isocyanate (e.g. toluene di-isocyanate or methyl di-p-phenylene isocyanate).[25,26] Polyurethane rigid foam is widely used as insulation material in building and construction, and flexible foams are used in the furniture and automobile industries.[26]

Phenol and its derivatives, for example bisphenol A, baprolactam and salicylic acid are basic ingredients for a broad range of industry products, such as phenolic resins, polycarbonates, epoxy resins, Bakelite, nylon, detergents, herbicides, and pharmaceuticals.[27] Phenol and polyol production are mostly derived from petroleum; therefore, their price is influenced by variations on crude-oil prices.

In 2013, rigid foam was the second largest segment in the global polyurethane market, after flexible foams.[26] The demand for polyols is predicted to reach over 10.4 $\mathrm{Mt \cdot yr^{-1}}$ by 2018 (growing at 5.5% Compound Annual Growth Rate (CAGR)).[19] Moreover, bio-based chemicals are expected to increase significantly and increase their share in overall chemicals production to an estimated 9% by 2020.[20,21] However, there are still challenges for the current technologies for production of bio-based chemicals and materials on a large scale. The manufacturing cost and uncertainty in market price and demand are still the key factors that prevent more investments in these bioproducts.

Some recent studies of the authors' group have demonstrated that depolymerized kraft lignin (DKL) and oxypropylated depolymerized kraft lignin (Oxy-DKL) were used as replacements for phenols and polyols with a replacement ratio higher than 50% in the synthesis of bio-based phenol formaldehyde and polyurethane resins. For instance, insulation polyurethane foams were prepared by partially (50%) replacing commercial polyols with DKL, or totally (100%) replacing with Oxy-DKL by Mahmood *et al.*,[16] and the bio-based polyurethane foams were found to present appropriate compression strengths and thermal conductivity comparable to those of the reference foams produced with sucrose polyol and PPG400. DKL was also used to replace phenol in the synthesis of phenolic resoles resins, and the DKL PF resoles as adhesives for plywood applications achieved bond strength higher than the minimum industrial standard.[7]

It should be noted that reviewing the production of polyol and phenol in detail is not of the focus of the present paper. More information on the production and utilization of bio-based polyol and phenol from lignin, for example production of polyurethane foams from renewable sources, production of bio-polyols by depolymerization of lignins and their application in the production of rigid polyurethane foams, and production of phenolic resins from lignin, can be found in other published work by Agrawala *et al.*,[31] Mahmood *et al.*,[32] and Effendi *et al.*,[33] respectively.

3.1.2 Process description

The designs evaluated are based on KL depolymerization and oxypropylation processes improved over 5 years of research at ICFAR (Institute for Chemical and Fuels from Alternative Resources). The technology is pending for patent, and the optimized process parameters can be found in two journal publications by Mahmood *et al.*[6,16] Therefore, a comprehensive process optimization is not presented here; instead, we focus on the preliminary cost analysis for this proprietary technology.

Through direct hydrolysis in polyalcohol, using NaOH (sodium hydroxide) as a catalyst, softwood KL was depolymerized into bio-based products of slightly high hydroxyl number and yield, with moderately low weight-average molecular mass (Mw) (Table 3.1). The KL was sourced from the FPInnovations Thunder Bay Bioeconomy

Technology Centre, where the KL was extracted via the LignoForce technology developed by FPInnovations.[6] Then, the depolymerized kraft lignin (DKL) was oxypropylated (Oxy-DKL) with 50 wt% (percentage by weight) of bio-contents (DKL) using propylene oxide (PO), acetone, glycerol and potassium hydroxide (KOH) mixture. The DKL and Oxy-DKL present a lower Mw and a higher total hydroxyl number comparing to the KL (Table 1). The Oxy-DKL in liquid form is preferable for the production of polyurethane foams.[16]

Table 3.1. M_w, hydroxyl numbers and viscosity of the bio-based feedstocks.[16]

Bio-based products	M_w ($g \cdot mol^{-1}$)	Aliphatic Hydroxyl num. ($mg\ KOH \cdot g^{-1}$)	Total hydroxyl number ($mg\ KOH \cdot g^{-1}$)	Viscosity @ 80 °C (Pa s)	State of product @ room temp.
KL	10,000	128	275	-	Powder
DKL	1,700	365	671	-	Powder
Oxy-DKL	3,600	-	350	0.61	Viscous liquid

A general schematic diagram of the proposed designs for production of DKL is illustrated in Fig. 3.1. For the processes summarized earlier, three base case scenarios (I, II, and III) were proposed to evaluate the economic feasibility of DKL and Oxy-DKL to replace, or substitute phenols and polyols. A summary of each scenario with more details regarding depolymerization and oxypropylation is now given.

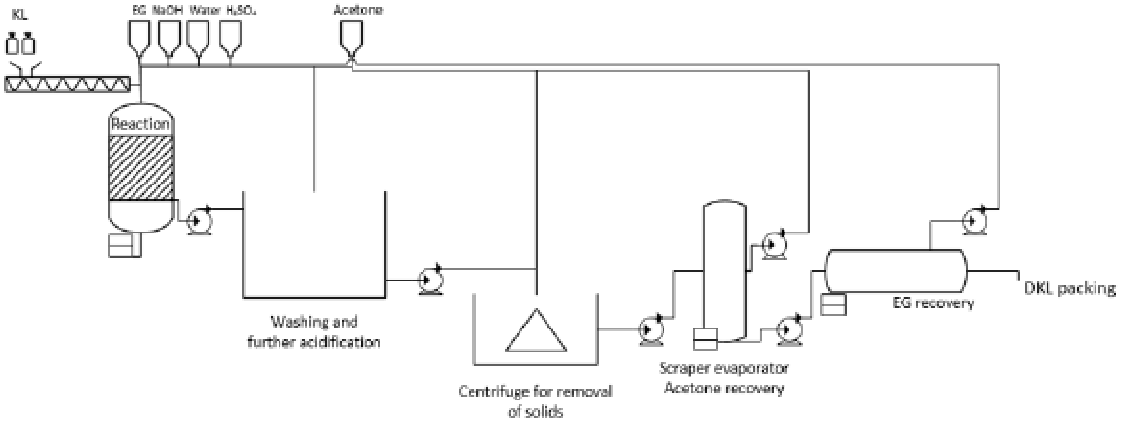


Figure 3.1. General schematic diagram of the proposed designs for production of DKL.

I. DKL_phenol: KL in the storage tank is fed into the reactor through a screw conveyor, and water, NaOH, and EG (ethylene glycol) are added to the reactor at specified mass ratio (KL:water:NaOH:EG = 1:0.21:0.28:3.51). Each run takes approximately 4 h, including a buffer time for possible delays, reactor feeding time, reactor heating time, reaction time, discharging and washing time, where in the reaction time is about 1 h and temperature is 250°C. The product consists of a cake that will be washed with distilled water, then transferred to an acidification tank where pH is adjusted to <4.0 and acetone is added to dissolve the DKL produced, then the mixture is discharged into a centrifuge filtration for removal of solid residues – a side product from the reaction, and finally to distillation in scraper evaporators to remove acetone and EG. The recycled chemicals return to the storage tanks, and the DKL powder is stored. DKL as a bio-based phenol should limit the amount of EG in its final composition to maintain a high phenolic hydroxyl number; thus, 100% recovery is assumed for this scenario (Table 3.2). The yield of final DKL product is equal to 90% of the KL weight, based on the experimental work of the authors' group (though in lab scale). [6,16]

II. DKL_polyol: DKL for polyols follows the same process described in Scenario I. The only difference is that up to 30% of EG is allowed in the final product composition, increasing the output volume, and decreasing the amount of EG recovered (Table 3.2). The yield of DKL_polyol is equal to 90% of the KL weight plus 10% of EG weight. Feasibility of producing DKL_polyol is evaluated considering its potential replacement of polypropylene glycol (PPG) and sucrose polyols for manufacture of bio-based polyurethane resins/foams.

III. Oxy-DKL_polyol: The DKL used for preparation of Oxy-DKL for polyols is produced from Scenario II. DKL, PO, acetone, and glycerol and KOH mixture are directed from the storage tanks to the pressure reactor. Each run takes approximately 4 h, wherein the reaction time is about 1.5 h and temperature is 150°C. Then the liquid solution flows to an acidification tank, then to a centrifuge for filtration and finally subject to distillation in a scraper evaporator to recycle acetone. The Oxy-DKL liquid product is stored. The yield of Oxy-DKL is essentially the weight of DKL plus PO and glycerol.[16]

Table 3.2. Savings from chemical recycle.

Scenario	DKL_polyol		DKL_phenol		Oxy-DKL_polyol
	EG	Acetone	EG	Acetone	Acetone
Consumption without recycle (Mkg·yr^{-1})	10.52	7.50	10.52	7.50	3.33
Consumption with recycle (Mkg·yr^{-1})	1.05	0.37	10.52	0.37	0.17
Reduction (%)	90	95	100	95	95
Saved costs (US\$·yr^{-1})	14.11	4.27	15.68	4.27	2.00
Saved costs (US\$·t^{-1} of product)	3,761.24	1,139.24	5,808.24	1,583.34	338.72

Chemical recycling is crucial for the feasibility of all scenarios, not only for the final product requirements, but also because EG and acetone account for the largest chemical volumes utilized in the processes. EG is also the most expensive chemical employed (Table 3.2).

3.2 Materials and methods

3.2.1 Analytical method and basis

The purchased equipment cost was estimated based on the scale-up design of the laboratory experiment using quoted purchase equipment prices for major pieces of equipment as base equipment costs and applying an appropriate scaling factor (Eqn (3.1)):

$$\text{Cost}_{\text{new}} = \text{Cost}_{\text{base}} \left(\frac{\text{Capacity}_{\text{new}}}{\text{Capacity}_{\text{base}}} \right)^{\text{Scaling factor}} \qquad \text{Equation 3.1}$$

Reliable heuristics and assumptions were applied based on Pham et al.[34] and Peter et al.[35] (Table 3.3). When necessary, the costs were updated to 2015 price indexes (Eqn (3.2))[34], and the 2016 indexes were not easily available. Quotes and literature were used when available to validate the cost estimates. As shown in Table 3, total Project Investment (TPI), i.e., the total capital cost, was estimated to be 4.32 times of the total purchased equipment cost.

$$\text{Current cost} = (\text{cost in year M}) \, \frac{\textbf{Current Index}}{\textbf{Index in year i}} \qquad \text{Equation 3.2}$$

Table 3.3. Methodology for capital and fixed operating costs estimate.[34,35]

Parameter	Estimate (%)	Factors
Total purchased equipment cost	100.0	
Purchased equipment installation	39.0	
Instrumentation and controls	26.0	
Piping	10.0	
Electrical systems	31.0	
Buildings (including services)	29.0	
Yard improvements	12.0	
Service facilities	55.0	
Total installed cost (TIC)	302.0	3.02
Engineering	32.0	
Construction	34.0	
Legal and contractors fees	23.0	
Indirect Cost (IC)	89.0	0.89
Total direct and indirect costs (TDIC)	TIC +IC	
Contingency	20.0	
Fixed Capital Investment (FCI)	TDIC + contingency	
Working capital (WC)	15.0	
Land Use	6.0	
Total Project Investment (TPI)	432.0	4.32
Labor (wages, salary and benefits)		Calculated
Overhead		60% of labor
Maintenance		2% of labor
Insurance and taxes (I&T)		1.5% of labor
Fixed Operating Cost (FOC)		Labor +overhead +maint+I&T

The price of each equipment or variable cost component was found in the literature, and commercial supplier's websites and quotes. Most suppliers provide a price range, for a minimum and maximum purchase amount. Therefore, the value assumed in this study is the average value obtained from all minimum, fixed, and maximum selling prices obtained from the suppliers. The capacity of the biorefinery scenarios varies according to the reaction yield and final product requirements. Main technical parameters, costs and revenue for the scenarios are summarized in Table 3.4. The biorefinery processes in both DKL scenarios (I and II) are basically the same, as described in the previous section, for example both have same capital and fixed costs (Table 3.4). The variable cost changes according to the production capacity, and chemicals consumption and recovery. The capital cost of the Oxy-DKL_polyol is lower than in the other scenarios because it uses DKL from Scenario II directly as a feedstock, and only one chemical needs to be recovered in this process.

Table 3.4. Main technical parameters and costs and revenue for the scenarios.

Parameter	Scenarios		
	DKL_phenol	DKL_polyol	Oxy-DKL_polyol
Total Project Investment (TPI) (MUS$)	4.03	4.03	3.33
Variable operating cost (MUS$·yr^{-1})	2.70	4.27	8.08
KL	1.80	1.80	-
NaOH	0.10	0.11	-
Water for the reaction	0.0003	0.0003	-
EG	0.00	1.57	-
Sulfuric acid	0.01	0.01	0.002
Acetone	0.23	0.23	0.10
DKL	-	-	3.63
PO	-	-	3.37
Glycerol	-	-	0.40
KOH	-	-	0.03
Utilities	0.55	0.55	0.55
Fixed operating cost (FOC) (MUS$·year^{-1})	0.72	0.72	0.69
Depreciation (MUS$·year^{-1})	0.03	0.03	0.02
Capacity (t·yr^{-1})			
Feedstock (KL or DKL)	3,000.00	3,000.00	2,500.00
Final product (DKL or Oxy-DKL)	2,700.00	3,752.50	5,610.00
Selling price (US$·t^{-1})			
Polyol average selling price	-	1931.11	1931.11
Phenol average selling price	1,412.51	-	-

The economic indicators most often used to evaluate the economic feasibility of industrial processes, such as biorefineries and energy plants, are the NPV, and the

Internal Rate of Return (IRR).[23,26,30,33] The NPV is the surplus generated by an investment at the beginning of the planning horizon in regard to the return rate applied (Eqn (3.3)). In order to calculate the NPV, a cash flow has to be created, including the cost and revenues of the project.

$$NPV = -Z_0 + \sum_{t=0}^{T} \frac{R_t + D_t}{(1 + DR)^t} \qquad \text{Equation 3.3}$$

$$IRR = DR, \text{by setting } NPV = 0 \qquad \text{Equation 3.4}$$

Where: Z_0 is the value of investment costs at time zero (t_0), R_t and D_t are the revenue and disbursement at the end of period t, respectively.

A break-even analysis was performed to identify the minimum selling price for the scenarios. It consists of the Present Value (PV) of fixed and variable costs divided by the present value of the units produced (Eqn (3.4)). In other words, the minimum selling price is the price that generates an NPV equal to zero.[34]

$$Minimum\ Selling\ Price = \sum_{t=0}^{T} \frac{PVcosts}{PVprodution} \qquad \text{Equation 3.4}$$

A linear depreciation method was applied considering an equipment's economic lifespan of 25 years, which is most commonly used for new technologies.[37-36] A one-year start-up time is considered; therefore, there is no profit in the first year, and the biorefinery works three 8 $h \cdot d^{-1}$ shifts for 250 $d \cdot yr^{-1}$ - which is a conservative estimate, a higher number of days per year would return even more profitable outcome. The return rate used in this study is 10%; the return rate, also called minimum attractive rate return, is used in cash flows to determine the present value of future cash flows. It reflects uncertainty on the process performance to introduce several hidden costs that cannot be foreseen, it also remunerates the investment. Other studies have considered a range of 8% to 15%; for example, 8.3%;[8] 10%;[8,38,39] 12%;[40] and 15%.[37]

3.2.2 Sensitivity and risk analysis

For the three scenarios, the NPV and minimum selling price were calculated using the most likely parameters (deterministic) shown in Tables 3.3 and 3.4 (represented by the X column). Then, a sensitivity analysis for the NPV, varying the TPI (i.e., the total capital cost), feedstock cost, operational costs, and polyol and phenol prices, was performed in Microsoft Excel® considering the minimum (X_{min}), X, and maximum (X_{max}) values of each parameter (Table 3.5).

The results from the deterministic sensitivity analysis helped to identify which uncertain parameters mostly affect the feasibility. Those parameters were then included in the investment risk analysis through a Monte Carlo simulation. The simulation was executed in the Analytic Solver Platform V2016-R3 (16.5.1.0) for Education, Copyright© 2016 Frontline Systems, Inc., and 10,000 runs were calculated considering random variables according to the probability distribution. A triangular distribution, frequently used in similar studies, for example Machado et al.[37] and Sastre et al.,[41] was assumed when the minimum, maximum a most likely values were available, and when there was no historical data available at no cost to analyze the price fluctuations.

Table 3.5. Variations assumed in the sensitivity and risk analysis.

Parameters	Scenario	X_{min}	X	X_{max}	Distribution
EG (US\$·kg^{-1})[a]	DKL_phenol, DKL_polyol	1.10	1.49	1.88	Normal (2s)
Polyol price (US\$·t^{-1})[b]	DKL_polyol, Oxy-DKL_polyol	1,000.00	1,931.11	2,600.00	Triangular
Phenol price (US\$·t^{-1})[b]	DKL_phenol	900.00	1,412.50	1,800.00	Triangular
PO (US\$·kg^{-1})[c]	Oxy-DKL_polyol	0.96	1.20	1.44	Normal (2s)
FOC (MUS\$)[d]	DKL_phenol, DKL_polyol	0.57	0.72	0.86	Triangular
FOC (MUS\$)[d]	Oxy-DKL_polyol	0.55	0.69	0.83	Triangular
TPI (MUS\$)[d]	DKL_phenol, DKL_polyol	3.43	4.03	4.63	Triangular
TPI (MUS\$)[d]	Oxy-DKL_polyol	2.83	3.33	3.83	Triangular
KL cost (US\$·kg^{-1})[c]	DKL_phenol, DKL_polyol	0.40	0.60	0.80	Normal (2s)
DKL cost (US\$·kg^{-1})[d]	Oxy-DKL_polyol	1.16	1.45	1.74	Triangular

a Historical data interval was used to estimate the standard deviation 13%.[42]
b Minimum and maximum prices obtained from quotations of commercial scale polyol and phenol producers. c Assuming a standard deviation of 10%. d Assuming 15% variation on the most likely value.

3.3 Results and discussion

3.3.1 Economic analysis for various scenarios

Considering the most likely values (X, Table 5) the economic analysis results for the three scenarios as described previously, for the production of DKL and Oxy-DKL as a bio-based substitute for petroleum-based phenol and polyols, are presented in Table 6. DKL as a replacement for phenol is unfeasible due to the current low market price of phenol. The minimum selling price (1,420.5 US\$·t^{-1}) of DKL_phenol is slightly higher than the average commercial price of phenols (1,412.5 US\$·t^{-1}).

The DKL_polyol and Oxy-DKL_polyol scenarios; however, showed similar promising economic results. The higher NPV for the DKL_polyol (MUS\$ 16.73) is a con- sequence of the lower variable costs (chemicals mainly) leading to a lower minimum selling price (1,440.0 US\$·t^{-1}) compared to Oxy-DKL_polyol (1,623.3 US\$·t^{-1}).

Table 3.6. Main economic indicators to evaluate project feasibility for the deterministic scenarios.

Indicator/scenarios	DKL_phenol	DKL_polyol	Oxy-DKL_polyol
NPV (MUS$)	-0.20	16.73	15.67
Minimum Selling Price (US$·t^{-1})	1,420.5	1,440.0	1,623.3
Average commercial Price (US$·t^{-1})	1,412.5	1,931.1	1931.1

It is important to stress that the results presented in Table 3.6 are before taxes for all scenarios. Assuming an income tax of 30%, the NPV would drop to the following, DKL_phenol MUS$ -1.3, DKL_polyol MUS$ 10.5, and Oxy-DKL_polyol MUS$ 10.0. The scenarios of DKL_polyol and Oxy-DKL_polyol are still feasible after 30% of taxes. Another factor to be considered is the form of the final product. The Oxy-DKL final product is in liquid form; therefore, it is not necessary to dissolve in a solvent before foam production, which is desirable, as opposed to DKL being in solid form that requires dissolving in a solvent, increasing costs for the foam production. Besides, the Oxy-DKL was proven to form better quality PU foam when replacing 100% of the petroleum-based polyol.[25]

Regarding the overall cost breakdown, the main cost for the production of DKL_polyol is the KL (33.3%) followed by the EG (29.0%). The EG is the most expensive chemical and has the highest consumption among the chemicals used in the reaction. Therefore, even recovering 90% of the EG, the remaining 10% needs to be purchased, which accounts for the second largest cost component in the DKL_polyol scenario (Fig. 3.2). For the DKL_phenol scenario where 100% of EG is assumed to be recovered, KL (46.9%) is also the principal cost component. Whereas, for Oxy-DKL_polyol, the DKL and PO account for almost 76% of the costs. The feedstocks are thus the principal source of cost in all scenarios (Fig. 3.2), as commonly reported in other studies.[6,7]

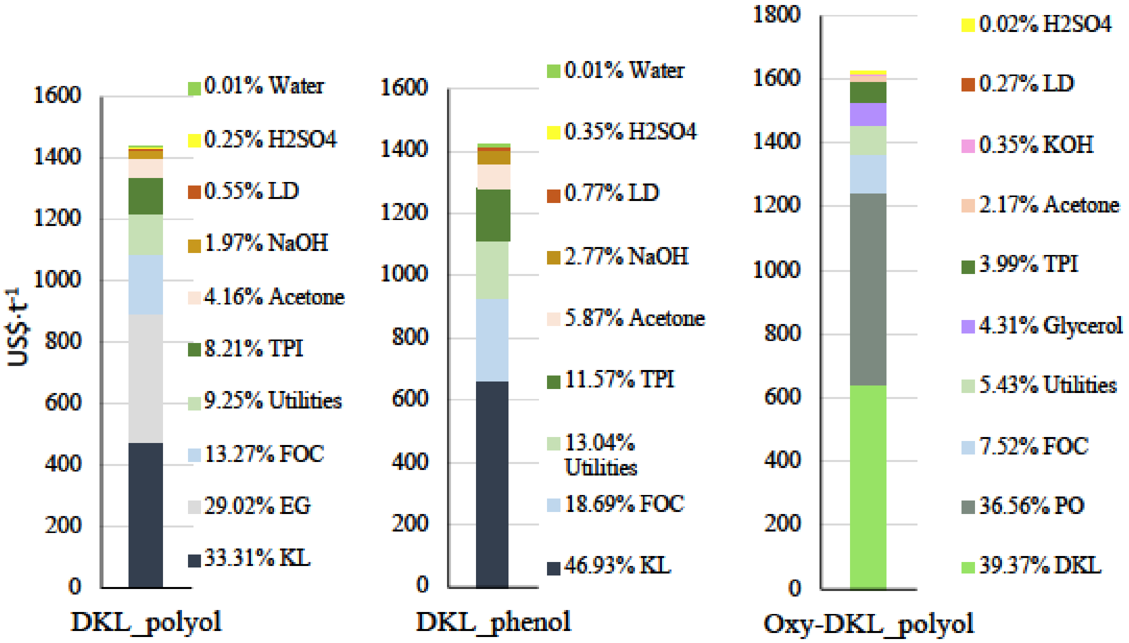


Figure 3.2. DKL-based polyol and phenol cost components' weight.

Abbreviations: H_2SO_4: sulfuric acid; NaOH: sodium hydroxide; TPI: total project investment; FOC: fixed operating cost; KL: kraft lignin; DKL: Depolymerized KL; PO: propylene oxide; EG: ethylene glycol; KOH: potassium hydroxide LD: linear depreciation.

As indicated in Fig. 3.2, the TPI (calculated from the total purchased equipment cost) accounts for only about 4–12% of the final production costs of the three products, being insignificant when compared with the costs of raw materials. In more detail, the total purchased equipment cost for production of DKL can be broken into the following: reaction and recycling 45%, filtration 20%, heat exchangers 14%, storage and feed system 10%, and other 11% (e.g. pumps, valves). Similarly, for the production of Oxy-DKL the total purchased equipment cost is as follows: reaction and recycling 39%, filtration 23%, heat exchangers 16%, storage and feed system 12%, and others 10% (e.g. pumps and valves).

Figure 3.3 presents DKL-based phenol and polyols MSP in comparison with their potential commercial products prices. As shown in Fig. 3.3, the MSPs fall within the price range of its potential commercial product, and phenol has a lower market value than polyols. Using Oxy-DKL_polyol to replace PPG400 seems to be the most promising option. As observed in Fig. 3.3, the industrial price range of phenol (CAS: 108-95-02) varies from 900 to 1800 US$·t^{-1}. The lower phenol price compared with polyols is the primary cause of the infeasibility of the DKL_phenol scenario. For further analysis of the economic feasibilities of various scenarios, sensitivity analysis has been performed and the results are presented in the next section to demonstrate changes in the NPV by varying the selling price of target products (phenols and polyols).

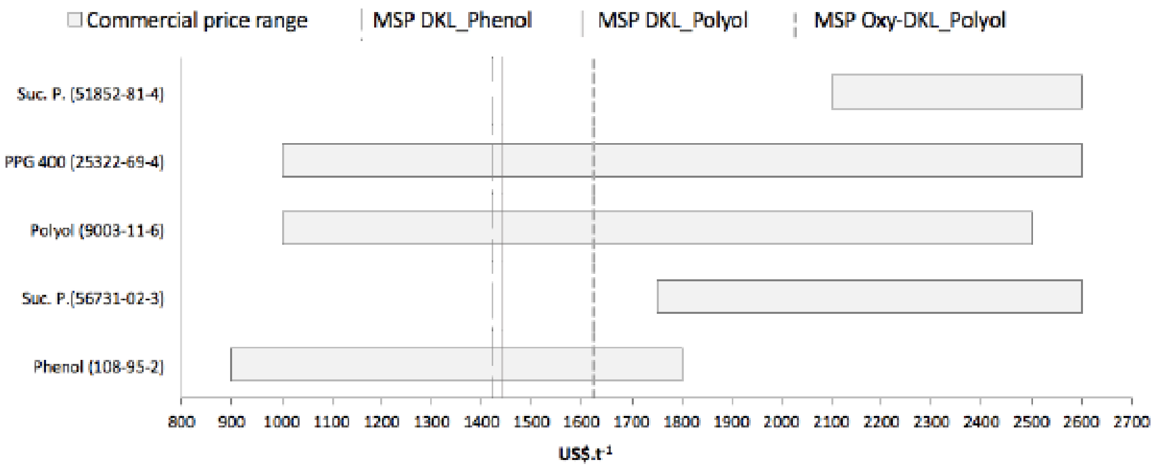


Figure 3.3. DKL-based phenol and polyols minimum selling price (MSP) in comparison with their potential commercial products prices.

Abbreviations: Suc. P.: sucrose polyol; PPG400: polypropylene glycol 400.

3.3.2 Sensitivity and risk assessment

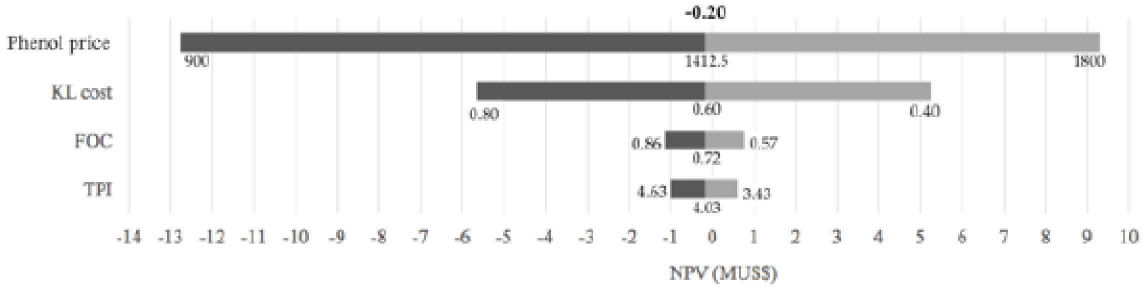
Feasibility of a new technology brings inevitable uncertain- ties, not only in the design to define equipment capacities and costs, but also on the final products prices and feedstocks costs. A deterministic sensitivity analysis was performed for all the costs (capital/fixed and variable) and the parameters with most significant impact on the feasibility are presented in tornado graphs (Fig. 3.4), where the NPV for each scenario is provided by varying one parameter at the time. The units of all parameters are presented in Table 3.5.

As shown in Figs 3.4 (a), (b), and (c), the NPV for all scenarios is most sensitive to the selling price of the final product, and the price range considered in this study was collected from online quotes with industrial scale suppliers. The DKL_polyol and Oxy-DKL_polyol scenarios result in a negative NPV if selling price of the polyol drops by 26.5% and 25.4%, respectively. A slight increase in the phenol price results in a positive NPV for the DKL_phenol scenario. The polyol and phenol prices are linked to petroleum price fluctuations, and market supply and demand.

In addition to the selling price of the final product, the feedstock cost also considerably affects the NPV. For instance, varying the price of KL in the DKL_polyol scenario and the price of PO in the Oxy-DKL scenario alters the NPV by 32.6% and 39.0%, respectively. On the other hand, all three scenarios are less sensitive to the fixed operating cost and total project investment. For instance, for the fixed operating cost and total project investment have a higher impact than the EG cost, they should vary at least ~ 85% from their fixed values in the deterministic scenarios.

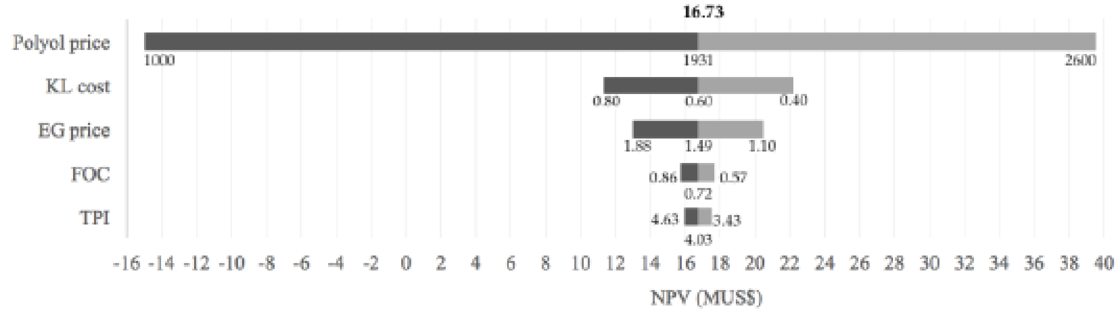
(a)

DKL_phenol



(b)

DKL_polyol



(c)

Oxy-DKL_polyol

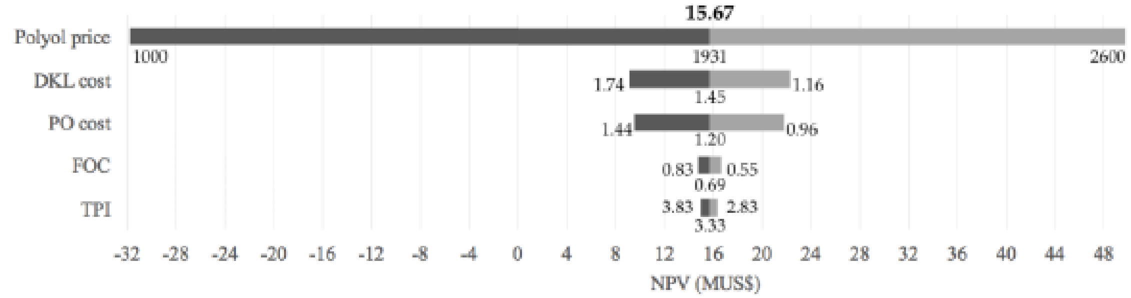


Figure 3.4. NPV deterministic sensitivity analysis of the scenarios by varying one parameter at the time.

A sensitivity analysis on the EG recovery was performed for the DKL_polyol scenario. It was found that the highest NPV (MUS$ 20.94) is obtained when 80% of the EG is recovered and 20% remains in the final product. This is explained by the increase in product yield; therefore, the revenue gains by remaining some EG in the product is higher than the savings from recycling EG.

Another important factor for consideration is the return rate. The rate that would generate zero returns (NPV = 0) for the scenarios, also called internal rate of return is as follows: DKL_phenol 9.4%, DKL_polyol 56.8%, and Oxy-DKL_polyol 62.84%. For all scenarios, the return rate considered is 10%; therefore, higher than the internal rate of return of found for the DKL_phenol scenario, which explains negative NPV for this scenario.

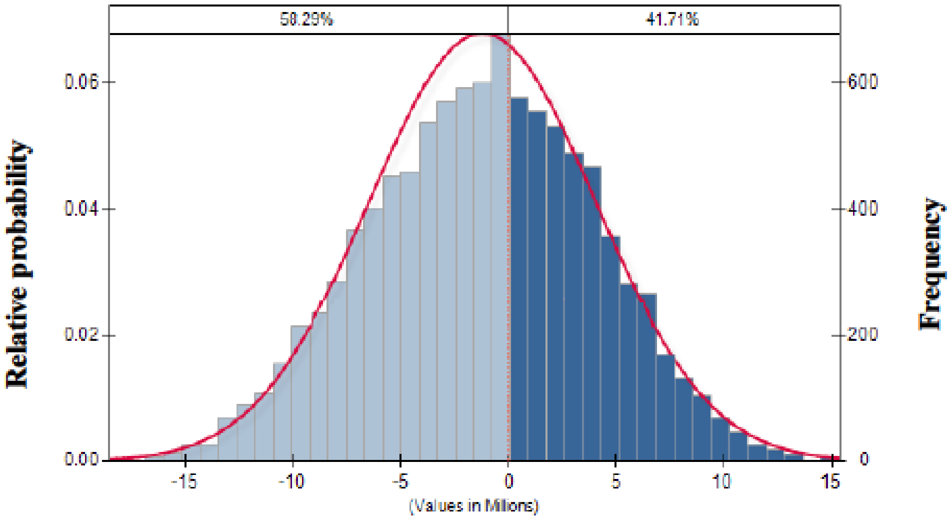
A Monte Carlo analysis was run for the three scenarios, varying randomly the parameters presented in Table 3.5. Figures 3.5(a), (b), and (c) show the results for the NPV with a 95% confidence interval for each scenario. The Monte Carlo analysis demonstrates that the DKL_polyol and Oxy-DKL_polyol scenarios are more feasible with and mean NPV of MUS$ 13.75 and 11.22, respectively, while the DKL_phenol scenario is less feasible, with 58.3% of the NPV results below zero, following the same tendency observed in the deterministic analysis as discussed previously.

The Monte Carlo analysis resulted in lower NPVs compared to those of the deterministic base case and sensitivity results (Fig. 3.5). This demonstrates that still with great variation in the main cost drivers the DKL_phenol and Oxy-DKL_polyol are attractive options to compete in the petroleum-based polyols market.

(a)

DKL_phenol

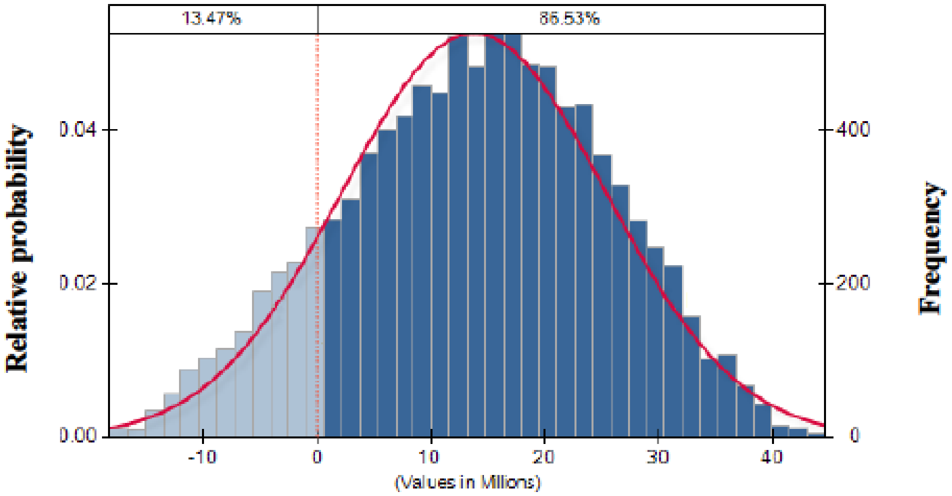
MC NPVs:
Mean: -1.22
Min: -18.54
Max: 15.32
Deterministic NPV: -0.20



(b)

DKL_polyol

MC NPVs:
Mean: 13.75
Min: -18.33
Max: 44.71
Deterministic NPV:
16.73



(c)

Oxy-DKL_polyol

MC NPVs:
Mean: 11.22
Min: -31.41
Max: 49.67
Deterministic NPV:
15.67

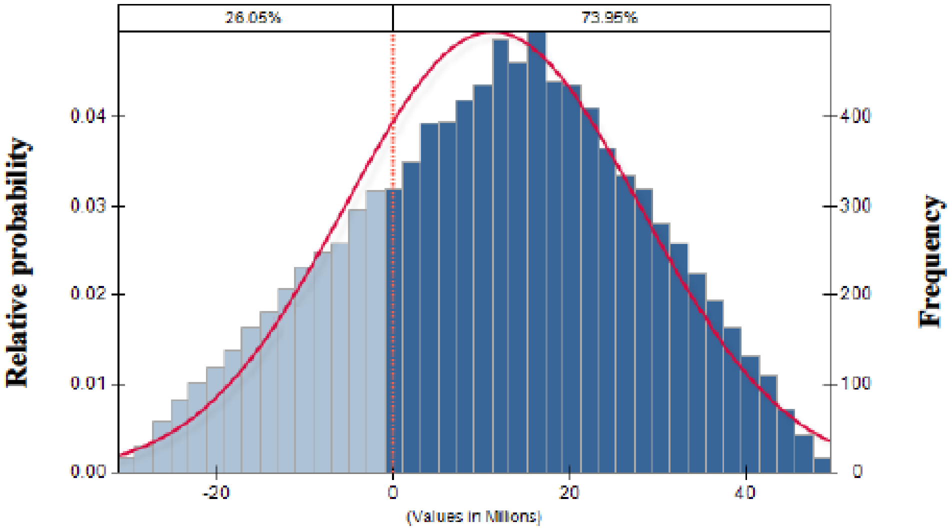


Figure 3.5. Monte Carlo analysis for NPV (MUS$) of various scenarios (mean value ±2 standard deviations).

3.4 Conclusions

Evaluating the market readiness of bio-based products is a challenging task, surrounded by uncertainty. Thus, this study provides a techno-economic and risk assessment of a kraft lignin biorefinery (3000 tonne of KL·year^{-1} capacity) for production of polyols and phenols. Three technology scenarios were evaluated for their feasibility represented by net present value results. A risk analysis was also performed through a Monte Carlo simulation varying final products price, main supply costs, fixed operational costs, and total project investment (i.e., total capital cost). Depolymerization of kraft lignin and further oxypropylation of the depolymerized kraft lignin are promising technologies for the production of substitutes for petroleum-based polyols. The Oxy-DKL_polyol scenario has the advantage of yielding a liquid product that can be directly used to replace commercial polyols in the production of polyurethane foams.

The sensitivity analysis showed that the selling prices of the final products and feedstock costs are the main factors influencing the feasibility of all scenarios. Although the total project investment (US$3.33–4.03 million) presented a lower impact on the probability compared to the other parameters evaluated, it is still a highly uncertain parameter. The lack of pilot and commercial scale production of bio-based chemicals adds to the challenge of providing accurate estimates for equipment costs. However, preliminary studies of these technologies can provide directions of lignin valorization for high-value bioproducts.

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CHAPTER 4 – Capacity Design of Kraft Lignin Biorefinery for Production of Bio-phenol via a Proprietary Low-Temperature/Low-Pressure (LT/LP) Lignin Depolymerization Process

ABSTRACT

In Canada, there is a kraft lignin (KL) surplus of ~1.06 million (M) t·year^{-1} (after ensuring pulp mills' recovery boiler demand). This KL supply can create a US$1.5 billion lignin-based bioproducts industry. Lower molecular weight and higher reactivity depolymerized kraft lignin is a promising bio-based replacement for petroleum-based chemicals such as phenols and polyols for the synthesis of biophenol formaldehyde or biopolyurethane resins. This work provides an economic analysis for biophenol production of a proprietary KL depolymerization process for eight scenarios with a KL treatment capacity ranging from 10,000 t·year^{-1} of KL to 120,000 t·year^{-1} and two recovery percentages (85% and 90%). The eight scenarios were examined on capital investment, manufacturing cost, net present value (NPV), and discounted payback period (PBP). A risk assessment through Monte Carlo analysis is presented to address uncertainties in capital investment, main raw materials cost, and biophenol selling price. From the analysis, the total variable manufacturing costs varies from ~1,081 up to 1,101 US$·t^{-1}, and the total fixed manufacturing costs from ~63 to 154 US$·t^{-1}. All scenarios are feasible; however, in small KL capacities, such as 10,000 t·year^{-1}, the investment is less attractive yielding a PBP longer than 5 years. Although, KL capacities above 40,000 t·year^{-1} lead to ~3-year PBPs and high NPVs (above US$35M). The risk analysis demonstrated that lignin-based phenol production is susceptible to biophenol price and KL cost variations.

Keywords: economic analysis, biorefinery, kraft lignin, depolymerized kraft lignin, biophenol, plant capacity, monte carlo simulation.

4.1 Introduction

A shift in industry preference to bio-based products due to the need of reducing dependence on fossil sources is expected to continue as a major key for bio-based products market growth. This will result in an increased interest in research on renewable lignocellulosic resources conversion for niche applications. A variety of lignocellulosic biomass resources have been used for producing bioenergy and biochemicals. These include agricultural residues (e.g., corn stover), herbaceous crops (e.g., switchgrass), forestry residues (e.g., sawdust) and industrial residue/waste (e.g., black liquor).[1] Among the lignocellulosic biomass resources, lignin – "complex three-dimensional bio-polymer of aromatic alcohols" [2]- has attracted growing interest in the production of bio-energy, and bio-based chemicals and materials because of its abundance and chemical nature. Lignin is the second largest available renewable bio-polymer on Earth, second only to cellulose. Considering that lignin makes up 20-35% of the dry mass of woody plants, in the biosphere lignin surpasses 300 billion tonnes. Although not all lignin is available, a renewable resource of this magnitude cannot be overlooked.[3]

Most of the technical lignin produced worldwide is a by-product of industrial processes and currently used for energy production. While producing energy is still of enormous importance, other biomass sources such as wood waste hog fuel of lower cost and not suitable for the production of high-value products should be considered for energy generation. In the conventional petroleum refinery, around 42% of its revenue is from petrochemical products (chemicals, plastics and rubbers) derived from 4% of total petroleum consumption, while a similar revenue is generated by transportation fuels that consume over 70% of the resource.[4] This suggests that producing chemicals and materials from lignin can create higher revenue than just energy production. Therefore, the goal of a biorefinery should be focused on production of high-value bio-based chemicals and materials rather than bioenergy only.

Fortunately, a shift in lignin utilization towards value-added applications is occurring in North America. Although kraft lignin is currently used mainly for the production of bioenergy in pulp mills, 60-70% of the recovery boilers in North America have capacity limitations (bottleneck) which results in a surplus of lignin. This excess of lignin is now beginning to be extracted for the production of bio-based chemicals and materials. For example, West Fraser adopting FPInnovations' LignoForce™ technology started to remove 30 $t.day^{-1}$ excess lignin in its pulp mill in Hinton, Alberta, aiming for higher value-added applications, such as resins.[5]

Due to the phenolic nature of lignin it can be utilized for a number of value-added applications,[6] such as oil and gas applications (as corrosion inhibitor, oil recycling enhancer), construction (as asphalt extender, concrete admixtures, non-wood resin), thermoplastics (as wood-plastic composites, activated carbon and carbon fibre), biochemicals (as dispersants, polyols and foams for insulation), and bio-phenol formaldehyde (BPF) resins used in engineered wood products (e.g. plywood and standard oriented boards).[5] However, the lower reactivity and high steric hindrance effects due to lignin's branched structure limit its direct use to substitute petroleum-based chemicals and materials.[7] Consequently, chemical modification is necessary to facilitate lignin use for bio-based products.[8] For instance, liquefaction of lignin to form monomeric and oligomeric phenolic compounds represents a promising route for production of phenolic resin precursors.[6]

Despite extensive research on bio-phenols production from lignocellulosic materials, its economic feasibility is still uncertain. According to Biddy et al.[9], biorefinery development relies on a technical and economic investigation to detect cost drivers, prioritize research directions and alleviate scaling-up risks. Sustainable feedstocks and cost-effective and efficient conversion technologies are the key to the production of bioproducts, biofuels and bio-polymers.[10] A preliminary study by the authors on a pilot scale-biorefinery to produce bio-phenol by lignin depolymerization showed that at 2017 market prices, bio-phenols production is not economic feasible.[11] Capital and labor expenses are not linear functions of capacity; they normally reduce as plant size increases.[12] Therefore, in this study we aimed to explore the impact of production capacity, selling price and chemicals recycling variations on economic feasibility of bio-phenols production.

The goal is thus to assist answering the question "Will lignin-derived phenols represent a new frontier in the technology of biomass conversion?".[10] This work presents economic assessment of a biorefinery based on a proprietary (LT/LP) kraft lignin depolymerization process developed by the authors' group for the production DKL as a bio-phenol in various capacities for the manufacture of BPF resins. In addition to plant capacity, effects of product price and chemical recycling on the economic assessment of this technology were also investigated in order to identify the best way to achieve economic production of bio-phenols from kraft lignin. Moreover, a risk analysis was performed to discuss lignin-based phenol production uncertainties.

4.2 Material and methods

4.2.1 Kraft lignin availability in Canada

Kraft pulp mills location and, pulp capacity data were gathered from Forest Products Association of Canada (FPAC), Pulp and Paper Technical Association of Canada (PAPTAC) and Natural Resources Canada (NRCAN) websites as well as pulp companies' websites and reports.

The KL availability data were estimated based on the recovery boiler capacities and requirements in the following manner: every 1 t of kraft pulp generates 1.7 t of black liquor solids of which about 35% is lignin, which corresponds to 0.595 t of KL per t of pulp. Considering that the recovery boiler requires a minimum calorific value of 2,890.8 $kcal \cdot kg^{-1}$ to avoid blackouts, every 1,000 t of pulp produced allows for the extraction of about 150 t of lignin in the case of softwood mills (the calorific value of the liquor is about 3,335.6 kcal·kg^{-1}) and 75 t in the case of hardwood mills (the calorific value is about 3,113.2 kcal·kg^{-1}). Since most of the Canadian kraft pulp mills use softwood, we assumed a weighted average up to 0.125 t of lignin available per 1 t of pulp produced.[13] For instance, a pulp mill with the capacity to produce ~540,000 t·year^{-1} of pulp could supply ~67,500 t·year^{-1} of KL.

On average a Canadian pulp mill has a KL surplus of 46,270 t·year^{-1}; therefore, from the 23 pulp mills around 1.06 Mt·year^{-1} are available and can be used for production of value-added bio-based products. The intensity map presented in Figure 4.1 gives a visual representation of the sources of KL in Canada and provides an overview of prospective locations for KL biorefineries. A summary of six main KL supply regions is described below and can be identified in Figure 4.1:

i. Three Canfor pulp mills located in Prince George, British Columbia (BC), with a total KL availability of 137,445 t·year^{-1}, are illustrated by the red circle in North BC on the map.

ii. Three mills located in Port Mellon (Paper Excellence, 53,104 t·year^{-1} of KL), Nanaimo (Harmac, 45,607 t·year^{-1} of KL) and Crofton (Catalyst, 47,106 t·year^{-1} of KL), are represented by the red circle in Vancouver Island on the map.

iii. Two pulp mills, Mercer in Castlegas, BC (64,974 t·year^{-1} of KL) and Domtar in Kamloops, BC (44,232 t·year^{-1} of KL), are shown in the highlighted region South of BC close to the US and Alberta (AB) borders.

iv. The Alberta-Pacific Forest Industries Inc. kraft mill, in Boyle, AB, alone generates 81,217 t·year^{-1} of KL, which is indicated by the circle concentrating just in North Edmonton.

v. The Resolute Forest Products in Thunder Bay, Ontario (ON) generates 67,348 t·year^{-1} of KL, indicated as a strong blue circle in Northwestern Ontario. A US$ 4.5M investment was announced in 2016 for the extraction of KL at the plant.

vi. A Domtar pulp mill in Windsor, Quebec (QC) generates a surplus of 55,853 t·year^{-1} of KL, represented by the blue circle close to Montreal on the map.

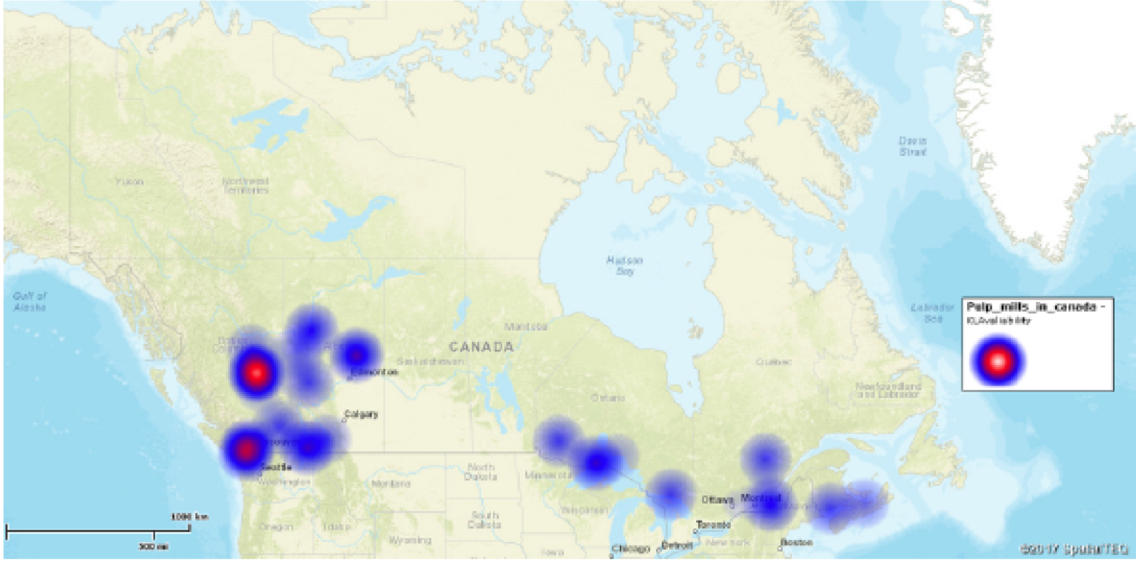


Figure 4.1. Kraft lignin availability in Canada. Developed in ESRI - Map Business Online (student free trial).

The above KL supply availability and location of the mills were considered to define the capacity scenarios. The West Fraser Timber Co. KL extraction plant, in Hilton AB, has a capacity of 30 t·day^{-1} of KL (rough estimate of 9,000 t·year^{-1}); hence, we assumed 10,000 t·year^{-1} as the minimum plant capacity for the scenarios. And, a maximum plant capacity of 120,000 t·year^{-1} based on the supply capacity of the Canfor plants in BC. Another two medium KL capacities of 40,000 t·year^{-1} and 80,000 t·year^{-1} were evaluated considering that on average each pulp mill can produce 46,270 t·year^{-1} of KL and in some regions the pulp mills are located near each other.

For the two low capacities the transportation cost was assumed to be zero because in these scenarios a lignin-based phenol biorefinery plant can be built in the mill itself; however, for high capacity scenarios, an average transportation cost of 2.0 US\$·t^{-1} and 5.0 US\$·t^{-1}, respectively, was added to the KL cost. These costs are an average based on a transportation problem designed to minimize transportation costs, considering the 6 locations presented previously, plant sizes, truck transportation costs and the road network connecting the mills.

4.2.2 Lignin-based phenol biorefinery design

The target lignin-based phenol biorefinery plant was designed based on a proprietary KL depolymerization process. In this process, KL was depolymerized through direct hydrolysis into depolymerized kraft lignin (DKL), using NaOH as a catalyst and ethylene glycol (EG) as the solvent. Under the optimized process conditions, the DKL product obtained has a high hydroxyl number (671 mg KOH·g^{-1}) and high yield (up to 90%), and a relatively low weight-average molecular weight M_w = 1,700 g·mol^{-1}.[14] A simplified process flow diagram of the KL depolymerization process is presented in Figure 4.2, and the mass flow balance for the KL depolymerization plant with 10,000.0 t·year^{-1} KL capacity and 90% EG recovery is available in the appendix (Table 4.S1). More details on the process technical optimization can be found in our research group previous publications.[14–19]

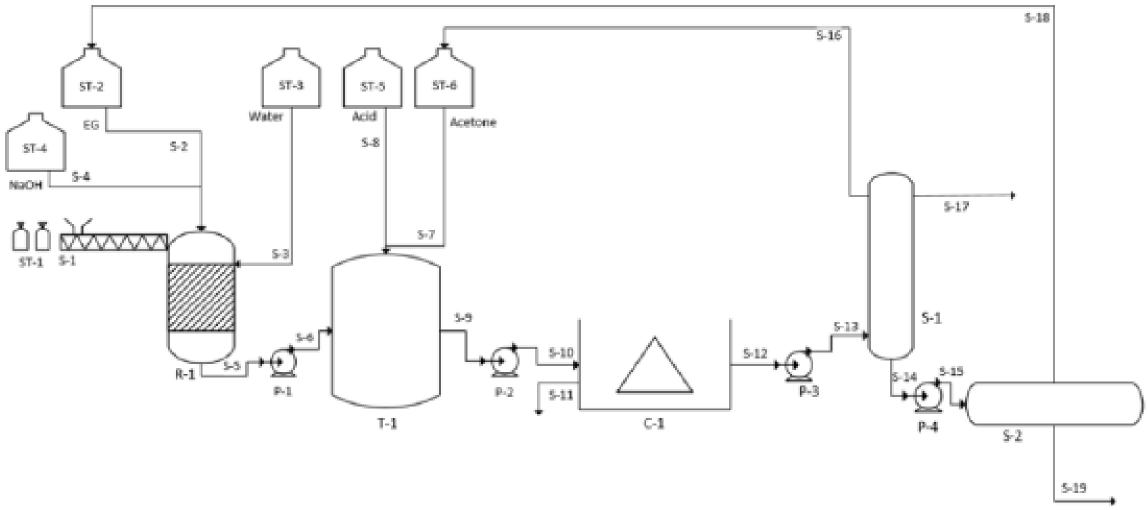


Figure 4.2. A simplified process flow diagram of the KL depolymerization process.

ST: storage tank; s: stream; R: reactor; P: pump; T; titration tank; C: centrifuge; and, S: scraper evaporator.[11]

The DKL as a substitute for phenol should not contain more than ~20% EG in its final composition to maintain satisfactory properties of BPF resins employing the DKL; thus, two recovery scenarios of 90% and 85% were considered. The yield of final DKL product is equal to 90% of the KL weight plus the amount of EG not recovered in each scenario.[14] As explained previously, four capacity scenarios are considered and two recovery percentages (Table 4.1). In this paper, the terms DKL and bio-phenol are used interchangeably to identify the end-product of the designed KL depolymerization process.

Table 4.1. Bio-phenol capacity and recovery scenarios examined.

Scenarios	Sc1	Sc2	Sc3	Sc4	Sc5	Sc6	Sc7	Sc8
KL capacity (t·year^{-1})	10,000	40,000	80,000	120,000	10,000	40,000	80,000	120,000
EG recycling (%)	85	85	85	85	90	90	90	90

4.2.3 Capital and manufacturing costs estimates

The equipment cost for a base-case design of a 3,000.0 $t \cdot yr^{-1}$ KL depolymerization pilot plant was reported in a recent publication of the authors.[11] To update the purchased equipment cost for higher capacities, Equation (4.1) [20] was applied when necessary, which is commonly used method for new processes/technologies when no cost data is available. [21,22]

$$\mathrm{Cost}_{\mathrm{new}} = \mathrm{Cost}_{\mathrm{base}} \left(\frac{\mathrm{Capacity}_{\mathrm{new}}}{\mathrm{Capacity}_{\mathrm{base}}} \right)^{\mathrm{Scaling\ factor}} \qquad \text{Equation 4.1}$$

This method should not be used alone because there are costs that cannot be estimated by this simplified method; for instance, reactor capacity limitations result in the need for multiple reactors instead of one unreasonably large reactor. Therefore, in our analysis the equipment cost was updated for each biorefinery capacity for each scenario in detail, considering the specifics of equipment size and material. When necessary scaling factors were used following some literature references.[23] For the major equipment, costs based on quotes and literature search were compared with graphical cost estimation methods.[24] All equipment costs were updated to 2016 when needed (2017 cost indexes were not yet available). The cost sources were examined, and the most reasonable costs were chosen for the calculations.

The fixed capital investment includes equipment purchase costs, installation, instrumentation and controls, piping, electrical systems, buildings, yard and service facilities, engineering, contractor fees, construction and contingency. [24] A high contingency value of 20% was considered to account for the uncertainty in the costs.

Manufacturing costs include variable costs, such as chemicals used in the manufacture and electricity. Fixed operating costs comprise labor, overhead, maintenance, insurance and property taxes. Lastly, 5% of the total fixed capital investment was assumed as working capital that a company needs to hold to cover its day-to-day operations.[25,26] The percentage (5-15%) is usually higher for companies manufacturing a variety of products.[24] More details on the costs, prices and financial assumptions, and sources are given in the appendix material Table 4.S2. It was assumed that the plant will be located within a pulp mill, so some costs can be reduced, such as site preparation, and wastewater treatment and utilities. The start-up time of one year is also assuming the advantages of co-locating the plant.

4.2.4 Economic analysis

The financial metrics of net present value (NPV) and payback period (PBP) were calculated for all scenarios. The NPV is the profit generated by a project discounted to the start of the planning horizon applying a return rate. The PBP corresponds to the period of time to recoup an investment based on a discounted cash flow.[11] The economic assessment was performed in Microsoft Excel®, as well as the mass flow, flowrate and equipment size calculations. Microsoft Visio® provided the platform for the block diagrams and process flowsheets. A hurdle rate of 16% was applied in the discounted cash flow.[25] Phenol price was calculated at 1,303.9 US$·$t^{-1}$ and EG 908.2 at US$·$t^{-1}$, based on the average historical prices in North America.[27–32] Kraft lignin was assumed at 600.0 US$·$t^{-1}$. And, a tax rate of 25% was applied to the profit. Table 4.S2 of the supporting information brings all costs, prices, sources and assumptions used in this study.

Sensitivity and Monte Carlo simulation: A deterministic sensitivity was first performed to identify the costs that most impact the feasibility of the scenarios. The scenarios of 40,000 t·year^{-1} KL capacity at 85% EG recovery (Sc2), and 10,000 KL capacity at 90% EG recycle (Sc5) were selected for the sensitivity analysis. Sc2 presents an approximate to the average KL availability in a Canadian kraft pulp mill, and the Sc5 was chosen because it presents the lowest economic performance among all scenarios.

For the deterministic sensitivity analysis, the inputs of bio-phenol selling price, EG cost, KL cost, acetone cost, capital investment, acid cost, NaOH cost and utilities cost were analyzed with regards to their impact on the NPV (output). Peters and Timmerhaus[24] suggested a variation ± 30% in the capital investment estimation; therefore, this variation was assumed in the sensitivity for all parameters, independently.

Further, the inputs with major impact on the sensitivity were run in the Monte Carlo simulation. The simulation uses probability distributions based on historical data, when available, to address uncertainties surrounding the investment in bio-phenol production from lignin. The sensitivity analysis was performed in Microsoft Excel®, and the simulations using the @Risk Analytic Solver Simulation Palisade. More details on all the steps performed in this analysis can be found in de Assis et al.[25]

For the capital cost and KL cost, for instance, a triangular distribution with a variation of 30% was assumed once historical information was not available. A triangular probability distribution, as its name suggests, consists of a continuous distribution with a probability density function shaped as a triangle. It is commonly used in situations when a limited amount of data is available, as it requires only three values: a minimum, a maximum, and a peak (most likely).[33]

Other distributions used in this study were Pert and Kumaraswamy. These distributions were chosen according to the best statistical fit to the historical data. Similarly, to the normal and triangular distributions, the Pert distribution focuses on the most likely value over the maximum and minimum; it constructs a smooth curve which progressively positions emphasis on values around the most likely value, in favor of values around the edges. It is designed to originate a distribution as close as possible to the realistic probability distribution of the data.[34] The Kumaraswamy distribution approximates the beta distribution; however, with much simpler cumulative density function (closed-form) than the beta distribution.[35] This advantage has increased its use in computation-intensive projects, such as simulation modeling.[36]

Next, the scenario's cash flow was linked to the uncertain variables probability distribution, and then the Monte Carlo simulation was run for 5,000 times simulating the probability distribution of the output (NPV), considering the variations of all the inputs.

Sensitivity analysis results can be hard to interpret isolatedly; therefore, they need to be organized in well-designed graphs. In this paper, the results are presented in tornado and spider graphs, these graphs have been commonly applied in economic risk analysis literature.[25,37,38] According to Eschenbac[39] spider plots and tornado diagrams are extensively used by engineering economists and decision making analysts, as they allow presenting sensitivity outcomes succinctly and simply. A tornado graph can show the impact of a large number of independent variables.[25] While a spider graphs can display a smaller number of variables. Both graphical methods present, for each independent variable, its impact on the dependent outcome. And in the spider plots it is possible to see the amount of change necessary to achieve a break-even point.[39]

In a further analysis of the simulation results, the regression coefficients were obtained and de-escalated to show how many units of the output would change by changing one unit of the input. Once the regression coefficients are normalized by the standard deviation, they are not expressed in US$ units. To convert the coefficients from standard deviations to units, in our case US$, the descaled coefficients were obtained by multiplying the coefficients by the standard deviation of the output and then dividing it by each input standard deviation.[40]

4.3 Results and discussion

4.3.1 Fixed costs

For discussion, the fixed costs were separated into three main categories: working capital, fixed capital investment that includes total direct costs, total indirect costs and contingency (derived from the total purchased equipment cost); and, the fixed manufacturing cost that accounts for maintenance, overhead, labor, depreciation and other fixed costs, such as property taxes and insurance. All values per unit production decrease with the increase in capacity, with the most significant drop shown from the 10,000 to 40,000 t·year^{-1} capacity scenarios. Since capital and labor expenses are not a linear function of the capacity, it is expected that those costs per unit produced will decline as plant capacity increases.[12] The fixed capital investment varied from US$ 5.9M to US$ 45.1M, from the lowest to the highest capacity.

As explained in section 3, two recovery EG scenarios were accessed and the amount of EG not recovered becomes part of the final DKL product. Therefore, as expected, the fixed costs per tonne of DKL are higher at 90% EG recovery (Figure 4.3) because less DKL is produced in those scenarios compared to those of the 85% EG recovery scenarios. It is clear that at the base case (pilot project) the fixed costs per tonne of DKL are much higher than those at large commercial scale; therefore, the pilot project is less likely to be feasible, which was demonstrated in our previous study for pilot scale production of DKL.[11] As the capacity increases, the fixed costs are spread out, and lower capital investment per unit of production is obtained.[12] At a certain point, however this cost starts to stabilize or even increase as the capacity keeps increasing.

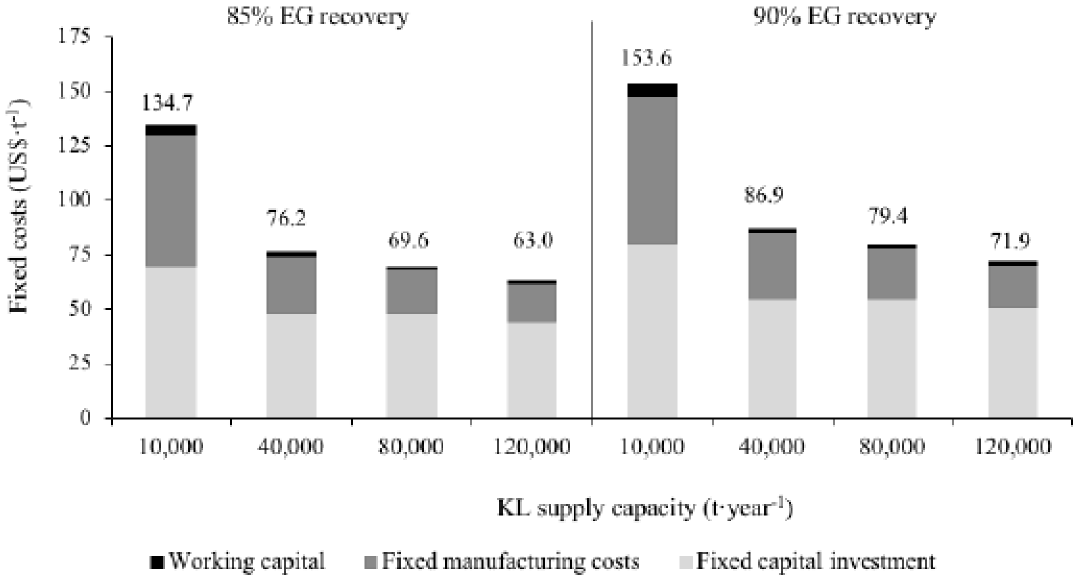


Figure 4.3. Overall fixed costs breakdowns for Sc1 to 8, at year zero.

4.3.2 Manufacturing costs

On the contrary to labor and capital investment, the total variable manufacturing costs have a linear relation to capacity.[12] The variable manufacturing costs per tonne of DKL are similar in all scenarios varying from 1,081 US$·$t^{-1}$ (Sc1) up to 1,101 (Sc8). The small difference comes from the amount of DKL produced that varies according to the amount of EG recovered. A higher amount of EG remains in the DKL with decreasing EG recovery rate, as mentioned previously. Besides, the DKL cost is slightly higher for the

Sc3, 4, 7 and 8 because of the KL transportation cost added for larger capacities scenarios. Finally, the tax amount also varies among the scenarios; lower production capacities generate lower profit and therefore lower taxes.

The most significant costs among the variable manufacturing costs are the KL (42.5% on average), followed by EG (27.8%), acetone (13.1%), NaOH (7.8%) and taxes (5.5%). The lowest cost participation comes from water (0.01%), waste water treatment (0.1%), acid (1.0%) and utilities (2.2%), respectively. The EG cost is lower in the 90% recycling scenarios than that in the 85% recycling scenarios; once less EG has to be purchased to compensate the amount not recovered. After all, main feedstock (KL in this study), is commonly found to be the primary source of variable manufacturing costs in many biorefining feasibility studies.[25,41] Moreover, the variable manufacturing costs commonly account for the major portion of the production costs. For instance, a study of the risk profile of cellulose nanocrystals manufacturing identified the variable manufacturing costs to be responsible for ~95% of the final product unit cost.[25] Similarly, in this study, the variable manufacturing costs correspond in average to ~92% of the DKL production cost, and the fixed costs to ~8%.

4.3.3 Deterministic economic analysis

All scenarios in this study were found economically feasible, thus demonstrating that scaling up the depolymerization of KL brings promising opportunities for production of bio-phenol for BPF resins. In our previous publication, a pilot scale 3,000 t·year^{-1} KL depolymerization plant was found unfeasible for bio-phenol produciton.[11] In this study, the base case plant of 10,000 t·year^{-1} KL depolymerization plant is feasible with PBP below 6.5 years for both recovery rates. However, it does not yield an attractive NPV

(US$ 7.5M and 4.7M) when compared to the higher capacities' scenarios (Figure 4.4). Therefore, increasing the size of the plant has a positive influence in the economic metrics. Combining the NPV and the PBP provides a better overview of the economic performance of the bio-phenol production from KL. A production capacity of 40,000 t·year^{-1} or more, and 85% EG recovery should be suggested for this technology.

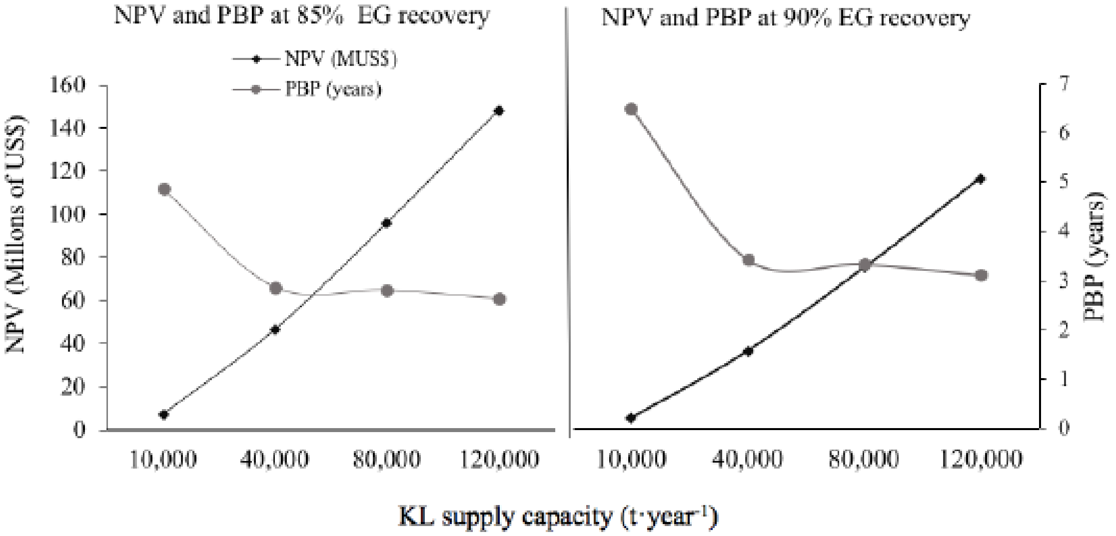


Figure 4.4. The NPV and discounted PBP for the Sc1 through 8.

The best economic performance is observed in the 85% recovery scenarios (Figure 4.4) as a result of the higher volume of final product. Nevertheless, this result is only possible when the EG price is lower than the phenol price. If the phenol price surpasses the EG price (current situation) it is better to have more EG in the final product (e.g., 15%) assuming that the presence of EG won't negatively influence the properties and applications of DKL in the production of BPF resins; on the other hand, if the EG price is higher than the phenol price it is more beneficial to recover more EG. Combined consideration of the NPV and the PBP suggests that a plant with a KL processing above 40,000 t·year^{-1}, and 85% EG recovery shows good results for the technology.

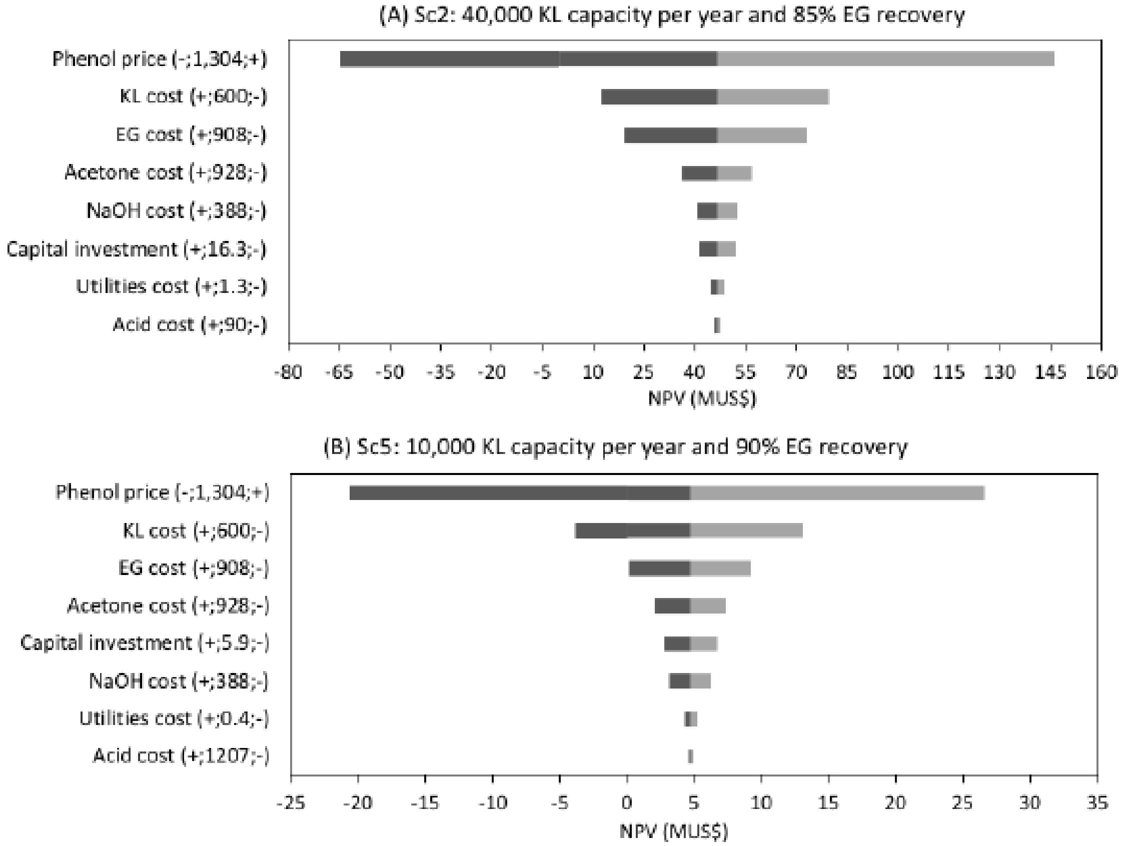
4.3.4 Sensitivity analysis

The tornado diagrams in Figure 4.5 show the inputs with higher influence on NPV, for Sc2 and Sc5. The longest the bars the strongest the impact on the NPV. The two colors differentiate the NPVs below and above each scenario's original NPV (US$ 46.7M for Sc2, and US$ 4.7M for Sc5). The Fig. 4.5 can be interpreted as follows: a bar extending to the right indicates a positive impact. For all costs, it means that decreasing the cost will increase the NPV. On the other hand, increasing of the selling price of the end-product (bio-phenol) markedly increases the NPV, as expected. Finally, the bar extending to the left indicates a negative impact. As such, an increase in the cost of the raw materials (KL, EG, acetone and NaOH), or the capital investment or utilities will decrease the NPV. And, a decrease in the selling price of bio-phenol will also decrease the NPV.

A similar order of inputs impact can be observed in both scenarios, where phenol price (bio-phenol selling price), KL cost and EG cost have the largest impact on the feasibility, respectively, while the acid and utilities costs have the lowest impact. However, a shift in the importance of the capital investment and NaOH cost is observed between the scenarios evaluated. The capital investment's impact on the feasibility increases for lower capacities. Other studies have also observed the main feedstocks cost to have a high impact on the financial results.[25,37,38]

The selling price of bio-phenol, assumed in this study as the same price of commercial phenol in North America, can drastically influence the profitability of both scenarios. The minimum selling price (NPV = 0) for bio-phenol is 1,165.7 US$$\cdot$t^{-1} in Sc2, and 1,240.2 US$$\cdot$t^{-1} in Sc5; therefore, a decrease in 30% in the base case bio-phenol selling price (1,303.9 US$$\cdot$t^{-1}) generates negative NPVs. On the other hand, a 30%

increase in the bio-phenol price strongly improves the NPV in both cases (Figures 4.5 (a) and 4.5 (b)).


(A) Sc2: 40,000 KL capacity per year and 85% EG recovery

(B) Sc5: 10,000 KL capacity per year and 90% EG recovery

Figure 4.5. Sensitivity analysis tornado diagram for Sc2 (A) and Sc5 (B).

Note: The bars met at the NPV value of each original deterministic scenario. The dark gray bars show a negative impact, and the light gray bars a positive impact on the NPV of the original scenarios. The 30% variation direction is shown in the brackets after the parameter name, where the minus (-) sign means a decrease in the parameter and the plus (+) sign means an increase.

Other parameters, such as the KL, EG, acetone, and NaOH costs, also profoundly affect the NPV. For Sc 2, variations of ±30% in those inputs result in a change in the NPV by ± 73%, 58%, 22% and 13%, respectively. The impacts are even stronger for Sc5, where ± 30% changes lead to an NPV variation of ± 183%, 97%, and 56%, and 43%, respectively. The capital investment affects the NPV by ± 33% for Sc5, but only by 12%

in Sc2 for variations of ±30%. For both scenarios the ±30% variation in utilities and acid cost have a marginal impact (less than 9%).

4.3.5 Probability analysis

The deterministic analysis provides a preliminary view of the project; however, further studies are necessary to incorporate uncertainties surrounding new technologies, i.e., the KL depolymerization to produce DKL as bio-phenols. Such risks come from the market price of final product and cost variations of raw materials, as observed in Figure 4.6.

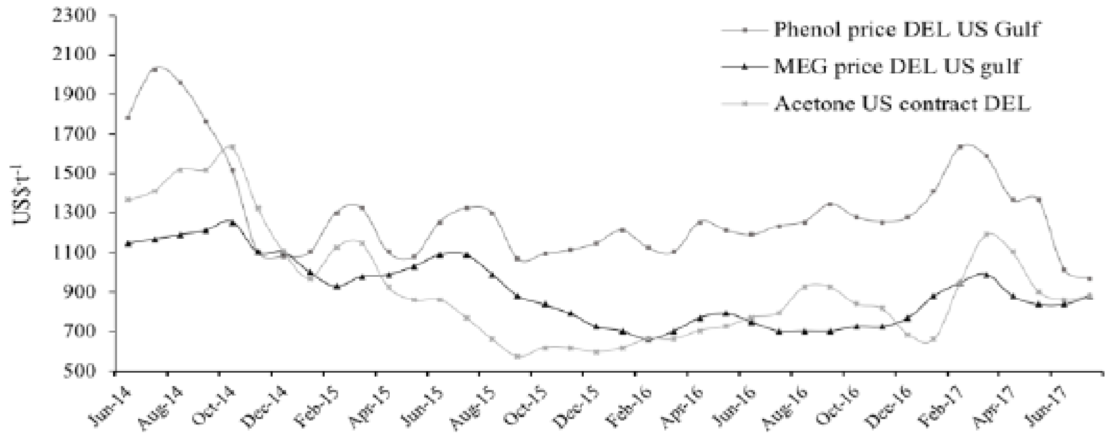


Figure 4.6. Historical monthly prices for phenol, acetone and ethylene glycol from June 2014 to July 2017.[27–29]

The uncertainties are calculated using probability distributions to model the uncertain variables in a Monte Carlo Simulation, as described in the methods section. From the deterministic sensitive analysis, we selected phenol price (US$·t^{-1}), KL (US$·t^{-1}), EG (US$·t^{-1}), acetone cost (US$·t^{-1}), and capital investment (US$) as inputs in the Monte-Carlo simulation. Figure 4.7 shows the data adjusted functions (lines) and the probability distribution (bars) for Sc2 (40,000 t·year^{-1} and 85% recovery, Table 4.1).

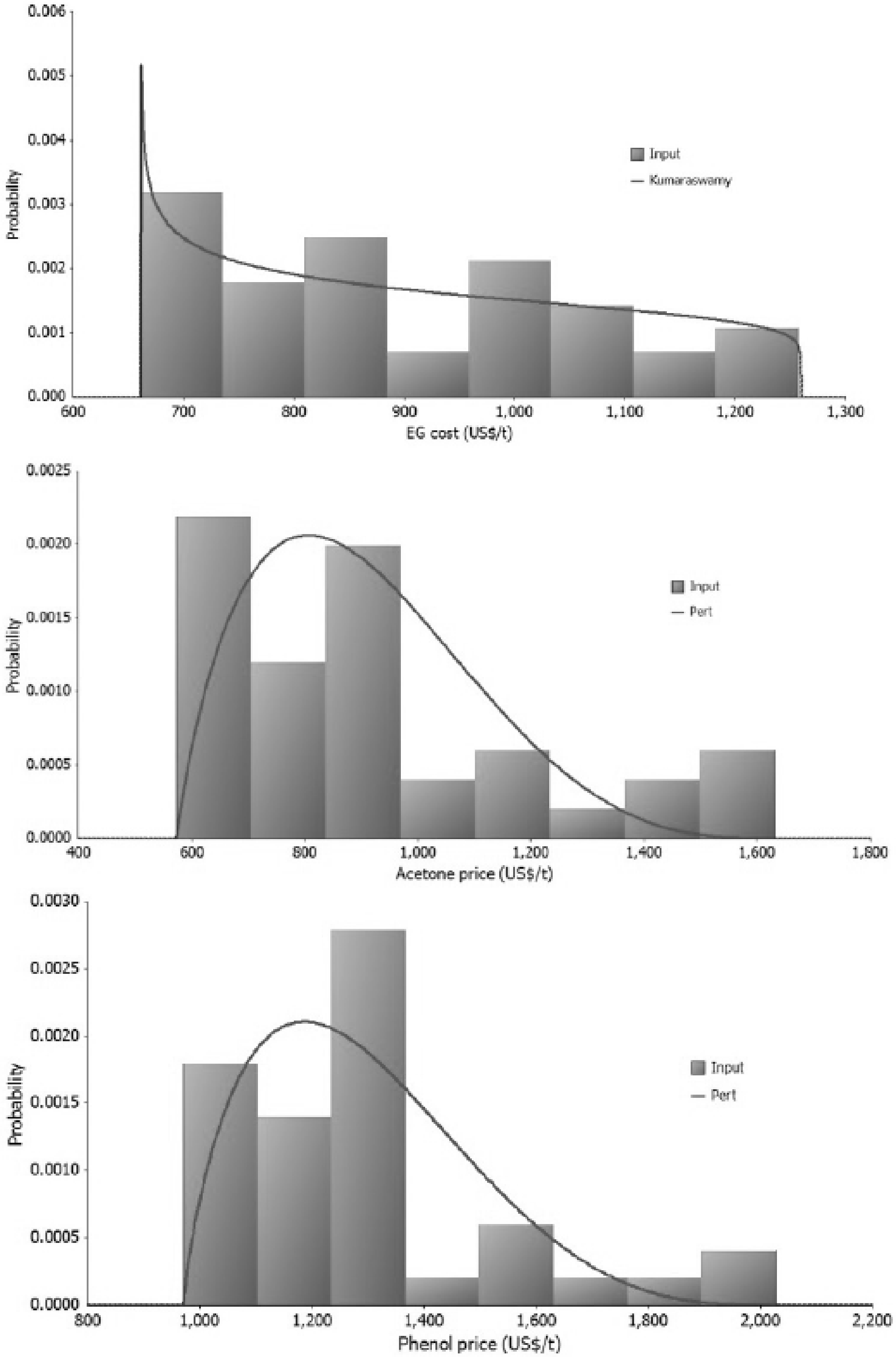


Figure 4.7. Adjusted distribution probabilities for EG, acetone, and phenol prices (US\$$\cdot$t^{-1}) for Sc2 (40,000 t$\cdot$year^{-1}, 85% recovery).

Note: The bars represent the probability distribution of the historical data, and the line the adjusted probability distribution.

Applying a probability analysis based on the historical data permits to observe the chances of an event to happen.[25] For instance, what are the changes of the NPV to be below a desired value. The Monte-Carlo results for the Sc2 NPV output are presented in Figure 4.8. The Figure 4.8 shows the output result (NPV) for all interactions ran in the simulation by varying all inputs according to their probability distribution. Each vertical bar represents an NPV probability interval. The top horizontal bar shows the chances of the NPV to fall on the area corresponding to the probabilities bars below zero, and between zero and US$ 229M (maximum).

The practical relevance of this analysis is to show the probability of the project to have an NPV close to the NPV value calculated in the deterministic scenarios. The probability of the NPV being between US$ 37M and 57M, for instance, is ~ 14.2%; this interval holds the NPV calculated in the deterministic analysis (US$ 46.7M). It is unlikely that an investor (e.g. pulp mill aiming to diversify its portfolio) would be interested in an investment at a high risk (probability of the NPV being below zero higher than 30%). Based on the assumptions made for lignin-based bio-phenol production, there is a 100% probability that the NPV falls below US$ 210M, and a 22.0% probability of NPV to fall below zero. The average NPV resulting from the 5,000 runs is US$ 42.6M, slightly lower than the deterministic calculated NPV. The above difference was resulted from the input uncertainties, which were incorporated by the probability curves.

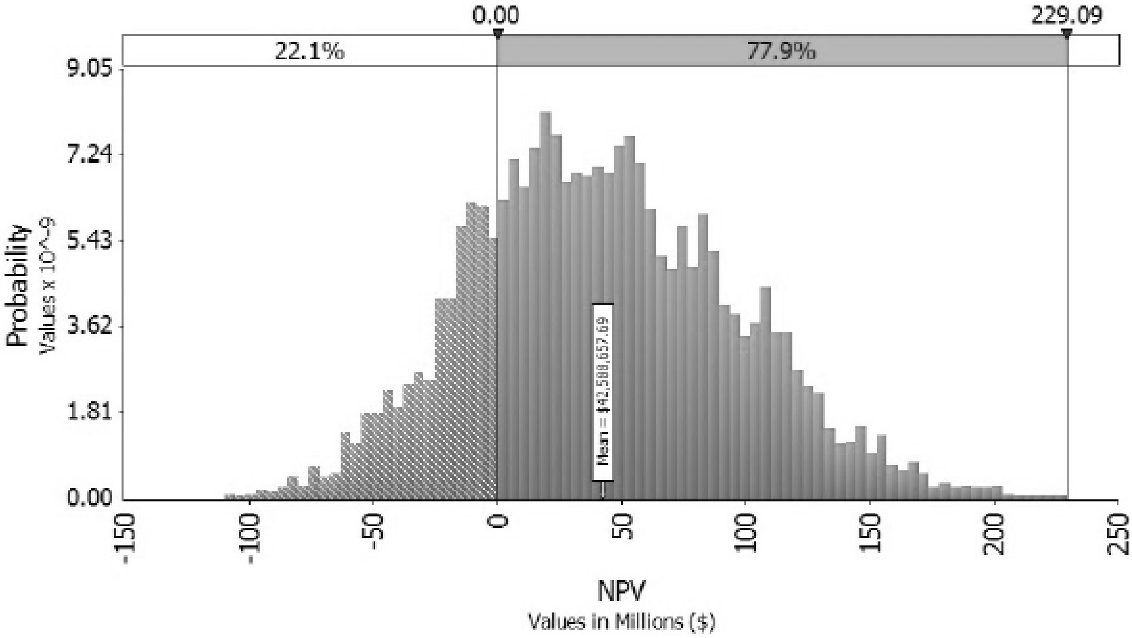


Figure 4.8. NPV (M US$) probability distribution curve for Sc2 (40,000 t·year^{-1} and 85% recovery).

Similarly, as the results previously presented in the deterministic sensitivity, the effects of multiple inputs in the output can be observed in Figure 4.9 for Sc2. However, these results consider historical price variation of a fixed variation. One can observe that the curves approach each other around the deterministic value (US$ 46.7M). For each input, the percentage change following its probability distribution is plotted in the Y-axis, with 5% boundaries, while the output result (NPV) is plotted on the X-axis. Whereas flatter the line is the less impact the input has on the output.

The bio-phenol selling price clearly carries the greater effect on the NPV, followed by EG, KL, acetone costs and capital investment, respectively. For instance, for the end-product selling price (represented by phenol price) an increase of at least 20% on its lowest possible value is necessary to generate an NPV above zero. On the other hand, for the KL and the other inputs, as they are costs not revenue, an increase in their value decreases the NPV (Figure 4.9). Practically, for all the cost inputs the NPV variation range from ~10M to 70M; therefore, all generating a positive NPV. This analysis shows the importance of the selling price of bio-phenol in the overall profitability of this process.

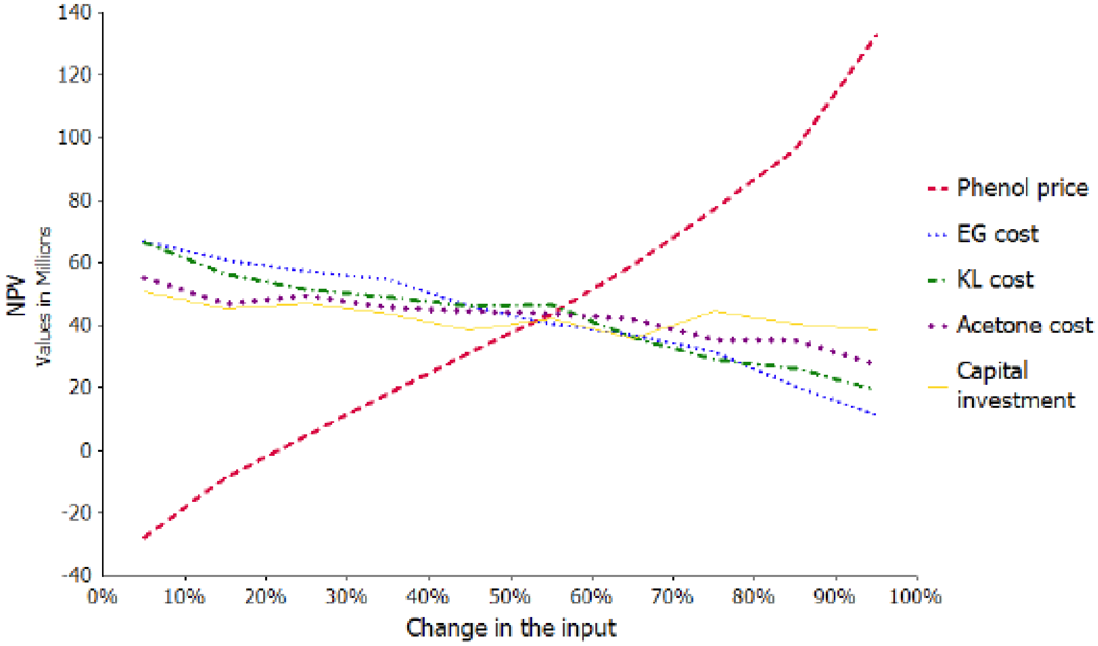


Figure 4.9. Spider graph for Sc2 showing the change in the NPV means (US$ M) across the change in the uncertain parameters.

Further interpretation can be drawn from the simulation de-escalated regression coefficients (Figure 4.10). A positive coefficient represents a positive effect, and a negative coefficient has a negative impact on the output, as observed in Figure 4.10. To facilitate the graphic presentation, the capital investment is shown in units of US$ 50,000 (50K). For instance, a change in US$ 50,000 in the capital investment results in a decrease of US$ 0.28M in the NPV, and an increase of US$ 1.00/t in the phenol price raises the NPV by US$ 0.26M (Figure 4.10).

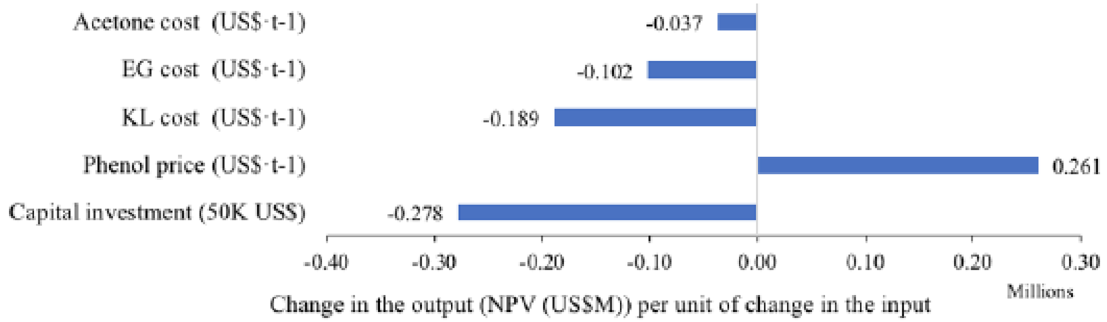


Figure 4.10. Descaled regression coefficients showing the change in the output (NPV (US$ M)) per unit of change in each parameter for Sc2.

4.4 Conclusion

This paper provides economic analysis for bio-phenol production based on a proprietary KL depolymerization process for 8 scenarios with the KL treatment capacity ranging from 10,000 t·year-^{1} of KL to 120,000 t·year-^{1} and two recovery percentages (85% and 90%). The main conclusions drawn from this study are summarized as follows.

Fixed costs per unit of DKL as bio-phenol produced decreased with the increase in capacity. Increasing the KL treatment capacity from 10,000 t·year-^{1} of KL to 120,000 t·year-^{1} could produce a 53% drop in the fixed costs per tonne of bio-phenol. The scenarios with 85% ethylene glycol (EG) recovery rate presented better economic performance than those with the 90% EG recovery rate if the bio-phenol selling price is higher that EG cost. Based on the deterministic results the largest capacity explored (120,000 t·year^1 of KL) with 85% EG recovery rate presents the most attractive NPV (US$ 148.4M) and PBP (2.7 years).

Considering that Canadian pulp mills can supply on average 46,000 t·year^1 of KL, without having to rely in external supply, the 40,000 t·year^{-1} capacity scenario is recommended for a KL-to-bio-phenol biorefinery plant in Canada; further expansion would be possible when the market for bio-phenol is established. The risk analysis considering variations on the main costs and phenol selling price resulted in a 78% probability of an NPV above zero, for the scenario with the KL capacity of 40,000 t·year^{-1} and 85% recovery rate. The variations in bio-phenol selling price, EG cost and KL cost are the parameters that most affect the feasibility of the biorefinery. For instance, historical data of the petroleum-based phenol price in North America varies from 970 to 2028 US$·t^{-1}. Based on this analysis, bio-phenol's selling price below ~1,160 US$·t^{-1} would result in unfeasibility of the biorefinery. Further studies can enrich this field by exploring the market demand and supply for phenols globally. Developing a supply chain model, for example, can provide the entire picture of the market helping high value-added products derived from KL to gain a greater share in the petroleum-based market.

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CHAPTER 5 – Forest biomass supply chain optimization for a biorefinery aiming to produce high-value bio-based materials and chemicals from lignin and forestry residues: A review of literature

ABSTRACT

Technological development has enabled the production of new value-added products from lignocellulosic residues such as lignin. This has allowed the forest industry to diversify its product portfolio and maximize the economic returns from feedstock, while simultaneously working towards sustainable alternatives to petroleum-based products. Although previous research has explored industrial-scale production opportunities, many challenges persist, including the cost of woody biomass and its supply chain reliability. While numerous studies have addressed these issues, their emphasis has traditionally been on bioenergy, with little focus on biochemical, biomaterials and bioproducts. This review seeks to address this gap through a systematic study of the work recently reported by researchers. A lot of work has been published from United States and Canada with an emphasis on bioenergy production (84.8%), 4.6% of the work is focused on biomass to materials and chemicals, and 10.6% addressed both. Between 2012 and 2015, the majority of published research focused on biomass to materials and chemicals, and both biomass to energy and biomass to materials and chemicals. This fact highlights recent interests in diversified biorefinery portfolios. However, further work concerning forest biomass supply chain optimization and new high-value bio-based materials and chemicals is necessary.

Keywords: biomass to energy, biomass to materials and chemicals, economic optimization, lignocellulosic residues, value-added bio-based products.

5.1 Introduction

Countries around the world are adopting laws or policies intended to lower greenhouse gas (GHG) emissions, which results in an increasing interest in alternative renewable sources for producing bioenergy, biochemicals, and biomaterials. Despite this interest, according to the International Energy Agency (IEA), oil, natural gas, and coal still account for almost 81.7% of the world's current primary energy supply (Bell et al. 2014). Moreover, many industrial chemicals and synthetic materials are still dependent on petroleum-derived products (Kurian et al. 2013). For instance, 42% of the petroleum revenue came from chemicals, plastic, and rubber. Surprisingly, this category consumes only 4% of petroleum (Werpy 2009).

As an alternative feedstock to petroleum-based products, lignocellulosic biomass has been recognized as a promising resource for the production of non-energy commodities such as chemicals, fibres, plastics, and construction materials because of its chemical properties and abundance (Fahd et al. 2012; Iqbal et al. 2013; Isikgor and Becer 2015). Additionally, lignocellulosic biomass provides the means to help the forest sector transition into a more diverse, market-driven industry, while concurrently improving its environmental footprint (Thiffault et al. 2014). Thus, the biorefining approach has become a favourable pathway to obtain value-added products from forest and mill residues. The biorefinery concept is defined by the IEA Bioenergy Task 42 Biorefining as the "sustainable and synergetic transformation of low-value biomass into marketable food and feed ingredients, products (chemicals, materials) and energy (fuels, power, heat)" (Bell et al. 2014).

In this context, researchers have been working intensively to improve biomass conversion technologies towards commercial-scale facilities (Hughes et al. 2013). However, despite the increased efficiency of the technology in the last decade, ongoing challenges related to the feedstock logistics and biomass valorization have resulted in only a small number of operational industrial biorefineries (Kurian et al. 2013).

While the biorefinery concept has emerged as an alternative way to petroleum dependence, the rising demand for biomass from the traditional forest industry and the emerging bioproducts industry have increased the complexity of multilevel supply systems. This creates a need for integrated biomass supply chain management (BSCM) approaches (Iakovou et al. 2010). Therefore, a method for designing profitable biomass supply chains (BSCs) that can also accommodate these aforementioned challenges is vital to the long-term economic viability of this emerging industry (Sukumara et al. 2014; An and Wilhelm 2014).

The development of an efficient BSC to provide a low-cost biomass feedstock requires detailed investigation and analysis. In recent years, there have been an increasing number of literature reviews on BSC. The following points summarize the subjects addressed by recent review papers:

- main concerns related to bioenergy BSC and logistics, e.g., Gold and Seuring (2011) and Kurian et al. (2013);
- effect of different feedstocks types on the BSCM, e.g., Iakovou et al. (2010) and Kurian et al. (2013);
- multicriteria decision-making methods addressing problems arising within the bioenergy sector, e.g., Scott et al. (2012);
- biofuel BSC under uncertainties, e.g., Awudu and Zhang (2012);
- deterministic and stochastic models applied in bioenergy value chain optimization, e.g., Shabani et al. (2013);
- assessment and optimization of forest biomass supply chain (FBSC), considering economic, social, and environmental aspects, e.g., Cambero and Sowlati (2014);
- development of energy BSC optimization frameworks, e.g., Elia and Floudas (2014);
- strategic challenges and issues with design, planning, and management of BSC, e.g., Mafakheri and Nasiri (2014);
- and, multiscale modeling and optimization of BSCs, e.g., Yue et al. (2014).

Additionally, there are a number of literature reviews regarding thermochemical technologies and the opportunities associated with lignocellulosic biomass (e.g., Iqbal et al. 2013; Isikgor and Becer 2015). While studies examining FBSC and conversion technologies to produce bio-based value-added products are quickly evolving, a review covering those subjects is very limited or missing. To fill this gap in the literature, this work endeavors to answer some questions, for example, what products shall be targeted in a biorefinery based on FBSC optimization. To accomplish this, the rest of this work is organized into two sections. The first part outlines recent advancements in conversion technologies and bio- based products from forest residues focusing on lignin. The second part presents a systematic review of FBSC studies. This paper contributes to the body of knowledge by (i) summarizing recent achievements in the production of bio-based products from lignin and forest residues, (ii) providing an overview of BSC studies based on their year of publication, research objectives, country of origin, and journal, and (iii) identifying the bioproducts targeted in the FBSC optimization studies and summarizing the number of articles that addressed bio-based materials and chemicals.

5.2 Methods

5.2.1 Narrative literature review

To provide background information on thermochemical technologies to produce value-added bio-based chemicals and materials from lignin and forest residues, a narrative review was performed in the first section of this paper. A narrative review is a combination of published information that typically summarizes the contents of each paper (Green et al. 2001). In this first section, we focused on the research work done by the research team of the Institute for Chemicals and Fuels from Alternative Resources

(ICFAR) and Lignoworks (the NSERC Biomaterials and Chemicals Strategic Research Network, http://www. icfar.ca/lignoworks/) in Canada, which have significantly contributed to the Canadian forest industry by generating alternative products and technologies from forest and mill residues.

Publications from Canada were reviewed in this paper, as this country is one of the leading countries in research in this field and can provide a considerable number of papers satisfying a narrative review to cover the topic.

5.2.2 Systematic literature review

In this section, the literature on supply chain optimization is collected through a search and screening of research and literature review papers that address different components of the BSC. Secondly, a systematic review is presented based on the process described below.

The systematic review helps to identify the difference between real and presumed knowledge by mapping out areas of uncertainty, determining the fields in which little research has been done, and identifying topics requiring more research (Petticrew and Roberts 2006). The systematic review followed five main steps: identifying key words or terms, locating and searching literature, checking publications applicable to the topic, classifying the literature, and writing the literature review.

The keyword "biomass* supply* chain*" was searched in the ISI Web of Knowledge (WOK), resulting in the retrieval of 979 documents. All database years of ISI were taken into consideration, and the results were saved in End Note Web for external review and verification (a complete list of documents can be obtained by contacting the first author). The data were then entered into Microsoft Excel for analysis. The review focused on English language peer-reviewed literature documenting FBSC technical and economic optimization. Therefore, to be included, the paper had to consider at least one forest-based feedstock and also perform a BSC techno-economic optimization.

5.3 A narrative literature review on alternative sources and thermochemical technologies for production of bio-based chemicals and materials

5.3.1 Alternatives sources for bio-based products

Energy crops and forest and agriculture biomass residues are renewable resources that can potentially offset future petroleum shortages while decreasing GHG emissions and not compromising food supply (Bell et al. 2014). Lignocellulose is a major structural component of woody and non-woody plants and consists of cellulose, hemicellulose, and lignin (Menon and Rao 2012).

Cellulose constitutes more than 40% of the wood and is present mainly in the secondary cell walls (Sjöström 1993). Hemicelluloses are heteropolysaccharides that also function as supporting materials in the cell walls (Sjöström 1993). Lastly, "Lignin is a complex three-dimensional biopolymer of aromatic alcohols" (Ferdosian et al. 2014). After cellulose, lignin is the second most abundant renewable natural polymer, accounting for between 15% and 40% of stem wood, depending on the species (Holladay et al. 2007; Novaes et al. 2010).

Recently, cellulose has become a source material for a variety of products, in addition to traditional products such as pulp and paper. The cellulose and hemicellulose-derived carbohydrates can be refined into various value-added bio-based products such as alcohols, esters, and carboxylic acids through so-called "sugar platform" biorefineries

(Cheng et al. 2010). Moreover, the world's first cellulose nanocrystalline plant was built in Canada with a capacity of 1 tonne (t)·day^{-1} (Hamel 2016).

Innovative technologies to create value-added and high-value bio-based products have led to improved usage of forest harvesting and mill residues such as kraft lignin. The primary source of technical lignin is the pulp and paper industry (Mahmood et al. 2013). According to Moshkelani et al. (2013), the kraft lignin pulping residues can increase the revenue margin of mills through conversion into higher valued marketable products such as bio- fuels, synthetic gas, and chemicals.

In the kraft pulping process, only 42% to 44% of softwood biomass after bleaching and about 50% of hardwood is converted into pulp, and the residue (mainly hemicelluloses and lignin) is combusted in the recovery boiler (Moshkelani et al. 2013). Laurichesse and Avérous (2014) estimated that annual global production of lignin is over 70 million tonnes, around 95% of which is burned in recovery boilers for steam and power generation. Only about 5% of lignin (mainly lignosulphonate) is utilized for production of value-added bio-based products such as dispersants, adhesives, and surfactants.

Lignin is an exceptionally abundant raw material and, therefore, offers an opportunity for lignocellulosic biorefineries. According to Hughes et al. (2013), biorefining technologies are available to utilize and fractionate lignocellulosic feedstock to produce intermediate and final products (Hughes et al. 2013). However, there are few kraft lignin plants in North America, including the MeadWestvaco in South Carolina, USA, which produces approximately 20,000 t·year^{-1} of kraft lignin (Huang 2014). In 2013, Domtar started to produce 75 t·day^{-1} of kraft lignin at its Plymouth, North Carolina, plant (Huang 2014). A commercial-scale kraft lignin production plant with a targeted capacity of 30 t·day^{-1} is under construction in Hinton (Alberta, Canada) based on the LignoForce system created by FPInnovations. Also, a lignin precipitation pilot plant, the first facility of its kind in North America, was installed at Resolute Forest Products in Thunder Bay (Ontario, Canada), with capacity for 100 kg·day^{-1} (Canadian Biomass 2013).

Holladay et al. (2007) considered six scenarios in which 225 million tonnes of lignin were utilized for power, transportation fuels, products, and chemicals, both individually and in various combinations. When lignin is used for purposes other than power, the overall revenue increase is US$12-$35 billion. However, significant technological development will be required to seize the full value benefit.

Research in non-traditional wood products that can be produced alongside traditional products has been playing a prominent role in expanding the current wood product portfolio to take advantage of new market opportunities (Blair 2013). A biorefinery model proposed by the Canada Bio-pathways Project is based on extracting the largest possible value from a forest feedstock. Products originating from this process include both traditional and novel ones that satisfy the primary criteria that the highest possible value must be generated at every stage. Ordinarily, heat and power are a necessary part of the combination (Browne et al. 2011).

Specialty chemicals are said to be promising elements of a forest biorefinery products portfolio because they have the highest profit margins compared with pulp and paper products and less competition within the market. This allows biorefineries to reduce their direct competition with well-established commodity petrochemical products (Mansoornejad 2012).

Browne et al. (2011) analyzed the relationship between annual market size and price of forest products. They concluded that the products with higher market price have a smaller market size, and vice versa. For instance, polyphenols (biomass-derived specialty chemicals) have a market size of 104 kg per year, and a market price higher than US\$100·kg^{-1}. In contrast, cellulose-based fibres have a world market of the order of 1011 kg, but regular sales prices are of the order of US\$1·kg^{-1}.

5.3.2 Thermochemical conversion technologies

Commercial-scale conversion of lignocellulosic materials to value-added bio-based products is still a challenging proposal. According to Ghatak (2011), an upgraded technology for lignin isolation from black liquor and breakthroughs in industrial chemistry and chemical technology for value-added products from lignin can profoundly improve a lignocellulosic biorefinery.

There are a number of conversion technologies available to convert biomass residues into a range of biofuels and chemicals (Srirangan et al. 2012). In this paper, a short overview of recent papers addressing lignin conversion technologies for chemicals and materials is presented. For an in-depth review, the following papers are recommended: Zhang et al. 2010*a*; Srirangan et al. 2012; Iqbal et al. 2013; and Shen et al. 2015. Additionally, especially for lignin conversion technologies, Pandey and Kim (2011), Huang (2014), and Laurichesse and Avérous (2014) are particularly useful literature sources.

Biomass gasification is a sustainable process that uses gasification agents such as air or oxygen, steam, CO_2, or their combinations for converting lignocellulosic biomass into low-to-medium-Btu (British thermal unit) fuel gasses (Hurley et al. 2010). In Feng et al. (2015), there are two pathways to obtain renewable phenol alternatives. The first is to extract chemical components such as lignin and alkaline extractives from lignocellulosic biomass. The second is to convert lignocellulosic biomass via various thermochemical processes (i.e., phenolysis, liquefaction, and pyrolysis) into phenolic bio-crude, bio-oil, or pyrolysis oil.

Lignin can be degraded or decomposed into oligomeric and monomeric phenolic compounds by different processes such as hydrolysis and pyrolysis (Pandey and Kim 2011). These compounds then become potential sources of bio-phenols for replacing petroleum-based phenols in the production of phenol formaldehyde (PF) resins (Cheng et al. 2011).

Direct liquefaction is considered a favourable route for converting biomass into liquid fuels and value-added chemicals (Feng et al. 2015). High-pressure direct liquefaction technology was found to be superior when compared with pyrolysis technology as it produces liquid oils with much greater caloric values (Yang et al. 2009*a*). Bio-oil products from fast pyrolysis contain high contents of water and oxygen leading to relatively low heating values. In contrast, biomass direct liquefaction processes produce liquid oil products (bio-crude) of a greater heating value than those from pyrolysis bio-oils (Li et al. 2011).

Another growing technology is supercritical water (SCW) gasification, which utilizes supercritical water as the reaction medium. It is an innovative hydrothermal process that converts wet biomass material or aqueous organic waste directly into a valuable hydrogen (H_2) rich syngas (Zhang et al. 2012).

Laurichesse and Avérous (2014) reviewed the chemical modification of lignin to produce bio-based polymers, which can be classified into the following main groups: lignin fragmentation or depolymerization into phenolic or other aromatic compounds for fine chemistry; synthesis of new chemical active sites to impart new reactivity to lignin; and functionalization of hydroxyl groups to enhance their reactivity or responsiveness. Pandey and Kim (2011), in their literature review on thermochemical conversions of lignin, concluded that pyrolysis, gasification, hydrogenolysis, chemical oxidation, and hydrolysis under supercritical conditions are the major thermochemical methods studied with regard to lignin depolymerization.

Another recent literature review concerning valorization of lignin to produce chemicals and materials was provided in a thesis by Huang (2014). The author concluded that lignin is a rich source of aromatics, which can be obtained by liquefaction or depolymerization. These lignins have smaller relative molecular mass, less steric hindrance effects, and more active functional groups, which are desirable for the synthesis of bio-based phenolic resins, polyurethane resins, and epoxy resins. Pyrolysis lignin has low yields, generating a considerable amount of char, and hydrothermal liquefaction provides various benefits when compared with gasification, wet oxidation, and pyrolysis.

5.3.3 Potential bio-based products from lignin and woody biomass

The term “bio-based product” includes the traditional products of the forest industry and a variety of bio-based chemicals, additives, plastics, fibres, reinforced plastics, and insulation materials (de Jong et al. 2012). Figure 5.1 summarizes the potential bioproducts from lignocellulosic materials identified by Iqbal et al. (2013). In this paper, we further classify the BSC for final products according to EIA Bioenergy (Bell et al. 2014) definitions:

- biomass to energy: power, heat, and fuels;
- biomass to materials and chemicals (non-energy) that can be further classified into two product groups: traditional wood, paper, and textile products (e.g., cotton, pulp), and synthetic chemicals and materials (e.g., plastics, fibres, and nitrogen fertilizers).

This review focuses on the bio-based chemicals and materials from forest residues, highlighting the potential lignin bioproducts. Biomass to bioenergy and biofuels production is widely discussed in previous reviews such as Hughes et al. (2013) and Williams et al. (2016). After an exhaustive screening, Kokossis et al. (2015) found that the promising products of a biorefinery portfolio are from C5 sugars, including the catalytic production of xylitol and C5 ethanol, from C6 sugars, including C6 ethanol and itaconic acid, and from lignin derivatives such as PF resins and polyurethanes.

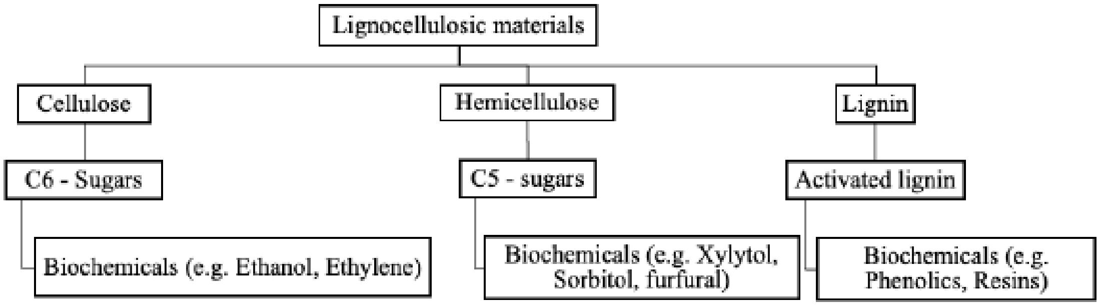

Figure 5.1. Potential value-added biochemicals of a lignocellulosic biorefinery.

Ferdosian et al. (2014, 2015) state that lignin may be the best candidate as a green alternative to bisphenol A for the production of epoxy resin because of its aromatic arrangement. Moreover, Mahmood et al. (2013) highlighted that kraft lignin is a source of polyols, due to lignin's particular phenyl propanol structure and aryl alkyl ether bonding. In the search for sustainable materials for building and construction, lignin was found to be a suitable substitute to phenol in the manufacturing of PF resins (Pandey and Kim 2011; Cheng et al. 2011).

Mahmood et al. (2013) proposed a process that produced renewable polyols from kraft lignin with desirable characteristics for rigid polyurethane foam synthesis such as low relative molecular mass, moderately high aliphatic hydroxyl number and functionality, and high yields.

PF resins are most broadly used as wood adhesives in the manufacturing of engineered wood products (e.g., plywood, particle board, and fibreboard). They are also employed in a variety of industrial products such as insulation, coated abrasives, paper saturation, and floral foam (Cheng et al. 2011). Bio-based PF resins from lignin can reduce the industrial consumption of various petroleum derivative elements such as phenol and bisphenol A, which have high toxicity and carcinogenic effects related to both environmental sustainability and human health (Wang et al. 2010, 2015).

Considerable efforts have been made in phenolic resin production to replace petroleum-based phenol either entirely or partially with lignocellulosic biomass. Browne et al. (2011) analyzed lignin as a replacement for phenol in the synthesis of PF resins and carbon black and as a feed for carbon fibre production processes considering lignin competitiveness against petroleum-based resins. Their findings indicate that lignin is capable of replacing up to 50% of the phenol in PF resins in the manufacture of plywood and possibly 30% in other kinds of composite wood panels with no primary alterations in strength properties.

Moreover, Feng et al. (2015) concluded that bark bio-crude and neat PF adhesive were successfully blended to produce novel formulated bio-PF adhesives. The authors found that the ratio depends on the bark species; they reached a ratio of 50:50 (by weight) for white birch bark, while the formulation ratio was up to 75:25 (by weight) for white spruce bark bio-crude and neat PF adhesive, respectively.

Cheng et al. (2011) studied wood bio-crude to replace phenol for the production of bio-based phenolic resol resins. They found that adding up to 75 wt% (weight percent) resulted in an efficient bio-based resol resin for plywood adhesives, which had comparable to better dry and wet bonding strength than the reference pure PF resin. Later, Cheng et al. (2013) tested phenolic resins and adhesives from lignin and forestry residuals, applying a high substitution ratio of degraded lignin PF (DLPF) to substitute phenol in the synthesis of bio-PF resins. Plywood samples glued with organosolv lignin PF (OLPF) and DLPF adhesives (phenol replacement ratio up to 75 wt%) showed higher dry and wet tensile strengths than those of PF adhesives. Zhang et al. (2015) demonstrated the use of kraft lignin as a promising curing agent for phenol-5-hydroxymethylfurfural (PHMF) resins for thermal stability and mechanical properties for the purpose of fiberglass-reinforced composite materials.

Within their literature review, Isikgor and Becer (2015) found that lignocellulosic biomass can be utilized as a raw material to generate more than 200 value-added chemical compounds, thereby proving the lignocellulosic biomass potential as a complementary platform to fossil resources. For example, other than bio-based PF resins and adhesives, bio-based rigid polyurethane foams were prepared by Mahmood et al.

(2015) using hydrolytically depolymerized kraft lignin via direct replacement or oxypropylation of depolymerized kraft lignin. The resulting foam displays an excellent combination of physical, mechanical, and thermal properties compared with the reference foam.

Table 5.1 summarizes papers addressing lignocellulosic conversion to generate various bio-based products, chemicals, and materials from lignin and forest residues (e.g., epoxy resins, polyols, adhesives, and PF resins among other materials and chemicals). The conversion technologies most studied for production of resin and adhesives are polymerization and liquefaction (Table 5.1).

Table 5.1. Summary of papers regarding thermochemical technologies for new bio-based products from lignin and forest residues.

Conversion technologies	**Raw material**	**Final product**	**Reference**
Co-catalysts and solvents	Glucose	5-hydroxymethyl furfural	Yuan et al. (2011)
Co-liquefaction in hot-compressed water	Secondary pulp/paper-mill sludge	Bio-crude	Zhang et al. (2011a)
Delignification	Bio-phenolic compounds from lignin/forestry residuals (pine sawdust)	Phenolic resins and adhesives	Cheng et al. (2013)
Depolymerization	Hydrolysis lignin	Polyurethane foams/resins	Mahmood et al. (2015)
	Kraft lignin	Depolymerized lignin Lignin-based epoxy resins	Huang et al. (2014) Ferdosian et al. (2015)
Depolymerization in supercritical acetone	Kraft lignin	Epoxy resin	Ferdosian et al. (2014)
Direct hydrolysis	Kraft lignin	Polyols	(Mahmood et al. 2015)
Direct liquefaction	Eastern white pine sawdust	Bio-oil Bio-based Phenolic Resol Resins	Cheng et al. (2010; 2011)
	Sawdust, cornstalks, pure lignin and pure cellulose as references	Phenol–formaldehyde resins	Tymchyshyn and Xu (2010)
Fast Pyrolysis	Hardwood sawdust	Pyrolysis oil	Reyhanitash et al. (2014)
Gasification	Pine sawdust	Combustible gas	Hurley et al. (2010; 2012)

Table 5.1. Continued.

Conversion technologies	**Raw material**	**Final product**	**Reference**
Glucose as the replacement of formaldehyde	Glucose	Novolac-Type Phenolic Resins	Wang et al. (2010)
Hydro-Liquefaction in Sub-Super-Critical Methanol	Woody biomass (birch powder)	Bio-crude	Yang et al. (2009a)
Hydrodeoxygenation	Bio-crude	Oily products	Yang et al. (2009b)
Hydrolytic degradation in hot-compressed water	Alkali lignin	Oligomers	Yuan et al. (2010)
Hydrothermal degradation		Bio-phenolic compounds	Cheng et al. (2012a)
Hydrothermal liquefaction	Birchwood sawdust	Bio-crude	Nazari et al. (2015)
	Eastern white pine sawdust	Methylolated bio-oil-PF resol resins	Cheng et al. (2012b)
Liquefaction	Bark (white pine, white spruce and white birch)	Bio-crude	Feng et al. (2014)
	White birch bark and white spruce bark	BPF adhesives	Feng et al. (2015)
One pot synthesis process	Kraft lignin	Formaldehyde-free phenolic resin	Zhang et al. (2015)
Organosolv extraction		Phenol–formaldehyde resol resins	Wang et al. (2009)
Phenol-5-hydroxymethyl furfural resins synthesized by reacting phenol with 5-hydroxymethyl furfural	Glucose	Glucose	Yuan et al. (2014)
Supercritical water gasification	Glucose	H_2	Zhang et al. (2012)
			Zhang et al. (2011c)
	Pulp/paper mill sludge, sewage sludges (primary, secondary, and digested)	Bioenergy	(Zhang et al. 2010)
	Sludge (secondary pulp/paper-mill)	H_2	Zhang et al. (2011b)

Even though there has been significant advancement in forest biomass biorefining conversion technologies for value-added bio-based chemicals and materials, there are still several barriers limiting their adoption within the market. Among the barriers for implementation of commercial-scale facilities, the two key ones are logistical constraints associated with maintaining a consistent supply of woody feedstock and lignin and the high capital costs of building a biorefinery (Blair 2013). Fortunately, many of these challenges can be addressed through a well-designed BSC (Gold and Seuring 2011; An et al. 2011; Zhang et al. 2014). A pivotally important task for developing a biorefinery is to create a reliable BSC for enough feedstock at a stable price. A BSC generally starts at the cultivation level (establishment and treatment of forest plantations and agricultural energy crops), going through harvesting, preprocessing, transportation, handling, and storage and ultimately ending at the final conversion unit such as a biorefinery or bioenergy conversion plant (Ba et al. 2016).

A systematic design of the entire BSC network that considers all stages, from the production of forest and wood residues to the end use of all bioproducts, is required to ensure that the economic and environmental benefits be optimized (Cambero et al. 2015). Therefore, an overview of BSCM and a systematic literature review of FBSC optimization based on literature papers up to 6 October 2015 are presented in the following section.

5.4 Systematic literature review on supply chain optimization studies and their targeted bio-based chemicals and materials

5.4.1 Supply chain optimization

A BSC integrates geographically dispersed facilities in which raw materials, intermediate products, or finished goods are acquired, transformed, stored, or marketed using transportation links that connect the facilities (Shapiro 2001; Chatfield et al. 2006). According to Shapiro (2001), there are two categories of mathematical models used in supply chain optimization. The first type, known as descriptive models, includes forecasting, cost relationships, resource utilization relationships, and simulation models.

The second type, known as normative models or optimization models, are classified as linear, integer, and nonlinear programming (Moore and Weatherford 2001).

Sharma et al. (2013) concluded that the majority of recent BSC papers utilize a mixed-integer (MIP) linear programming approach, an optimization approach. The MIP models are generalizations of linear programming models in which integer variables (most commonly the binary values of 0 and 1) are constrained to take on a nonnegative integer value, whereas the remaining continuous variables are allowed to take on any nonnegative values (Shapiro 2001).

The BSC can be classified in three main planning scales: strategic, tactical, and operational (Stadtler 2005; Shahi and Pulkki 2013). BSC design (BSCD) and strategic planning consider a horizon of years and involve, for example, network design, facility location(s), and process capacities. Alternatively, tactical planning and operational planning involve analyses on shorter time scales and commonly address inventory location and control process scheduling and material flows. All scales should be analyzed collectively in an overall BSCD (Garcia and You 2015).

There have been an increasing number of papers addressing BSC optimization reported in some previous literature reviews. For instance, Shabani et al. (2013) analyzed 31 papers published prior to 2011. Their review focused on BSC design and analysis of bioenergy production. They concluded that environmental and social objectives should be included in the BSC models in addition to economic objectives. Cambero and Sowlati (2014) reached the same conclusion. The BSC network models were reviewed by Shahi and Pulkki (2013) from the retrieved 22 papers. They found that there is a need for an integrated simulation-based optimization modeling approach to address uncertainties in the BSC demand and supply.

In an exhaustive literature review, Elia and Floudas (2014) located 80 BSC studies regarding the production of heat, power, and transportation fuels from coal, biomass, and natural gas, both individually and in combination. They concluded that optimization models are most frequently applied; also, future studies considering multiple feedstock inputs (e.g., biomass and coal) with the focus on downstream operations and methods to address large-scale BSCs are necessary.

The most common objective of supply chain management is to minimize the total BSC cost. This includes raw materials and other acquisition costs, inbound transportation costs, facility investment costs, direct and indirect manufacturing and distribution costs, inventory holding costs, interfacility transportation costs, and outbound transportation costs (Shapiro 2001). The most effective approach to supply chain management is to maximize the net revenue by maximizing the revenue while minimizing total cost (Shapiro 2001).

An optimal BSCD is vital for the forest industries' long-term success. A forest biorefinery BSCD incorporates a wide range of biomass sources spreading out over vast geographic areas and utilizes a variety of transport modes, ultimately generating a large number of potential BSC options. The main goal is to find the optimal logistical arrangement that minimizes annual system-wide costs, including harvesting, collection, or purchasing costs, facility (storage, handling and fixed) costs, inventory holding costs, and transportation costs, within the parameters of a predetermined set of requirements (Toka et al. 2010).

At the strategic level, the results from the BSCD become constraints for the aggregate planning that takes place at the tactical decision-making level. However, the BSCD not only has to be efficient on the expected conditions, but also robust and flexible enough to adapt to potential changes in these circumstances (Toka et al. 2010). The number of studies addressing forest BSCD has increased rapidly. Table 5.2 presents a summary of four papers addressing BSCD. For more references, we refer to previous literature reviews: Sharma et al. (2013), which reviewed 32 papers, and Cambero and Sowlati (2014) with 54 papers.

Table 5.2. Summary of recent BSCD papers for bioenergy and biochemicals production.

Reference	**Mathematical model**	**Model objective**	**Main findings**
Zhang et al. (2014)	Mixed Integer Linear Programming (MILP)	Maximizing profit for commodity chemicals production via woody biomass fast pyrolysis and hydro processing pathways.	For a case study of Minnesota, U.S., the model demonstrated that distributed biomass chipping facilities are more profitable than roadside chipping, rich biomass sites are preferable locations for building a biorefinery, also that biomass availability and facility capital costs are the most significant variables affecting the project profitability.
Cambero et al. (2015)	Multi-period MILP model	Optimize the BSCD of forest residues for the production of bioenergy.	The model recommended the installation of small biomass boilers coupled with steam turbines for electricity production and pyrolysis plants to supply the needs of Williams Lake timber supply area, in British Columbia, Canada.
Čuček et al. (2014)	MILP	Optimally integrate regional biomass and bioenergy supply network including production processes from different sources of biomass producing first, second and third generation biofuels.	It is feasible to produce second and third generation biofuels. Biomass and waste, especially switchgrass and algae, were found to be promising raw materials for producing biofuels. Biorefinery supply networks could reveal significant unburdening capabilities of GHG emissions.
Tong et al. (2014)	Multi-period MILP model	Optimizing the BSCD for an advanced drop-in hydrocarbon bio-fuel BSC, integrating with existing. petroleum refineries under uncertainty.	Their model demonstrates, through a case study of Illinois, that advanced hydrocarbon biofuel BSC integrated with existing petroleum refinery infrastructure significantly reduces capital cost and total annualized cost, when compared to traditional biofuel BSCs.

Selecting the optimal location for the biorefinery site is an important decision that has a significant impact on the overall transportation cost (Eksioglu et al. 2009). The single and multi-facility methods for biorefinery location(s) require the knowledge of biomass feedstock locations (latitude and longitude), as well as biomass cost, availability, and quality and income from by-products (Johnson et al. 2012). Transportation costs are of prime importance when calculating the overall costs of biomass. Consequently, local or regional production of biomass is most favourable (Demirbas 2010).

The location problem has been addressed extensively in some publications. For a comprehensive review of BSC location models, we recommend Johnson et al. (2012). They examined the methods for optimally locating a forest biomass to a biofuel facility, re- viewing 57 papers from 2005 to 2012 addressing this BSC problem. The authors also classified the methodology used in the papers, concluding that mixed integer programming (MIP) is the most applied method because it provides the most comprehensive assessment for locating biorefineries overall. Nonetheless, Shahi and Pulkki (2013) found that, in general, the problems solved with linear programming and MIP models often needed several oversimplifications to render them solvable; they suggest an integrated simulation-based optimization modeling approach as a better method. According to Kocoloski et al. (2011), locating facilities in a way that minimizes transport cost can reduce the overall cost significantly compared with uninformed employment.

The majority of the optimal location studies focus on bioenergy production, including fuels, heat, and power (e.g., Leduc et al. 2008; Velazquez-Marti and Fernandez-Gonzalez 2010; Parker et al. 2010; Tittmann et al. 2010; Bai et al. 2011; Kim et al. 2011; Natarajan et al. 2012, 2014; Palander and Voutilainen 2013; Marvin et al.

2013; Pantaleo et al. 2014). However, some publications addressed BSC optimization for chemicals and materials production, including location problems, for example, Zhang and Wright (2014), Santibañez-Aguilar et al. (2015), Kokossis et al. (2015), Zhang et al. (2014), Sukumara et al. (2014), Dansereau et al. (2014).

5.4.2 The targeted products in biorefineries involving forest biomass supply chain optimization

It is evident that the number of published papers on economic optimization of FBSCs has increased significantly in the past 10 years (Fig. 5.2 (b)). New challenges and more sophisticated models have been developed indicating the importance of efficient BSC design and the evaluation of production of various products, e.g., energy, materials, and chemicals from forest biomass. Regarding the number of papers on BSC optimization, the Journal of Computer and Chemical Engineering published more papers than any other journal, accounting for 13.8% of the total papers, followed by Bioresource Technology, Energy, and Biomass and Bioenergy, each ac- counting for 8% of the total papers (Fig. 5.2 (a)). The United States (US) (35%) and Canada (11%) contributed to more publications than any other country (Fig. 5.2 (c)).

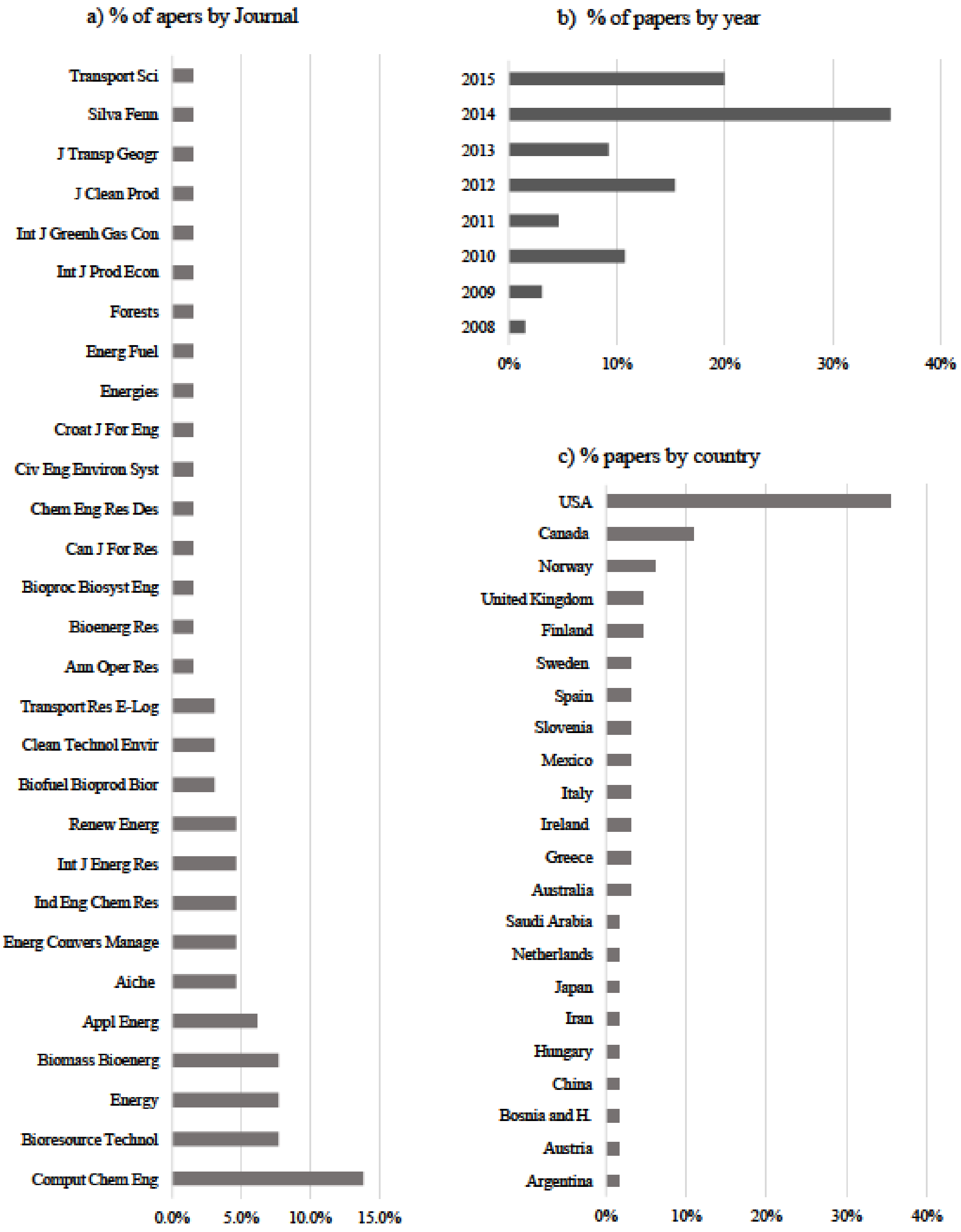

Figure 5.2. Papers reviewed percentage by journal (a), by year (b), and by country (c). The review includes publications up to October 6, 2015.

The Canadian forest products industry needs to diversify its portfolio to remain competitive, and the underutilization of forest resources has lowered its competitiveness in the global market (Shahi and Pulkki 2013). A reliable BSCD is crucial to utilize the forest resources better and achieve their highest possible value. Hence, BSC optimization studies are essential for the introduction of high-value bio-based products. Once such BSC optimization studies are completed, analyses can be done to determine the most appropriate strategies of fibre use to maximize value generation based on current forest market conditions (Shahi and Pulkki 2013).

The relatively larger number of publications from Canada on BSC optimization indicates that the research community has endeavored to explore solutions and alternatives for the Canadian forest industry. Additionally, the Canadian government, through Natural Resources Canada (NRCan), has supported development and implementation of bioenergy and biorefinery technologies (Paleologou et al. 2011). For instance, FIBRE (Forest Innovation by Research and Education) was founded in 2008 with the goal of developing innovative products, applications, and processes, as well as policy for the forest industry (FIBRE, available from http:// www.fibrenetwork.org/, accessed 21 July 2016). Under the umbrella of FIBRE, there were seven research networks funded by NSERC (i.e., Value Chain Optimization Network, Bioconversion Network, Lignoworks, Sentinel Bioactive Paper Network, NEWBuilds, Innovative Green Fibre Network, and For Value Net Network).

In the US, the Energy Independence and Security Act of 2007 (Public Law 110-140 (2007), https://www.epa.gov/laws-regulations/ summary-energy-independence-and-security-act) and the U.S. Environmental Protection Agency (EPA) regulate the supply of renewable transportation fuels consumed through the Renewable Fuel Standard (RFS2) program. According to Zhang and Wright (2014), biorefiners, renewable fuel producers, and other stake- holders are mandated to meet annual bio-fuel production and environmental requests to obey the RFS2. The large number of papers on BSC optimization from the US highlights the efforts of American researchers in the production of various products using renewable feedstock replacing petroleum. Regarding renewable feedstock, there have been a variety of lignocellulosic sources explored within the literature such as wood chips, energy crops, forest residues, agricultural residues, corn, switch grass, mill residues, and pulp and paper residues, among others. Studies focusing solely on wood as a primary feedstock comprised 44.6% of the publications collected in this work, while the remaining 55.5% are papers involving at least one non-wood feedstock source.

Biorefineries integrate biomass conversion processes to produce various products including fuels, power, heat, and value- added chemicals and materials. Their goals are to optimize the use of bio-based resources and minimize wastes, thereby maximizing benefits and profitability (Kokossis et al. 2015). According to the International Energy Agency, a biorefinery should produce at least one energy product and one non-energy product (Bell et al. 2014). From the papers reviewed, it can be inferred that there is a misunderstanding of the biorefinery concept, as some papers claimed biorefinery while producing only bioenergy.

Figure 5.3 presents a classification of the targeted products in the papers reviewed in this work. The majority of the papers (approx. 85% or 56 papers) focused on bioenergy and biofuels production. Only about 10% of the papers targeted both bioenergy and bio-based materials and chemicals such as specialty chemicals, pulp and wood products, newsprint products, lignin products, furfural, and commodity chemicals. Finally, less than 5% of the papers focused solely on bio-based materials and chemicals. More specifically, the main products targeted were ethanol (40%), electricity (23%), and heat (23%). However, none of the papers focused on carbon black, PF and PU resins, epoxy resins, and carbon fibre, discussed in a previous section of this article.

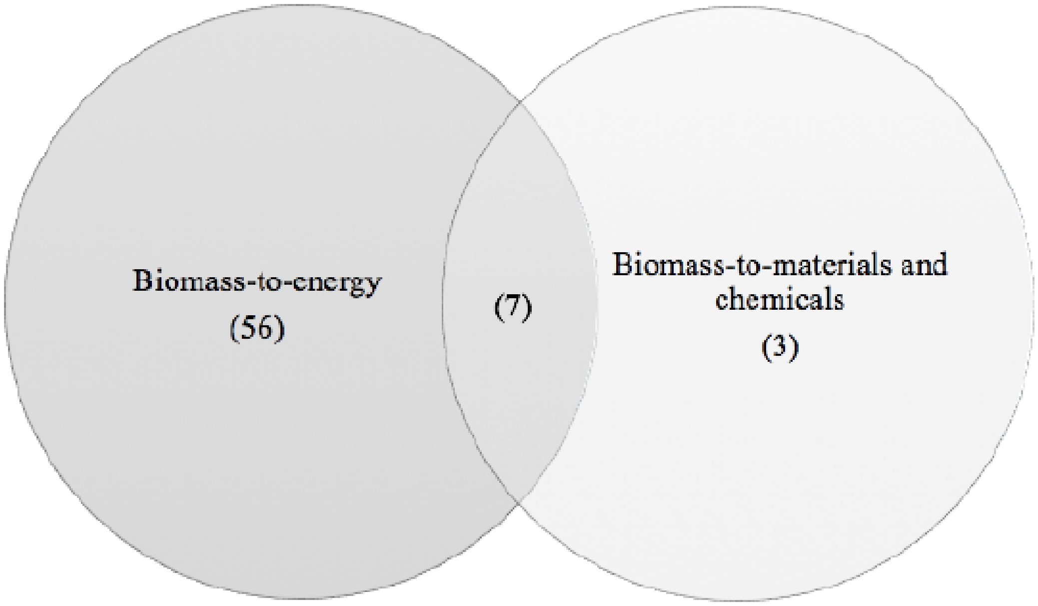

Figure 5.3. Final product of the FBSC economic optimization from the 66 reviewed papers.

Overall, 10 papers were targeting bio-based materials and chemicals and bioenergy (Table 5.3). These papers were published between 2012 and 2015, implying the emerging research interest in this field in the last couple of years.

Table 5.3. Summary of the 10 papers addressing bioenergy, biochemicals and biomaterials.

Reference	Research objectives	Feedstock	Target Products	Main findings
Zhang et al. (2014)	See Table 5.2	Forest residues.	Commodity chemicals	See Table 5.2
Kokossis et al. (2015)	Developing a systems approach for the design of integrated biorefineries, finding the most profitable biorefinery portfolio.	Wheat straw, rice; poplar and birch.	37 chemical compounds, 20 intermediates, and 17 final products.	Total site integration was found to offer savings of up to 88% when compared with the non-integrated case. The final products selected were xylonic acid, polyamide$_2$, polyester, polyamide$_3$, lignin-based castor oil, polyurethane coating, and resins.
Mesfun and Toffolo (2015)	Integration of a pulp and paper mill and a wood-pellet plant that share a heat and power plant.	Pulp wood, round wood sawdust and wood chips.	Heat, power, pulp, lumber and wood pellets.	The integrated cases studied performed better economically than the standalone ones in terms of
Santibañez-Aguilar et al. (2015)	Optimal planning of a distributed biorefinery system, accounting for the time dependence of the involved variables and parameters.	Wood chips, sugar cane, sorghum grain, sweet sorghum and corn grain.	Bioethanol and specialty chemicals.	BSCs based on biomass conversion are seriously affected by the availability of biomass resources over the time.
Kong et al. (2012)	To develop an optimization model to integrate the roundwood and forest biomass value chains in the initial stage of the FBSCs. Minimizing costs of procurement, chipping, inventory, and transportation.	Sawlogs, pulpwood, and forest residues, and wood chips and bark.	Heat, pulp and wood products.	In an integrated market there may be competition between heat generation and pulp because pulpwood can be used as raw material in both.
Kong et al. (2013)	Improvements the model published in 2012 in order to address log-term planning. They presented a new approach that can jointly choose areas and define price levels for different assortments at the chosen supply points of the BSC in the long-term planning.	Sawlogs, pulpwood, forest residues, wood chips and bark.	Heat, pulp and wood products.	With their model different equilibrium prices for roundwood and forest biomass can be generated, and possible unprofitable supply points can be excluded.

Table 5.3 Continued.

Reference	Research objectives	Feedstock	Target Products	Main findings
Sukumara et al. (2014)	A region-specific optimization model which links various aspects of the biofuel supply chain, such as feedstock source location, upstream and downstream logistics, as well as thermochemical and bio-chemical processing.	Corn stover and forest residues.	Ethanol, electricity and chemicals.	The model was proved to be the basis for a decision support tool that can guide investors and policy makers in making critical assessments on a local level in any particular region of interest.
Dansereau et al. (2014)	Integrating BSC planning and framework to optimize a superstructure that would ultimately assist decision makers to create BSC policies that can readily adjust to market changes.	Recycles paper, logs, and chips.	Newsprint products, lignin products, furfural, ethanol and heat.	By applying key concepts of the margins-based framework a company could increase its performance and robustness through BSC planning.
Zhang and Wright (2014)	Determinate the optimal plant sizes, locations, and product distributions for an integrated fast pyrolysis biorefinery BSC.	Forest residues.	Hydrogen, liquid fuels, commodity chemicals, and lignin.	Liquid fuel prices influence the annualized profit more than the commodity chemical price.
Čuček et al. (2014)	See Table 5.2	Corn grains, wood chips municipal solid waste, corn stover, organic manure and timber.	Heat, electricity, Ethanol, Corn-food, digestate boards, and distillers dried grains with solubles.	See Table 5.2

5.5 Conclusions

Lignocellulosic sources are one of the most promising renewable alternatives to fossil fuels for the production of bio-based chemicals and materials, as well as bioenergy and biofuels, including transportation fuels, heat, and power. Forest biomass can be used as a potential feedstock for biorefineries, which can help to ensure long-term environmental sustainability of the industry. Supply chain optimization has been addressed and emphasized in many publications. Although there are many review papers on biomass supply chains in the literature, some questions such as “what products shall be targeted in a biorefinery based on FBSC optimization” have not yet been answered.

In this review, various lignocellulosic feedstock, potential products, and conversion technologies were overviewed. FBSC to increasing forest industry competitiveness, enhance the sustainability of the forest sector, and decrease petroleum dependence.

- The BSC optimization has gained intensive attention in the past two years, in particular in the US and Canada.
- The target products in the BSC studies published so far are mainly ethanol, electricity, and heat, with little focus on bio- based chemicals and materials.
- A complete economic analysis and BSCD is crucial to the introduction of bio-based products into the market.
- There is a need for further studies focusing on biorefinery and supply chain optimization for the production of high-value bio-based materials and chemicals from forest biomass.

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CHAPTER 6 – Towards Commercial Lignin-Based Polymers: Supply Chain Cost Minimization

ABSTRACT

This paper brings vital information on variable cost, capacity, and supply chain design for the renewable production of phenols and polyols from kraft lignin (KL) in Canada. The technology proposed here is a low-pressure/low-temperature approach that results in DKL (Depolymerized Kraft Lignin) - a bioproduct with economic and technical capability to compete with non-renewable alternatives. Our supply chain variable cost minimization model was applied to several demand scenarios (20% to 50% demand) for a case study of the Canadian kraft pulp industry. At 30% polyols and phenols demand the model installs 8 biorefineries resulting a DKL minimum selling price varying from: 1,573 US$/t to 1,108 US$/t small to larger capacities respectively. Both, capacity and transport cost impact the feasibility of DKL.

Keywords: kraft lignin, supply chain, lignin polymers, cost minimization, kraft lignin depolymerization

6.1 Introduction

Lignin is recognized as the world's most abundant renewable aromatic polymer [1]. Its potential as an alternative to petroleum-based polymers is well established by extensive research over the years, as described in several review papers, for example, sources and characteristics [2], conversion [3], and biorefining portfolio [1,4]. One of the questions that remain is why the lignin-based market is still emerging at a slow pace? For the lignin market to take off, its derivative products have to be produced at a low-cost and perform at the same level as petroleum-based equivalents [1]. The performance side of the equation has been largely studied and improved methods are frequently published; on the other hand, the low-cost production and distribution side faces many challenges.

The lignin-based products manufacture can intensely benefit from research towards value-added products characteristics, costs, markets and supply chain (SC). Focusing on entering an existing market and established SCs can accelerate the growth of lignin biorefining [4]. Successful recovery processes, e.g., LignoForce and LignoBoost, have opened the opportunity for kraft pulp mills to create a new stream of products from lignin. Having the strength of well-established biorefining process, such as the kraft pulping industry, can increase the probability of success of kraft lignin (KL) bioproducts.

Having a reliable and robust lignin source stream is an advantage of pulp mills; nevertheless, it is just one step towards lowering the cost of lignin-based products. Other aspects to be considered are target markets and portfolio flexibility. KL can be utilized directly after recovered from black liquor or undergo conversion processes to achieve desired characteristics for value-added applications. Examples of KL potential applications developed in laboratory scale range from, but not limited to, hydrogels and nanocomposites for water purification [5,6], nanoparticles [7], vanillin [8], polyurethanes (PU) [8–10], carbon fibre [11], bio-dispersants [12], electrode materials [13], phenol-formaldehyde (PF) [14] and epoxy resins [15]. Furthermore, Téguia et al. [16,17] identified that KL as a replacement for phenol in PF resins, polyols in PU foams, and polyacrylonitrile (PAN) in carbon fiber are promising revenue diversification and competitive positioning strategies for kraft mills.

The volatility of the petroleum-derived polyols market from the crude oil price and demand instability results in a demand-supply unbalance which became an opportunity for lignin-based substitutes or replacements. PU are one of the most demanding applications of the polymer family. They are a result of the reaction of polyols and isocyanates which are both petroleum-derived [18]. Polyols are compounds containing multiple -OH groups which are precursors for polymers [19]. They consist of value-added chemicals their cost varied from ~1,800 to 3,000 US$/t in the last three years. Polypropylene oxide (PPG), for instance, is used in the manufacture of PU foams, it is formed in smaller quantities during the production of propylene glycol by hydration of propylene oxide [20].

As cited earlier, another often explored potential lignin product are phenolic resins. Phenol is an industrial commodity obtained from crude oil by-products; consequently, its price is influenced by crude-oil prices, production and demand variations. Around 95% of the petroleum-based phenol production is originated via the cumene oxidation process [21]. This process uses benzene and propene as feedstock (3:1 ratio) [22], to produce cumene then it goes under partial oxidation via the Hock rearrangement [19]. Acetone is produced as a by-product at ratio of 1/0.6 phenol/acetone [23]. Therefore, the demand for acetone also drives the phenol market. The average price of phenol in 2016 was 1,220 US$/t, and acetone 760 US$/t , both in US gulf [24]. One of the phenol's most important applications is in the manufacture of PF resins. Which are the most commonly used adhesive in the production of engineered wood products (EWP), like plywood, oriented strand board and laminated veneer lumber. The EWP market is growing and North America is the largest market of PF resins for EWP [25].

It is time to move lignin products research and industry initiatives to commercialization to obtain valuable information for further improvements that cannot be observed in laboratory scale. Canada is a leading country in the extraction and modification of KL for further value-added utilization and its pulp and paper industry is moving towards commercialization of KL. Therefore, considering the KL availability in Canada, potential markets and the conversion technology, we developed a variable cost minimization model to provide insights on the potential commercialization of DKL as an alternative petroleum-based phenol for the synthesis of phenolic resins, and polyols for polyurethane foams.

6.2 Methods

Direct use of KL in PF resins is limited to around 25% replacement of phenol, and in PU foams to around 10% replacement of polyols. To improve KL reactivity and increase replacement, several fractionation and modification methods have been studied. For instance, phenolation – mixing phenol and KL in certain conditions, allows up to 40% phenol replacement in PF resins [16]. The hydrolytic depolymerization of KL presented in this paper is a novel method that allow higher replacement ratios of 50 to 75%.

6.2.1 Low-temperature/low-pressure lignin depolymerization process

Over extensive research a novel low-temperature/low-pressure KL depolymerization technology to produce phenols and polyols was optimized by our research group, details on the process parameters, design, cost analysis and scaling-up can be found on our previous publications [14,26–30]. In this process, KL is depolymerized via direct hydrolysis at 250 °C, <150 psi pressure for 1 h for 20 wt% KL concentration using Ethylene Glycol (EG) as solvent and NaOH as a catalyst [28,30]. Washing and filtration with acetone and water are performed followed by recovery assuming a 5% loss in the process. Besides, the EG must be recovered as well to obtain the desired characteristics of the final product also to save costs, as EG is the most consumed chemical in the process. For the SC problem, we considered an EG recovery of 90%; therefore, 10% of EG remains in the final product with this characteristic the final product could be sold as phenol or polyol. The major parameters used in this paper are listed in Table 6.1.

The fixed cost estimated by the equations include working capital; fixed capital investment that includes total direct costs, total indirect costs, and contingency (derived from the total purchased equipment cost); and the fixed manufacturing cost that accounts for maintenance, overhead, labor, depreciation, and other fixed costs, such as property taxes and insurance [26].

Table 6.1. Summary of plant parameters relevant to the SC design.

Parameters	Value/Equation	Explanation
Production yield (t of DKL per 1 of KL processed)	1.29	Calculated based on the yield of 90% KL weight [29] also considering the not recovered (10%) EG that remains in the final product.
Manufacturing cost (US$/t)	1,076	Assuming the manufacturing costs have a linear relation to capacity [26].
Maximum plant capacity (KL processing t/y)	120,000	Maximum capacity and equations adjusted based on [26] (Supplementary material E). Where "x" is the amount of DKL produced by the plant, L: Linear and NL non-linear.
Fixed Cost (FI) (M US$)	FI (L): 65.225*x + 1,000,000 FI (NL): $18,207*x^{0.6944}$	

6.2.2 Identifying phenols and polyols market demand regions

Several market consulting companies, such as ICIS, Markets and Markets, PR Newswire, Grand View Research, provide detailed market reports on polyol and phenols. However, as information and data analysis are their core business, their reports are costly. Hence, in this study, we have gathered information from various sources to discuss and draw reasonable assumptions on market regions and demand for phenols and polyols.

As summarized in Fig.6.1, several keywords were introduced in various search engines. First on Google, to retrieve free information published by the chemical consulting companies. They release summaries of the market of polyols and phenols with specific key-data, such as expected growth and total demand, to draw costumers' attention to their full market report content. Secondly, the keywords were introduced into the database ProQuest which allowed filtering content to find trade and market journals and magazines (e.g., ICIS Chemical Business). Short articles and news available in these publications provided data on historical price variations and leading players in the market. Narrowing the search further, the keywords were introduced into industry suppliers catalog websites. These sources provided a list of companies by region and by country. Lastly, government websites helped to identify imports and exports and the demand by country in North America.

As a result, a list of demand locations was developed in excel. Every company website was accessed to determine potential market regions following the query presented in Fig. 6.1, resulting in a list of ~ 90 potential demand locations for phenol and polyols in North America.

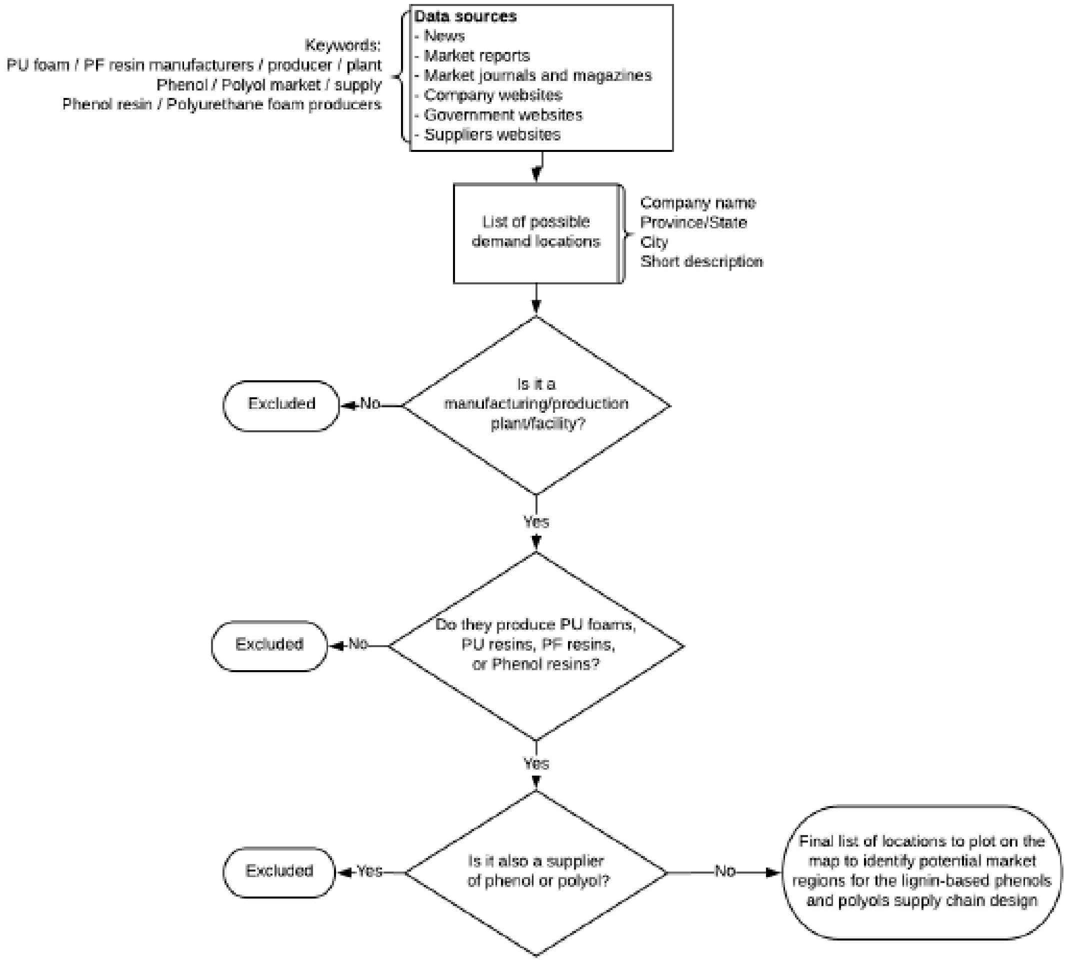


Figure 6.1. Phenol and polyol market data gathering and processing.

With the list of locations, a heat map was designed, using the software MapBusinessOnline, to show the possible demand regions in North America, the map is presented and discussed in a later section of this paper. The demand was established based on the market analysis, where 15 regions were identified as potential markets in North America (Appendix Table 6.S1). Once we could not find enough information to consider Mexico's demand; the country was not included in the study. Besides the model would unlikely choose to sell KL-based phenols and polyols to Mexico due to the high transportation cost; instead, it should prefer to serve the high-demand regions in the border of the US and Canada.

6.2.3 Supply availability and transport cost

The KL availability was gathered and presented by our research group in a previous publication [26], a table summarizing the availability by pulp mill location is presented in the Appendix (Table 6.S2). The truck transportation cost matrixes (Appendix Tables 6.S3 and 6.S4) were calculated from supply-to-biorefinery possible location and from biorefinery possible location-to-market region. The application *Worldfreightrates* was used to calculate the transport cost for all combinations one by one, for a 53 ft truck with a capacity to transport 19 t of chemicals.

A reference city was used to calculate the transport cost to each market region, which was determined according to the manufacturer's concentration in that region. Or, for the regions where only a few spread-out manufacturers were found, a central-region city was chosen as a reference to calculate the transport cost. The regions and transport cost reference cities are identified in a map presented in the results section.

6.2.4 Variable cost SC minimization model

The model aims to identify the distribution flow in the transport matrix that minimizes the total transport and manufacturing variable cost. The supply locations (s) consist of 23 pulp mills which can potentially supply KL – assuming that the 23 kraft mills can precipitate 12% of KL from the BL and sell it at the mill gate for 600 US$/t. The possible biorefinery locations (b) also correspond to the pulp mill locations in Canada, once they can beneficiate from the already installed infrastructure of the mills. The set of potential markets (d) are 15 locations distributed between the United States of America (US) and Canada. The overall SC and boundaries of this study are given in Fig. 6.2. The indexes, decision variables, and parameters are described in Table 6.2. The constraints and the objective function are detailed in the Eq. (6.1 to 6.7) below.

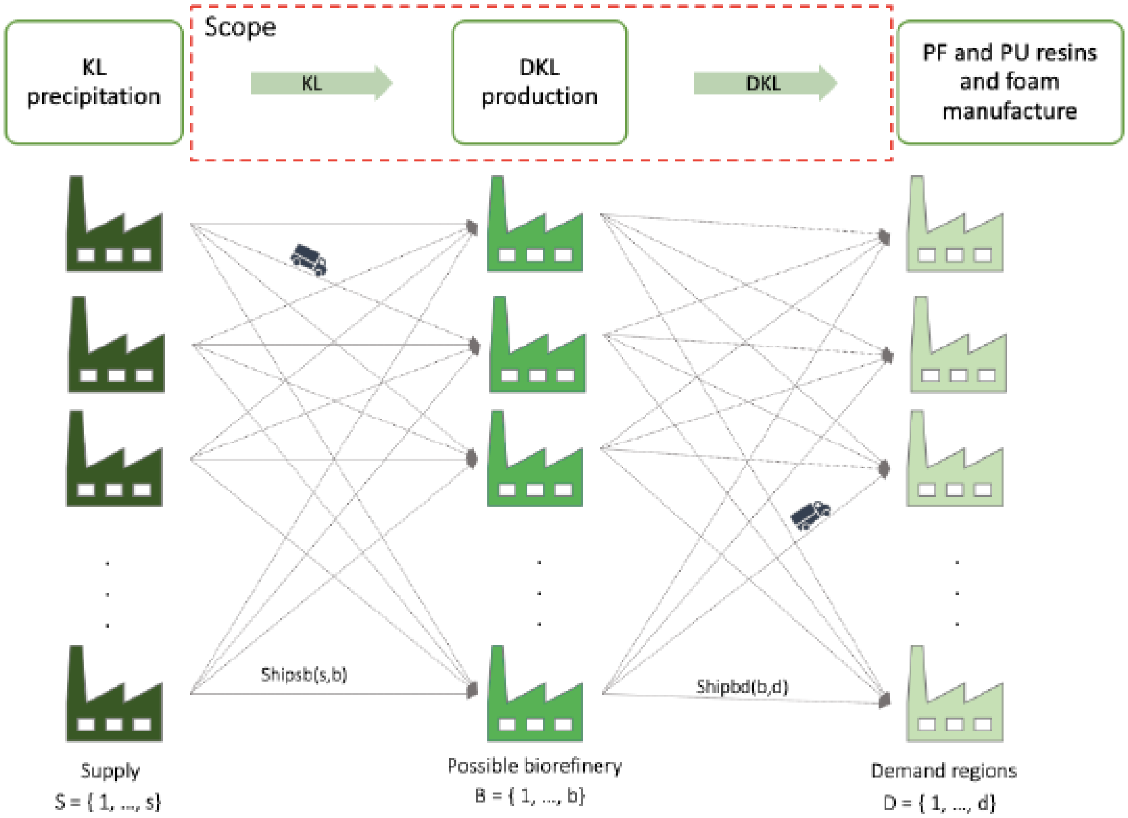


Figure 6.2. Simplified SC configuration and study scope.

Objective function

Total cost (tcost) is the sum of the cost of transporting the raw material to each selected facility plus the cost of transporting the products to each costumer plus the variable manufacturing cost.

Minimize:

$$tcost = \sum_{s}^{S}\sum_{b}^{B} \mathrm{cost}_{\mathrm{sb(s,b)}} \times \mathrm{shipsb(s,b)} + \sum_{b}^{B}\sum_{d}^{D} \mathrm{cost}_{\mathrm{bd(b,d)}} \times \mathrm{shipbd(b,d)} \times \mathrm{yield(b)} + \sum_{b}^{B}\sum_{d}^{D} \mathrm{shipbd(b,d)} \times \mathrm{yield(b)} \times \mathrm{varcost(b)}$$

Equation 6.1

Constraints

Supply(s): define that the amount purchased from a supply location (pulp mill) can't exceed the supply availability at that location.

$$\sum_{s} \mathrm{shipsb(s,b)} \leq \mathrm{supplya(s)}$$

Equation 6.2

Demand(d): the amount supplied to a demand region can't exceed the amount demanded by the region.

$$\sum_{d} \mathrm{shipbd}(\mathrm{b}, \mathrm{d}) \leq \mathrm{demandr}(\mathrm{d})$$ Equation 6.3

Balance(b): the sum of KL shipped from the supply location to the biorefinery location is entirely transformed in DKL.

$$\sum_{b} \mathrm{shipsb}(\mathrm{s}, \mathrm{b}) \leq \sum_{d} \mathrm{shipbd}(\mathrm{b}, \mathrm{d})$$ Equation 6.4

Capacity(b): Each biorefinery, if open, has a maximum DKL processing capacity.

$$\sum_{b} \mathrm{shipsb}(\mathrm{s}, \mathrm{b}) \leq \mathrm{maxcapacity}(\mathrm{b})$$ Equation 6.5

Maxdemandeq: Maximum overall demand to be fulfilled in each demand scenario.

$$\sum_{b} \mathrm{shipbd}(\mathrm{b}, \mathrm{d}) \times yield(b) \leq \mathrm{maxdemand}$$ Equation 6.6

Non-negativity constraints:

$$\mathrm{shipsb}(\mathrm{s}, \mathrm{b}), \mathrm{shipbd}(\mathrm{b}, \mathrm{d}),\ tcost, \leq 0$$ Equation 6.7

Table 6.2. Model nomenclature.

Sets	Description*
S= {1, 2, …, s}	Supply locations
B= {1, 2, …, b}	Potential biorefinery locations
D= {1, 2, …, d}	Demand regions
Parameters	
supplya(s)	Amount available at each supply location (t/y)
demandr(d)	Amount demanded at each market region (t/y)
$cost_{sb}$(s,b)	Transport cost from the supply location to each potential biorefinery location (US$/t)
$cost_{bd}$(b,d)	Transport cost from each potential biorefinery location to each market regions (US$/t)
maxdemand	DKL demand target scenarios (t/y)
yield(b)	Production yield (t of DKL/t KL processed)
maxcapacity(b)	Maximum plant capacity (KL processing t/y)
variablecost(b)	Manufacturing variable cost (US$/t)
Variables	
tcost	Total variable cost (US$)
shipsb(s,b)	Amount shipped from the supplier to the biorefinery (t/y)
shipbd(b,d)	Amount shipped from the biorefinery to the market (t/y)
Equations	
Supply(s)	Supply constraint at the supply locations
Demand(d)	Amount demanded at each the market region
Balance(b)	Supply and demand balance
Capacity(b)	Maximum biorefinery capacity equation
Maxdemandeq	Maximum demand to be fulfilled equation

*Calculated in 2016 US$ (United States Dollars)

Demand scenarios considering targets of 20%, 30%, 40%, and 50% of the total (891,744 t/y) phenol and polyol demand were considered. The model was validated and verified; it consists of a linear problem (LP) that was developed in GAMS and run though the NEOS platform using the CPLEX optimizer. The problem contained 876 single variables and 3,474 non-zero elements. The configuration obtained that minimized the tcost for each scenario was then used to calculate the minimum selling price (MSP) in two different cases: variable costs only and variable costs plus fixed cost (based on the fixed cost equations presented in Table 6.1). The MSP consists of the present value of the costs divided by the present value of the units produced considering the planning horizon of the project and a discount rate [31].

6.3 Results and discussion

6.3.1 Phenols and polyols market demand and KL availability

In 2012 the phenol market in North America demanded 2.63 M t/y with an expected growth rate of 2.8% per year; therefore, a demand of approximately 2.86 M t/y in 2016 [32]. The key players for the phenol market are presented in Fig. 6.3, some companies, such as Honeywell, Sabic, Harverhill and Dow Chemical, not only demand but also produce phenol [32]. Phenols are employed in various sectors, as shown in Fig. 6.4 (a). Among them, PF resins account for approximately 30%, from which it is segmented between resoles and nolovacs [33].

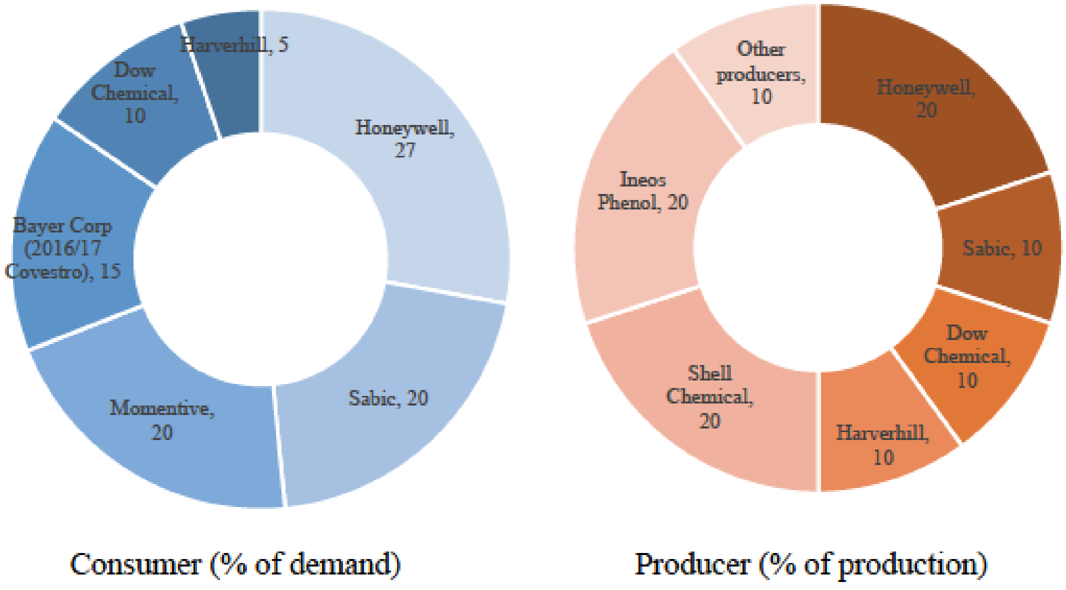
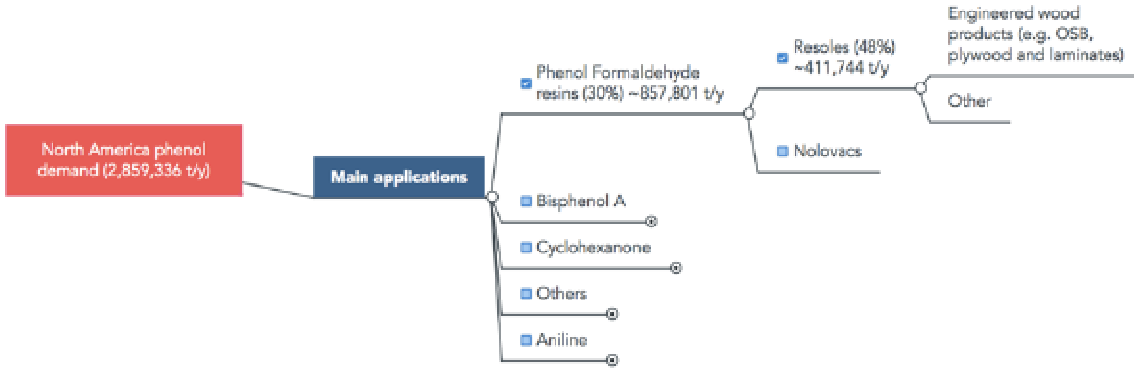


Figure 6.3. North America phenol demand and production [32].

Polyol is another significant ingredient in different segments, in 2016 its demand reached 1.6 M t/y. It is largely used polyurethane formulations for industrial applications (Fig. 6.4 (b)). Around 30% of the polyol demand is estimated for rigid foams [34]. Main companies in the polyol for PU and PF rigid foams are Woodbridge Foam Corporation, Delemec, Accella Polyurethane Systems, UFP Technologies, BASF, Norseman, and Huntsman Corporation.

(a) Phenol and phenolic resins demand in North America



(b) Polyol and rigid foam demand in North America

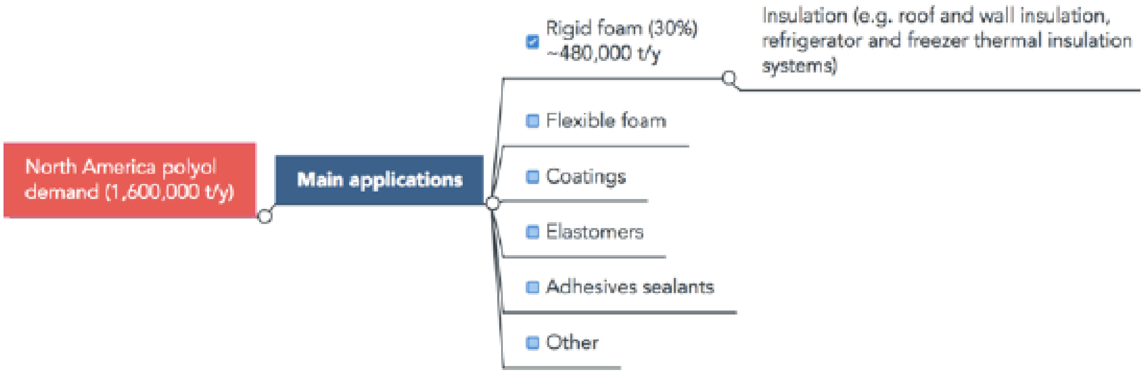


Figure 6.4. Phenol and polyol market in North America, base year 2016 [32–37].

Based on the locations retrieved according to the methods section "Identifying Phenols and Polyols Market Demand Regions" a heat map was plotted to give an idea of the demand density based on the number of manufacturing/production plants. We observed that phenols and polyols demand follow the same tendency; therefore, there were considered together in the optimization analysis. The US regions were separated based on the US census territories. To represent the demand regions in Canada and calculate transportation costs we created sub-regions (represented by the circles in the map, Fig. 6.5), as de demand is spread out in the east and west. The largest concertation of manufacturers demanding phenol and polyols was observed in East North Central in the US and Southeast Ontario in Canada (Fig. 6.5).

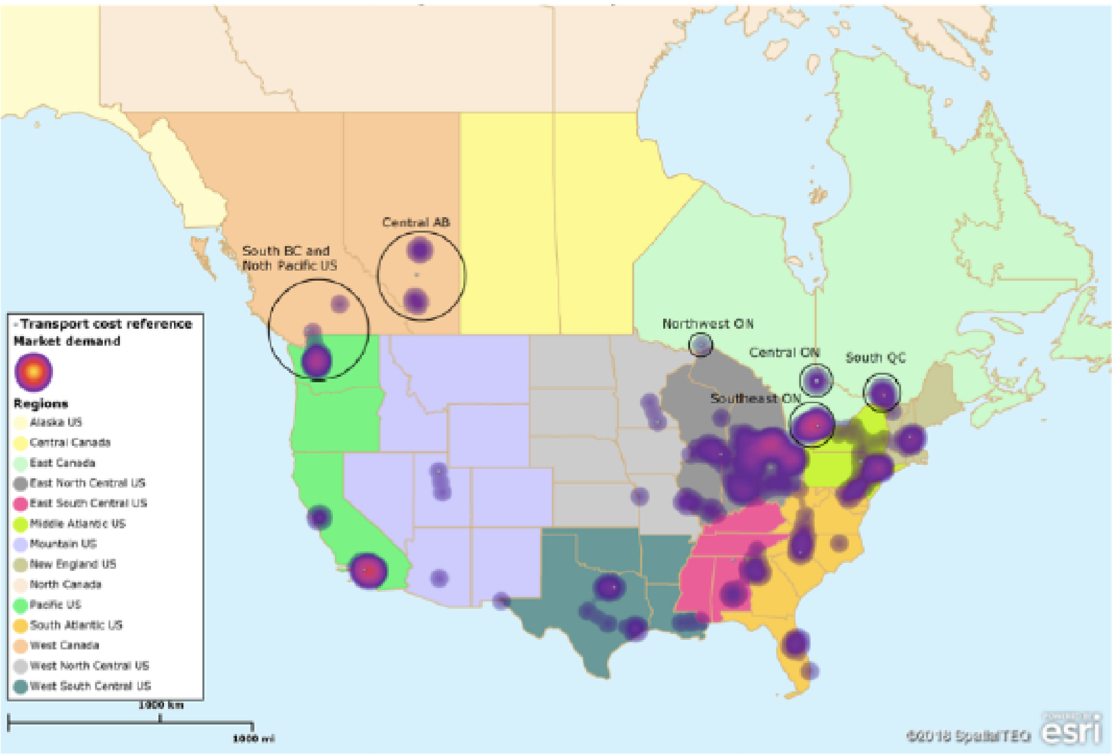


Figure 6.5. Heat map of phenol and polyol manufacturers distribution and potential demand regions in Canada and the US.

The Figure 6.6 brings a heat map for the KL availability in Canada. The yellow-orangish heat region in Central-North British Columbia (BC) represent three pulp mills located in Prince George. Other three mills located in South BC (Port Mellon, Nanaimo and Crofton) are represented by the yellow-greenish heat region close to Vancouver

Island. Two pulp mills, one in Castlegas and another in Kamloops, contribute to the blue-greenish area South of BC close to the United States and Alberta (AB) border. In AB, Boyle alone represents the circle indicated North of Edmonton. In East Canada one can also point out two large zones one in Thunder Bay and Terrace Bay in Northwestern Ontario, another in Trois-Rivières, Windsor and Thurso in Quebec.

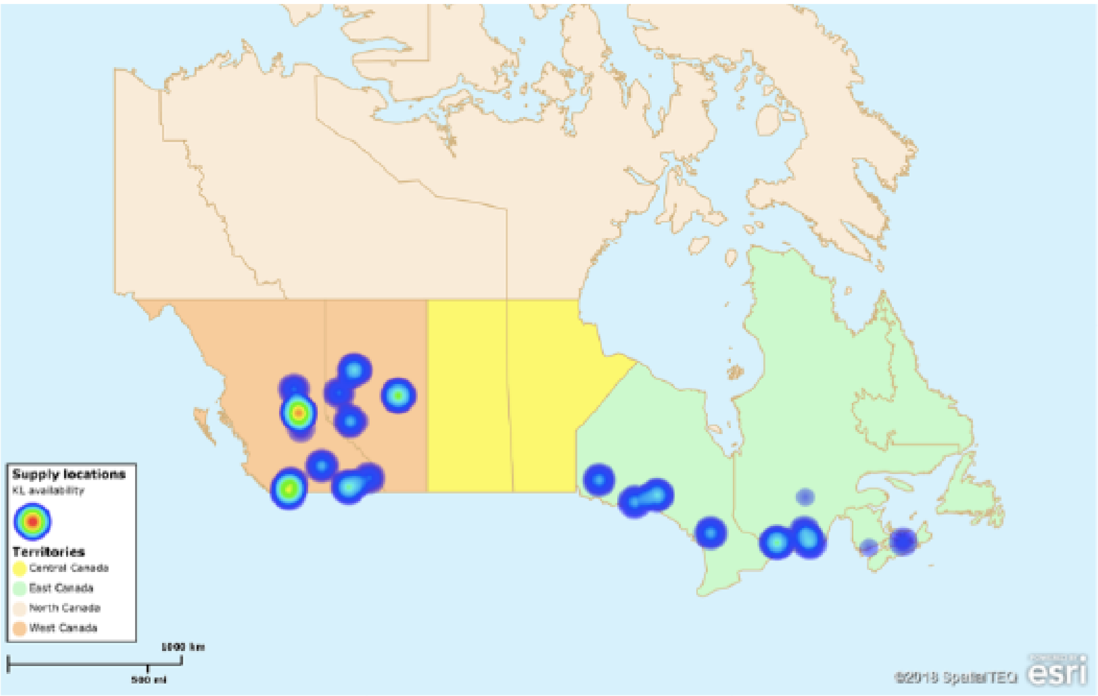


Figure 6.6. Heat map of KL availability in Canada.

In the context of lignin extraction and commercialization some initiatives have been observed. For instance, a commercial-scale lignin recovery plant is operating in Hinton, Alberta. Their extracted KL will be developed for use as a natural adhesive in the engineered wood products produced by West Fraser Timber Co., which owns the Hinton mill [38]. Also, the Ministry of Northern Development and Mines Ontario is supporting innovative research and a new lignin pilot project in Thunder Bay. The province's

Northern Ontario Heritage Fund Corporation is investing MUS$ 4.5 to help FPInnovations establish a fully functioning biorefinery plant [39].

6.3.2 SC variable cost minimization: a case study 30% DKL

The configuration resulted in the 30% demand base-case scenario is presented in Fig. 6.7. The model opens eight biorefinery locations (Trois-Riviéres, QC, Crofton, BC, Thunder Bay, ON, Espanola, ON, Windsor, QC, Boyle, AB, Nanaimo, BC, and Thurso, QC). One can observe in Fig 6.7 that the plants selected (large yellow triangles in the map) correspond to some of the KL high-supply areas discussed in the previous section. Only variable costs were minimized in this preliminary investigation. Therefore, the model chooses to install a larger number of plants in locations close to the market, minimizing DKL transport cost.

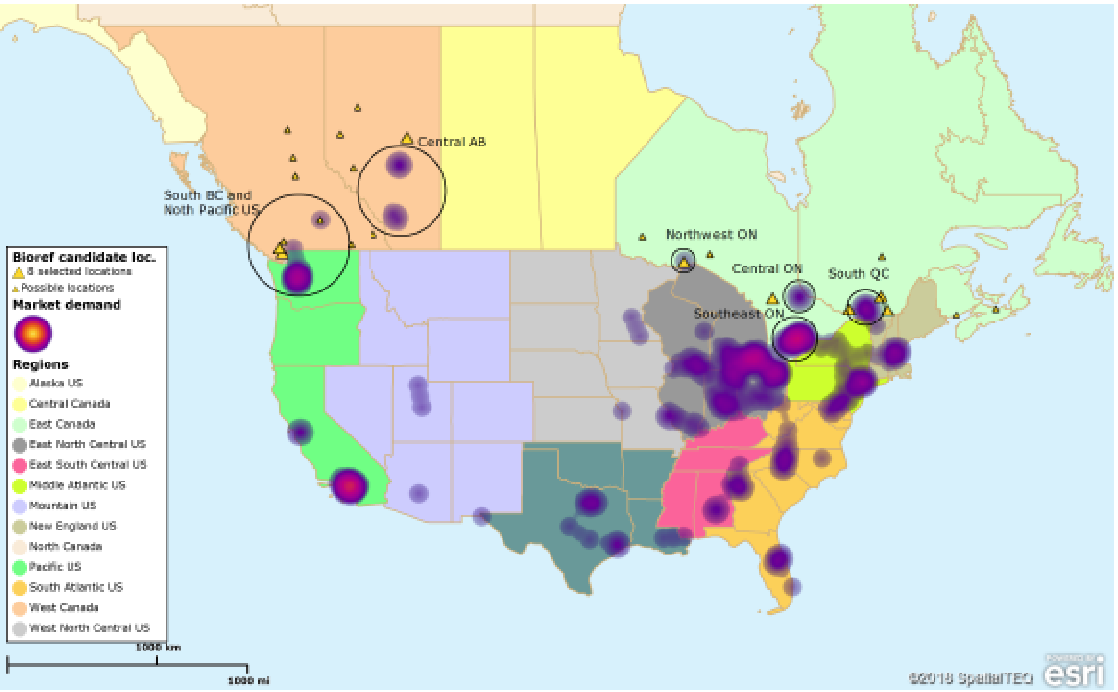


Figure 6.7. Results for the base-case scenario for 30% DKL demand.

Table 6.3. Installed plants and the markets supplied for the 30% DKL demand scenario.

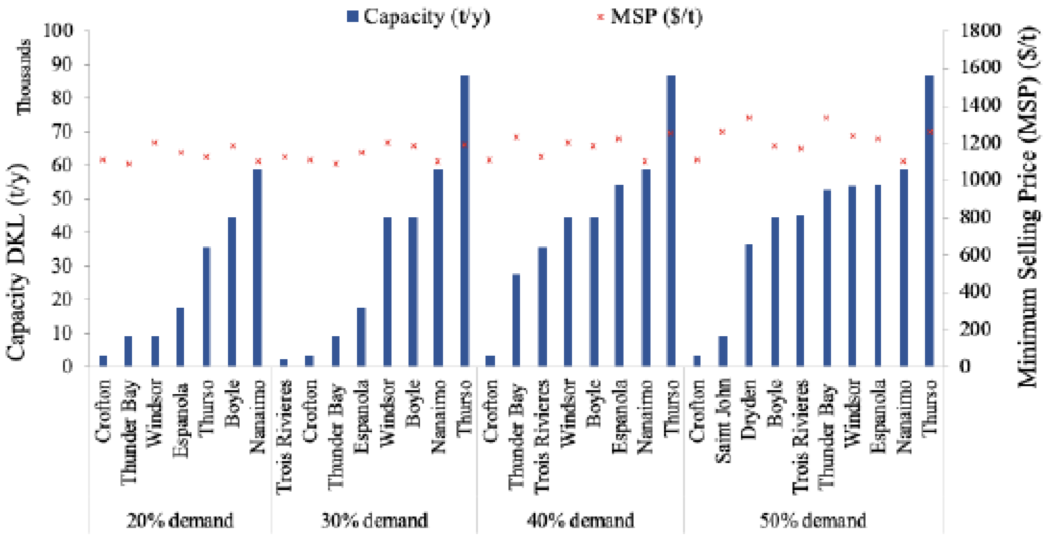
Installed plant	DKL capacity (t/y)	Market supplied / amount (t/y)
Trois-Riviéres, QC	2,261	South QC / (2,261)
Crofton, BC	3,566	South BC and North Pacific US / (3,566)
Thunder Bay, ON	8,917	Northwest ON / (8,917)
Espanola, ON	17,835	Central ON / (17,835)
Windsor, QC	44,587	New England US / (44,587)
Boyle, AB	44,587	Central AB / (44,587)
Nanaimo, BC	58,856	South BC and North Pacific US / (58,856)
Thurso, QC	86,914	Southeast ON / (53,505) and South QC / (33,409)

All DKL production plants showed in Table 6.3, are self-sufficient in KL feedstock; for instance, to produce 86,914 t/y of DKL the Thurso plant would require 67,375 t/y of KL which corresponds to the maximum availability assumed in this study (12.5% of the total KL generated at the mill). Our previous study found that higher profit margins can be obtained for plants with a capacity above 25,000 t/y of DKL providing some price elasticity to compete with petroleum-based polymers [24]. Fixed costs per unit produced tend to decrease as capacity increases. For the configuration presented in this case study, the average DKL MSP including all costs (fixed and variable at a 10% hurdle rate) was 1,273 US$/t varying from 1,108 (Nanaimo) to 1,573 US$/t (Trois Riviéres).

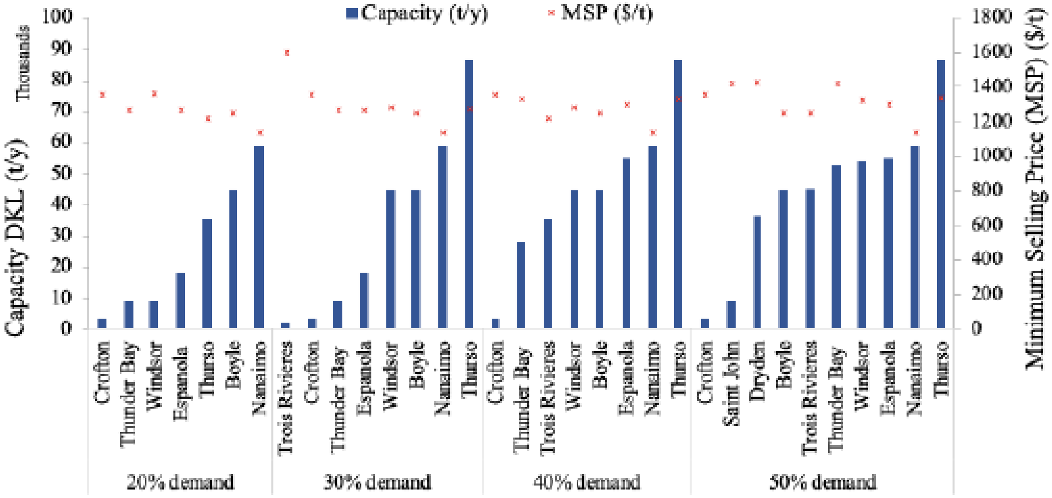
From June 2014 to July 2017 the phenol prices in the US varied from ~970 to 2,028 US$/t [24,40,41], and polyols varied from ~1,800 to 3,000 US$/t in North America [27]. Thus, DKL as a replacement for phenols is less attractive pricewise than for polyols. Once, this technology allows replacement of up to 75% in phenols and 50% in polyols with the same production configuration, the plant has the flexibility to target one product over another given the market constrains aiming the highest possible return. In the next section, we explore the impact of the fixed costs in the MSP for the SC configurations of four demand scenarios.

6.3.3 Demand scenarios

The capacity and MSP of the four demand scenarios are given in Fig.6.8 (a and b). Looking at the locations selected, six sites appeared in all scenarios (Nanaimo, Espanola, Windsor, Thunder Bay, Boyle and Crofton) because of its proximity to large markets.



a) Demand scenarios with MSP including variable cost only



(b) Demand scenarios with MSP including variable and fixed cost*

Figure 6.8. Capacity and MSP for various phenol and polyol demand scenarios, (a) accounting for variable cost only, and (b) variable and fixed cost. Note: Capacity cost estimated based on the equations FI (L): 65.225*x + 1,000,000 and FI (NL): 18,207*x0.6944. Both showed similar results; therefore, only FI (L) is presented in the figure.

In Fig. 6.8 (a) fixed costs are not amounted for; therefore, the MSP variation is small among the scenarios, becoming more noticeable in the 50% demand scenario. Larger the demand, higher is the transport cost to the market in order to deliver DKL further away from the biorefinery. On the other hand, in Fig. 6.8 (b), the MSP variation is noticeable in all scenarios. Keeping the SC configuration same, the addition of the fixed cost to the MSP results in higher costs for smaller capacities. The savings from transport cost might not compensate installing small DKL plants.

The locations showed in Fig. 6.9 were selected in all scenarios at capacities above 20,000 DKL t/y and an overall average MSP of 1209 US$/t. Therefore, these locations are recommended for DKL production. However, this study does not consider the mill specific information; therefore, capabilities of these mills to extract KL and their interest in functionalising it is unknown.

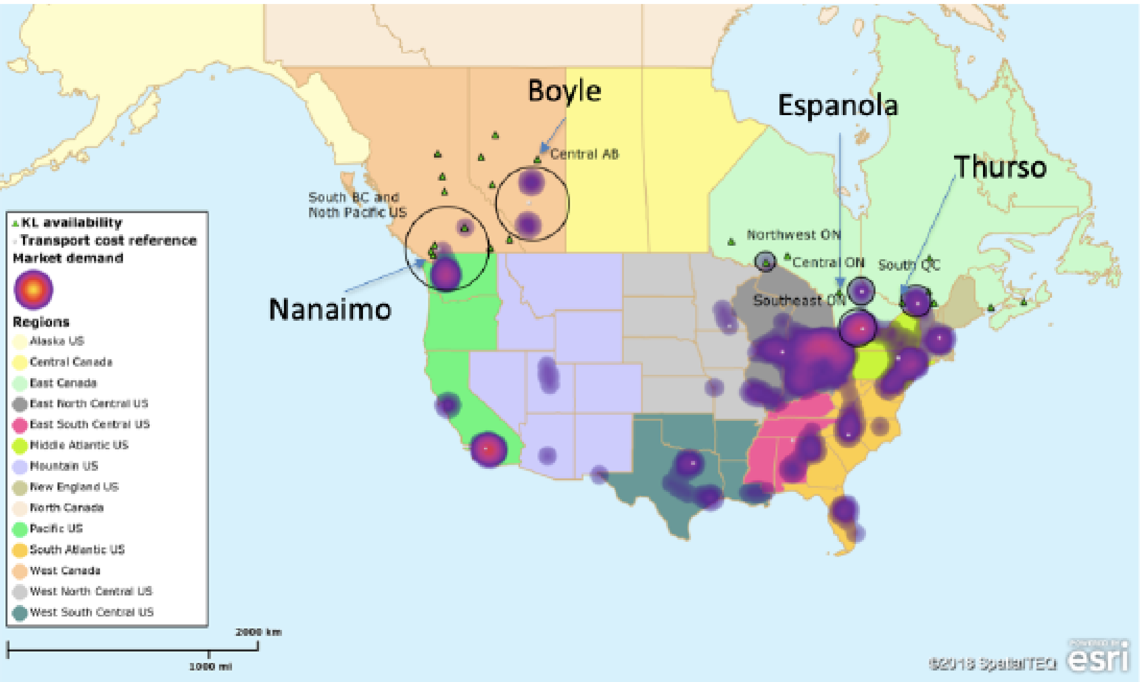


Fig 6.9. Locations selected in all scenarios with capacities above 20,000 DKL t/y.

6.4 Conclusion and recommendations

Most of the technologies remain at laboratory scale because of the lack of information on the economic feasibility and market competitiveness of KL bioproducts. To obtain a low-cost competitive bioproduct from lignin it is necessary to optimize not only the technology but the entire supply chain. This study brings a start to the modeling of KL-based products' supply chain. Here we present a market analysis for phenol and polyol in North America, and a supply chain variable cost minimization model. This study identified potential biorefinery locations, such as Nanaimo, BC, Boyle, AB and Thurso QC are located close to demanding markets, for example, South BC and North Pacific US, Central AB, Southeast ON, and South QC. In the base-case eight plants are installed resulting a DKL MSP ranging from: variable costs only: 1,204 US$/t to 1,085 US$/t; and, variable and fixed costs: 1,573 US$/t to 1,108 US$/t for larger capacities.

The next step is to incorporate the fixed costs equations directly into the supply chain model to obtain a better understanding of the tradeoff between transport costs and fixed costs. Additionally, it is important to account for plants that are already extracting KL from black liquor, companies that own pulp mills and plywood manufacturing plants. It would also add immense value to consider various KL applications with and without further conversion after extraction from black liquor. It is necessary to identify the border line between using KL directly and DKL considering their replacement limitations and the price of its petroleum-based substitutes. In the long-term, higher margins could be achieved by producing the resin and foam instead of supplying alternatives for phenols and polyols. Finally, partnerships among KL pulp companies to target specific market needs as well as government incentives and the academy engagement can also account a great deal into the success of KL bioproducts ventures.

Adding capacity flexibility and uncertainties in price and demand in the supply chain add complexity to the problem resulting in a MINLP - under uncertainty; nevertheless, it is a necessary step to further identify the best configuration to minimize cost and maximize the profit of KL bioproducts. Therefore, it is the challenge for an additional publication to complement the findings of this paper.

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CHAPTER 7 – Conclusions and recommendations

7.1 Overall conclusion

Lignin valorization is a massive opportunity for revenue increase in the kraft pulp industry. The list of lignin potential applications is extensive, especially for KL. KL is not as expensive to obtain as high-grade lignin, at the same time it has improved quality when compared to the low-cost lignosulfonates. Commercial scale production of KL is growing around the world allowing manufacturer testing of lignin as a substitute or a replacement for commodity chemicals, such as phenols.

The groundwork in lignin's extraction, characterization and modification are well covered in the literature, and it continues to grow. The majority of academic research stops at the laboratory level, limiting the efforts to proving the concept and showing the technical aspects of the application proposed. A minimal focus is given to lignin products feasibility, availability of feedstock, market price and demand estimations. It is a challenge to design and gather reliable techno-economic estimates for new technologies. However, it should not prevent this vital area of research to grow.

In this work, we demonstrate that it is possible to provide valuable feasibility information on new technologies. This was achieved through collaborative efforts involving multidisciplinary expertise, allied to well-established methods of chemical engineering design and cost estimation, and an analysis of risks associated with the uncertain parameters. Further, competitive advantages are tied to supply chain strategies; therefore, this work demonstrated that the location and capacity of biorefineries determines the viability of lignin phenols and polyols. Specifically, this research adds to the knowledge through:

- Covering the supply and market side of lignin applications extensively, while also highlighting pathways for lignin modification targeting improved substitution and applications.
  - KL most promising applications in the short to mid-term are phenols and polyols.
  - KL modification improves its performance and increases the level of substitution.
  - The vast majority of supply chain studies focus on biomass-to-energy.
  - There is a lack of techno-economic studies for biochemicals and biomaterials.
- Developing a process design at pilot scale for a novel depolymerization process using low-pressure and low-temperature created at Dr. Xu's research group (patent pending). The DKL products have suitable characteristics, such as high hydroxyl a moderately low weight-average molecular weight, for synthesis of biopolymers. Which can substitute up to 75% petroleum phenol in the manufacture of phenol-formaldehyde resins and up to 50% in the formulation of polyurethane foams.
- Investigating the feasibility of DKL as a biopolyol and biophenol alternative.
  - DKL as total variable manufacturing costs varies from ~1,081 up to 1,101 US$/t, and the total fixed manufacturing costs from ~63 to 154 US$/t, (capacity 10,000 to 120,000 t/y DKL). For an average size Canadian kraft pulp mill, a DKL production above 25,000 t/y is recommended.
  - KL-based polyol and phenol is a feasible alternative for revenue generation for the Canadian kraft pulp industry.
  - The novel depolymerization low-pressure and low-temperature technology presents good economies of scale as the cost per unit decreases with plant scale expansion.

- Performing a risk analysis to address uncertainty in feedstock cost, capital investment, and based on historical data of target products selling price.
    - The parameter that most affects the KL-based chemicals feasibility is the fluctuation of polymer prices.
- Modeling a preliminary SC design for DKL as a substitute for phenols and polyols
    - Fixed manufacturing cost varies substantially with capacity; as capacity increases fixed manufacturing cost decreases. Plant location is a critical variable for competitive advantage.

The theoretical contributions of this study are the lignin availability in Canada and potential market of lignin-based chemicals and materials. Additionally, we demonstrated the significant impact of the SC in the feasibility of lignin-based chemicals. Furthermore, the methods and the framework presented here are suitable for the assessment of other bioproducts. The Canadian forest industry is undergoing a transformation; several pulp mills are investing in portfolio diversification. This work provides practical information for this industry to support decision making on DKL as a lignin valorization strategy.

7.2 Future research

The study presented here is an example of what should be developed for all lignin potential applications. Then, when a substantial body of knowledge is available covering design and cost of possible lignin products, an overall analysis can take place addressing various applications to select the most feasible option given supply and demand constraints. Some limitations of our work are, lack of information on mill-specific KL extraction limitations, technology maturity risks, competition with other KL modification technologies and unmodified KL, and assessment of environmental and social implications. Therefore, the list below offers suggestions for future research.

1. Introducing capacity flexibility to the SC, modeling the capital investment non-linear relationship with capacity.
2. Investigate several scenarios, such as varying substitution levels considering modified and non-modified KL, demand by proximity to markets.
3. Investigate integration with an existing pulp mill or biorefinery plant. Where site-specific synergies, such as energy balances, current products and waste treatment can contribute to KL valorization.
4. Investigate the interaction of KL bioproducts within existing supply chains of the forest and chemical industry.
5. Model the entire SC in a multiple criteria framework (environmental, social and economic), from the source of biomass to the consumer of the final product which was manufactured using bio-based chemicals.

So far, the studies lack the end-user inputs because we are still trying to engage and understand the needs of the manufacturers (e.g., panels and foams producers) – say the middle of the chain. The pull should come from the end-user. When they see the value proposition and participate in the development process; it will be possible to identify the most promising approach for the successful lignin biorefinery expansion.

Appendix Chapter 4

Table 4.S1. Mass flow balance for a DKL plant with 10,000.0 t·year^{-1} KL capacity and 90% EG recovery.

Flow	Stream	Material	Flow rate (t·day^{-1})
ST-1 to R-1	s-1 - in	KL (raw material)	33.3
ST-2 to R-1	s-2 - in	EG (raw material)	116.9
ST-3 to R-1	s-3 - in	Water (raw material)	6.9
ST-4 to R-1	s-4 - in	NaOH (raw material)	9.4
R-1 to P-1	s-5 - in	Reaction product	166.6
P-1 to T-1	s-6 - in	Reaction product	166.6
ST-3 to R-1	s-3 - in	Water (raw material)	83.3
ST-6 to T-1	s-7 - in	Acetone (raw material)	83.3
ST-5 to T-1	s-8 - in	Acid (raw material)	5.2
T-1 to P2	s-9 - in	Reaction product + acetone + water + acid	338.6
P-2 to C-1	s-10 - in	Reaction product + acetone + water + acid	338.6
C-1 to waste treatment	s-11 - out	Solid residues (10% KL) + NaOH	12.8
C-1 to P-3	s-12 - in	DKL diluted in acetone + water + acid	325.8
P-3 to S-1	s-13 - in	DKL diluted in acetone + water + acid	325.8
S-1 to P-4	s-14 - in	DKL	146.9
P-4 to S-2	s-15 - in	DKL	146.9
S-1 to ST-6	s-16 - out	Acetone	76.7
Acetone losses	out	Acetone	6.7
S-1- to waste treatment	s-17 - out	Water + acid	95.5
S-1 to ST2	s-18 - out	EG	105.2
S-2- to storage	s-19 - out	Purified DKL (end product)	41.7
In flow (t.day^{-1})	338.6		
Out flow (t.day^{-1})	338.6		
Purified DKL (t·year^{-1})	12,508.1		

Table 4.S2. Major cost information and financial assumptions.

Parameter	Value	References
Phenol selling price ($\$\cdot\text{t}^{-1}$)	1,303.9	Dietrich (2016, 2017)[1–3]
KL cost ($\$\cdot\text{t}^{-1}$ at pulp mill)	600.0	FPInnovations (2017)[4]
NaOH cost ($\$\cdot\text{t}^{-1}$)	388.0	de Assis et al. (2017)[5]
EG industrial grade (MEG) ($\$\cdot\text{t}^{-1}$)	908.2	Tarun (2017),[6,7] Mirasol (2016)[8]
Acetone cost ($\$\cdot\text{t}^{-1}$)	928.3	Dietrich (2017)[9]
Sulfuric acid cost ($\$\cdot\text{t}^{-1}$)	90.0	ICIS (2017)[10]
Water cost ($\$\cdot\text{t}^{-1}$)	0.13	Pham et al. (2013)[11]
Electricity cost ($\$\cdot\text{kWh}^{-1}$)	0.062	Pham et al. (2013)[11]
Waste water treatment ($\$\cdot\text{t}^{-1}$)	0.6	Ulrich and Vasudevan (2006)[12]
Equipment life span (years)	25.0	Assumed
Start-up time (years)	1.0	Assumed
Production capacity 1st year (%)	80.0	Assumed
Production capacity remaining years (%)	100.0	Assumed
Acetone recovered (%)	92.0	Assumed
Depreciation method	straight line	de Assis et al. (2017)[5]
Planning horizon (years)	25.0	Assumed
Total direct costs (%)	3.6 x equipment cost	Peters and Timmerhaus (2003)[13]
Total indirect costs (%)	1.4 x equipment cost	Peters and Timmerhaus (2003)[13]
Contingency (%)	0.2 x equipment cost	Peters and Timmerhaus (2003)[13]
Fixed capital invest. (FCI) (%)	5.2 x equipment cost	Jordan (2001)[14]
Working capital (%)	5% of FCI	Tan et al. (2016)[15]
Maintenance cost (%)	2% of FCI	de Assis et al. (2017)[5]
Overhead costs (%)	60% of labor	Peters and Timmerhaus (2003)[13]
Other fixed costs (%)	1.5% of labor	Peters and Timmerhaus (2003)[13]
Hurdle rate or return rate (%)	16.0	de Assis et al. (2017)[5]
Taxes (%)	25.0	assumed
Operating season ($\text{h}\cdot\text{year}^{-1}$)	7200.0	assumed
Labor (US\$ $\text{operator}\cdot\text{year}^{-1}$)	~52,000	de Assis et al. (2017)[5]

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Appendix Chapter 6

Table 6.S1. List of potential markets and estimated demand for phenols for resoles and polyols for rigid foam.

Market regions	Phenols for resoles and polyols for rigid foam demand (t/y)
East North Central US	178,349
Middle Atlantic US	89,174
West South Central US	80,257
South BC and North Pacific US	71,340
Pacific US	71,340
South Atlantic US	71,340
Southeast ON	62,422
Central AB	44,587
East South Central US	44,587
New England US	44,587
South QC	35,670
Mountain US	35,670
West North Central US	35,670
Central ON	17,835
Northwest ON	8,917
Total demand	891,744
Target DKL based (30%) supply chain	267,523

Table 6.S2. Kraft lignin availability

Supply	KL availability (t/y)
sdryden	40,875
sespanola	42,375
swindsor	41,875
skamloops	44,250
ssaintfelicien	13,913
sthunderbay	40,875
shinton	47,500
squesnel	21,250
sprincegeorge	137,500
scastlega	65,000
scrofton	47,125
sboyle	81,250
speaceriver	60,000
sthurso	67,375
sportmellon	53,125
sskookumchuck	29,250
snewglasgow	22,125
smackenzie	30,000
ssaintjohns	11,250
stroisrivieres	35,000
sterracebay	55,875
snanaimo	45,625
sgrandorairie	31,250

Table 6.S3. Transport costs matrix (US$/t of KL) from supply to potential biorefinery locations.

	Potential biorefinery locations											
Supply Region	bdryden	bthunderbay	bterracebay	bespanola	bthurso	bsaintfelicien	btroisrivieres	bwindsor	bsaintjohns	bnewglasgow	bkamloops	bhinton
sdryden	0	14	19	39	57	60	62	64	125	96	72	60
sthunderbay	14	0	8	32	47	50	47	54	104	86	82	70
sterracebay	19	8	0	22	41	41	40	19	74	82	80	77
sespanola	39	32	22	0	21	34	27	31	92	60	106	97
sthurso	57	47	41	21	0	19	10	12	70	42	124	117
ssaintfelicien	60	50	41	34	19	0	12	18	61	39	131	120
stroisrivieres	62	47	40	27	10	12	0	27	27	34	121	122
swindsor	64	54	19	31	12	18	27	0	20	36	135	124
ssaintjohns	125	104	74	92	70	61	27	20	0	14	177	185
snewglasgow	96	86	82	60	42	39	34	36	14	0	168	156
skamloops	72	82	80	106	124	131	121	135	177	168	0	18
shinton	60	70	77	97	117	120	122	124	185	156	18	0
squesnel	78	88	94	114	134	137	140	141	202	173	16	19
sprincegeorge	74	85	91	104	131	134	136	138	198	170	21	17
scastlega	64	75	81	103	122	124	141	142	203	174	18	28
scrofton	83	93	100	118	136	142	155	157	217	189	14	30
sboyle	53	84	70	89	110	113	115	116	177	149	32	17
speaceriver	66	77	83	103	123	126	129	130	191	162	31	15
sportmellon	84	95	101	119	138	144	157	158	219	191	16	31
sskookumchuck	86	97	103	121	140	146	160	161	222	193	19	34
smackenzie	78	89	192	114	135	138	82	142	200	174	27	22
snanaimo	77	87	102	109	139	131	158	109	102	192	15	32
sgrandprairie	59	69	83	92	122	113	128	92	83	162	26	13

Table 6.S3. Continued.

Supply Region	Potential biorefinery locations										
	bquesnel	bprincegeorge	bcastlega	bcrofton	bboyle	bpeaceriver	bportmellon	bskookumchuck	bsmackenzie	bnanaimo	bgrandprairie
sdryden	74	64	83	53	66	84	86	78	77	74	59
sthunderbay	85	75	93	84	77	95	97	89	87	85	69
sterracebay	91	81	100	70	83	101	103	192	102	91	83
sespanola	104	103	118	89	103	119	121	114	109	104	92
sthurso	131	122	136	110	123	138	140	135	139	131	122
ssaintfelicien	134	124	142	113	126	144	146	138	131	134	113
stroisrivieres	136	141	155	115	129	157	160	82	158	136	128
swindsor	138	142	157	116	130	158	161	142	109	138	92
ssaintjohns	198	203	217	177	191	219	222	200	102	198	83
snewglasgow	170	174	189	149	162	191	193	174	192	170	162
skamloops	21	18	14	32	31	16	19	27	15	21	26
shinton	17	28	30	17	15	31	34	22	32	17	13
squesnel	5	31	24	34	26	26	28	12	28	5	22
sprincegeorge	0	31	33	30	22	31	34	7	33	0	18
scastlega	31	0	21	33	39	23	25	37	24	31	35
scrofton	33	21	0	40	39	5	5	36	4	33	37
sboyle	30	33	40	0	16	42	44	29	43	30	19
speaceriver	22	39	39	16	0	41	43	17	42	22	8
sportmellon	31	23	5	42	41	0	4	37	4	31	35
sskookumchuck	34	25	5	44	43	4	0	39	8	34	41
smackenzie	7	37	36	29	17	37	39	0	32	7	16
snanaimo	33	24	4	43	42	4	8	32	0	39	39
sgrandprairie	18	35	37	19	8	35	41	16	39	0	0

Table 6.S4. Transport cost matrix ($ per tonne of bioproduct) from potential biorefinery locations to potential markets.

Potential biorefinery locations	Potential market regions														
	South BC and North Pacific US	Central AB	Northwest ON	Central ON	Southeast ON	South QC	Pacific US	Mountain US	West South Central US	West North Central US	East North Central US	East South Central US	South Atlantic US	Middle Atlantic US	New England US
bdryden	87	56	14	47	56	62	112	77	70	28	39	69	78	75	75
bthunderbay	98	67	1	36	45	51	118	83	66	24	34	64	72	63	64
bterracebay	98	74	9	33	38	48	126	90	73	32	40	64	64	56	60
bespanola	124	92	33	8	19	27	133	100	80	38	35	56	53	33	37
bthurso	143	112	49	17	18	6	147	114	90	62	43	61	49	20	20
bsaintfelicien	150	119	52	33	36	19	164	130	105	78	58	77	65	34	29
btroisrivieres	152	121	55	24	24	6	153	120	95	68	48	67	55	26	19
bwindsor	153	123	56	25	25	7	154	121	96	69	49	68	54	28	14
bsaintjohns	187	147	81	48	48	33	177	143	112	91	71	79	64	36	20
bnewglasgow	187	157	90	57	57	39	188	154	124	103	83	91	76	48	32
bkamloops	15	27	86	117	131	135	75	53	115	86	102	132	142	139	155
bhinton	31	16	75	110	122	125	91	61	110	77	94	124	133	130	147
bquesnel	24	32	93	128	140	144	84	64	126	95	112	142	151	148	165
bprincegeorge	28	28	89	124	137	140	88	67	123	91	108	139	147	145	161
bcastlega	22	27	79	110	127	128	70	43	104	78	99	121	136	135	151
bcrofton	4	38	68	130	142	148	66	51	117	95	115	138	153	152	168
bboyle	42	12	67	102	114	118	94	58	103	69	86	117	125	123	139
bpeaceriver	41	22	81	116	128	132	105	68	117	83	100	131	139	137	153
bportmellon	7	38	99	132	144	150	69	52	118	95	116	138	153	152	168
bskookumchuck	32	20	73	104	118	122	77	41	100	73	90	118	129	127	143
bmackenzie	35	35	93	128	141	144	94	73	128	95	112	143	151	149	165
bnanaimo	3	39	100	133	145	151	67	53	119	96	116	139	154	153	169
bgrandprairie	39	21	80	115	128	131	104	67	116	82	99	130	138	136	152