NOVEL CONCEPTS ON THE RECOVERY OF BY-PRODUCTS FROM ALKALINE PULPING

BY

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ABSTRACT

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Novel Concepts on the Recovery of By-products from Alkaline Pulping

Innovative biorefinery concepts were developed for the separation and utilization of organic materials, especially aliphatic carboxylic acids, lignin, and extractives, which are formed as by-products during wood-based alkaline delignification processes.

The partial recovery of sodium as NaOH and aliphatic carboxylic acids from hardwood soda-AQ black liquor was studied via electrodialysis. The lignin was partly (about 59 % of the initial lignin) precipitated from black liquor by carbonation (pH to about 8.5) followed by electrodialysis or H_2SO_4 (pH to about 2), with subsequent precipitation of more lignin and the liberation of aliphatic acids. The Na_2SO_4 formed was successfully separated from the acidified liquor by precipitation with methanol and treated by electrodialysis to recover NaOH and H_2SO_4 for recycling. The electrodialysis of Na_2SO_4 was effective and almost 90 % of the sodium was recovered.

Volatile formic and acetic acids were recovered from acidified black liquor (pH about 2) by simple distillation and the recovery of the significant low-molar-mass hydroxy carboxylic acids (glycolic, lactic, and 2-hydroxybutanoic acids) by means of their methyl esters for chemical utilization. The residual high-molar-mass acids (3,4-dideoxy-pentonic, 3-deoxy-pentonic, xyloiso-saccharinic, and glucoisosaccharinic acids) present in the form of their lactones were then utilized in the production of surfactants with tall oil fatty acids. The esterification of the model compound α-glucoisosaccharino-1,4-lactone with lauric, oleic, and tall oil fatty acids was studied separately in a microwave reactor in the presence of *p*-toluenesulfonic acid as a catalyst, and the total yields varied in the range of 40-62 %.

The precipitated lignin obtained by carbonation and acidification with H_2SO_4 was separated and characterized with Fourier transform infrared, ultraviolet, energy dispersive X-ray fluorescence, and nuclear magnetic resonance spectroscopy. In addition, the molar weight distributions of these lignin fractions were determined using gel permeation chromatography. The lignin obtained by acidification was employed in synthesis of an acid catalyst. This lignin-based acid catalyst was made by phenol formaldehyde condensation, followed by a sulfonation reaction. The esterification of tall oil fatty acids with methanol was studied in a microwave reactor in the presence of various catalysts, such as lignin-based acid catalyst, *p*-toluenesulfonic acid, and

Amberlyst 15. Compared to other catalysts, the lignin-based acid catalyst showed a good activity, and it also could be easily recycled.

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, which are referred into the text by Roman numerals (I-V):

I Kumar, H., and Alén, R., Partial recovery of aliphatic carboxylic acids and sodium hydroxide from hardwood black liquor by electrodialysis. *Industrial & Engineering Chemistry Research,* 2014, 53(22), 9464-9470.

II Kumar, H., and Alén, R., Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor. *Separation and Purification Technology,* 2015, 142, 293-298.

III Kumar, H., and Alén, R., Microwave-assisted catalytic esterification of α-glucoisosaccharino-1,4-lactone with tall oil fatty acids. *Sustainable Chemical Processes,* 2016, 4(4), 1-5.

IV Kumar, H., Alén, R., and Gokarneswar, S., Characterization of hardwood soda-AQ lignins precipitated from black liquor through selective acidification. *BioResources,* 2016, 11(4), 9869-9879.

V Kumar, H., and Alén, R., Microwave-assisted esterification of tall oil fatty acids with methanol using lignin-based solid catalyst. *Energy & Fuels,* 2016, 30(11), 9451-9455.

Author´s contribution

The author wrote the publications together with Professor Raimo Alén. The experimental work and preliminary planning in publications was performed by the author. Gokarneswar Sahoo made the NMR analyses in publication IV.

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OTHER SUPPORTING PUBLICATIONS

Christopher, L.P., Kumar, H., and Zambare, V.P., Enzymatic biodiesel: Challenges and opportunities. *Applied Energy,* 2014, 119, 497-520.

Christopher, L.P., Zambare, V.P., Zambare, A., Kumar, H., and Malek, L., A thermo-alkaline lipase from a new thermophile *Geobacillus thermodenitrificans* AV-5 with potential application in biodiesel production. *Journal of Chemical Technology & Biotechnology,* 2015, 90, 2007-2016.

Christopher, L.P., and Kumar, H., Clean and sustainable biodiesel production. In: J. Yan, Ed. *Handbook of Clean Energy Systems*, 2015. John Wiley & Sons, Inc., Chichester, UK, pp. 139-154 (DOI: 10.1002/9781118991978.hces155).

Kumar, H., and Alén, R., Production of biodiesel from TOFAs and methanol by esterification with a lignin-based catalyst – 11th International Conference on Renewable Resources and Biorefineries, York, UK, 3-5 June, 2015.

Kumar, H., Lehto, J., and Alén, R., Biorefinery concepts integrated to alkaline pulping – 6th International Conference on Nordic Wood Biorefinery, Helsinki, Finland, 20-22 October, 2015.

Kumar, H., and Alén, R., Recovery of aliphatic carboxylic acids from black liquor – 24th European Biomass Conference & Exhibition, Amsterdam, The Netherlands, 6-9 June, 2016.

Kumar, H., and Alén, R., Recovery of value-added chemicals from alkaline pulping – IX Iberoamerican Conference on Pulp and Paper Research, Espoo, Finland, 4-8 September, 2016.

PREFACE

This doctoral thesis is based on experimental work carried out in the Laboratory of Applied Chemistry at the Department of Chemistry, University of Jyväskylä, from April 2012 to August 2016.

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Jyväskylä, August 2016

Hemanathan Kumar

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CONTENTS

LIST OF ABBREVIATIONS AND SYMBOLS

α-GISA	α-Glucoisosaccharinic acid
α-GISAL	α-Glucoisosaccharino-1,4-lactone
AQ	Anthraquinone
ASM	Anion selective membrane
β-GISA	β-Glucoisosaccharinic acid
BL	Black liquor
BOD	Biological oxygen demand
BPM	Bipolar membrane
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
$C_{18:0}$	Stearic acid
$C_{18:1}$	Oleic acid
$C_{18:2}$	Linoleic acid
$C_{18:3}$	Linolenic acid
CBL	Carbonated black liquor
COD	Chemical oxygen demand
CSM	Cation selective membrane
CTO	Crude tall oil
CTOS	Crude tall oil soap
DMSO	Dimethyl sulfoxide
ED	Electrodialysis
FA	Fatty acid
FAME	Fatty acid methyl ester
FID	Flame ionization detection
FTIR	Fourier transform infrared
GC	Gas chromatography
GISA	Glucoisosaccharinic acid
GISAL	Glucoisosaccharino-1,4-lactone
GPC	Gel permeation chromatography
HMM	High-molar-mass
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometric
ICP	Inductively coupled plasma
I.D.	Internal diameter
IS	Internal standard
LMM	Low-molar-mass
MC	Model compound
MF	Microfiltration
MM	Molar-mass
MMD	Molar-mass distribution
M_n	Number-average molar-mass
MS	Mass spectrometry
MSD	Mass spectrometric detection
M_w	Weight-average molar-mass

M_w/M_n	Polydispersity
MWD	Molar weight distribution
m/z	Mass to charge ratio
NF	Nanofiltration
NMR	Nuclear magnetic resonance
o.d.	Oven dry
OES	Optical emission spectrometer
PDA	Photodiode array detector
ppm	Parts per million
PTFE	Polytetrafluoroethylene
*p*TSA	*p*-Toluenesulfonic acid
PVC	Polyvinyl chloride
SCAN	Scadinavian Pulp, Paper and Board Testing Committee
TLC	Thin layer chromatography
TMCS	Trimethylchlorosilane
TMS	Trimethylsilylated
TOFA	Tall oil fatty acid
TOS	Tall oil soap
UF	Ultrafiltration
UV	Ultraviolet
Vis	Visible
XISA	Xyloisosaccharinic acid

1 INTRODUCTION

A more sustainable use of natural resources throughout the world is essential. Recently, renewable feedstocks are becoming increasingly viable in the conversion to green chemicals. The pulp and paper industry is one of the most widely established industries and well placed to contribute to sustainable development. For example, in chemical pulping, a substantial amount of wood fibrous material is dissolved in the cooking liquor ("black liquor", BL) during the delignification process. Along with residual inorganic cooking chemicals, BL also contains significant amounts of degraded hemicelluloses (in the form of aliphatic carboxylic acids), together with degradation products of lignin and a minor fraction of extractives (e.g., "crude tall oil", CTO). In the pulp mill, after the recovery of these extractives, BL is concentrated and burned in the recovery furnace to recover cooking chemicals and energy. It should also be emphasized that when surplus energy is generated, partial recovery and utilization of dissolved organic solids offers a natural platform for integrated biorefining [Alén, 2011b; 2015].

Aliphatic carboxylic acids have a wide range of applications in chemical industries. However, the aliphatic acids present as sodium salts in BL should be totally liberated from sodium prior to their recovery and utilization [Alén, 2011b]. This is traditionally done by acidification (pH to 2−3) with strong mineral acids (primarily H_2SO_4). A key issue is to find the appropriate way to handle substantial amounts of Na_2SO_4 that is formed as a by-product from the aforementioned process (including the recovery of sodium). On the other hand, electrochemical membrane process techniques (e.g., electrodialysis, ED; the reaction $Na_2SO_4 \rightarrow H_2SO_4 + NaOH$ [Raucq et al., 1993; Paleologou et al., 1997]) offer one interesting possibility of recovering and recycling at least part of the H_2SO_4.

Further main challenges faced in the recovery and purification of hydroxy carboxylic acids are due to their low vapor pressure, properties of water solubility, tendency to undergo self-esterification (especially "low-molar-mass", LMM hydroxy acids, such as glycolic, lactic, and 2-hydroxy-butanoic acid), and also the presence of other impurities [Alén, 2015]. Their

laboratory-scale purification could be carried out either through straight-forward distillation under reduced pressure [Alén and Sjöström, 1980c] or by ion-exclusion chromatographic techniques [Alén et al., 1990]. On the other hand, the large-scale separation of formic and acetic acids after their liberation has been accomplished by azeotropic distillation with the aid of ethylene dichloride [Biggs et al., 1961].

Esterification is a common chemical reaction in which an ester is derived by the reaction of an acid and an alcohol with the simultaneous removal of water [Sakamuri, 2003]. Esters are usually less polar than alcohols, and, due to the lack of ability of forming intermolecular hydrogen bonds, they do not associate with each other [March, 1992]. Thus, esters are also more volatile (i.e., have lower boiling points) than carboxylic acids with a similar molar-mass (MM), and their effective distillation without yield losses is possible. This kind of approach has been applied to the purification of lactic acid from fermentation broth [Joglekar et al., 2006; Zhao et al., 2009]. Similarly, it can be concluded that free LMM hydroxy acids in acidified BL could be easily separated and purified by this type of esterification. Further, their individual separation by distillation seems possible due to the difference in their relative volatility. However, residual free high-molar-mass (HMM) hydroxy acids such as 3,4-dideoxy-pentonic acid, 3-deoxy-pentonic acid, xyloisosaccharinic acid (XISA), and glucoisosaccharinic acid (GISA), exist as intramolecular cyclic esters (i.e., lactones) [Alén and Sjöström, 1980c; Alén, 2011b]. These lactones could be suitable for further esterification with long-chain fatty acids (FAs) (e.g., with a conventional acid fraction from CTO) to obtain emulsifying agents [Sjöström, 1991; Alén, 2015].

In addition, it is also necessary to find potential applications of large amounts of lignin that is precipitated during the acidification process. In addition to extractives (tall oil), lignin is the most important by-product of chemical pulping. Lignin can be treated under different conditions to obtain a wide range of industrial products [Alén, 2011b; 2015]. For example, a solid acid-based catalyst can be prepared from lignin by a chemical process [Liang et al., 2013; Zhang et al., 2013] and potentially used to catalyze the esterification of tall oil fatty acids (TOFAs) to biodiesel [Keskin et al., 2007]. Research of this type can lead to the synthesis of value-added green catalysts and biofuels from by-products of pulping.

Therefore, it can be concluded that in addition to recovering energy by burning, various attractive products can be recovered and synthesized from BL. Up to now, far too little attention has been paid towards the production of valuable materials from industrial by-products of forest waste. This research provides new insights in developing socio-economic and environmentally sustainable process possibilities towards the recovery and utilization of chemicals from low-cost by-products and industrial waste. In addition, the research can add value to the Finnish economy by diversifying the product range of Finnish pulp mills.

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2 OBJECTIVES OF THE STUDY

The purpose of the present work was to develop potential techniques for the separation and utilization of the organic and inorganic materials present in alkaline BL. In order to achieve this target, the following general objectives were set:

To develop new techniques for the recovery of LMM and HMM aliphatic carboxylic acids from alkaline BLs.

To recover NaOH with minimal energy consumption by ED either through the diluted carbonated black liquor (CBL) or Na_2SO_4 formed during the acidification of CBL with H_2SO_4.

To analyze the lignin precipitated from differently processed alkaline BLs.

To clarify possibilities to esterify HMM aliphatic carboxylic acid lactones (mainly glucoisosaccharinic acid lactone, GISAL) with fatty acids.

To prepare fatty acid methyl esters (FAMEs) using a lignin-based acid catalyst.

The overall objective was to find a more efficient utilization of part of BL as an alternative to its burning by means of the manufacturing of various value-added products.

3 ALKALINE PULPING PROCESSES

Pulp is the generic product of wood. Predominantly used for the manufacturing of paper and paperboards, some pulps are chemically processed into various products, such as regenerated fiber and cellulose derivatives [Sjöström, 1993; Sixta, 2006]. Pulping refers to processes that involve the liberation of fibrous pulp from wood or other lignocellulosic feedstock by either chemical, mechanical, or combinatory processes [Rydholm, 1965; Grace and Malcom, 1989; Biermann, 1993; Sjöström, 1993; Sixta, 2006; Alén, 2011b]. Currently, chemical pulping accounts for over 70 % of the total global pulp production; the kraft (sulfate) process is the most versatile and economical pulping process, which is now the dominant process for chemical pulp production [Alén, 2011b; Christopher, 2012]. In chemical pulping, lignin is almost completely removed from wood fibers and dissolves in the cooking liquor. However, the selectivity of delignification is rather low, as simultaneously with lignin removal, a large amount of fibrous feedstock material along with extractives are also degraded [Sjöström, 1993; Pakkanen et al., 2005; Pakkanen and Alén, 2012; Lehto and Alén, 2013]. In this regard, one of the potential approaches is pretreatment of the wood chips under chemical (mild acidic or alkaline), biological, or enzymatic processes prior to the chemical pulping to recover part of the feedstock hemicelluloses already at this stage [Tunc and van Heiningen, 2008; 2011; Yoon et al., 2008; Mendes et al., 2009; Li et al., 2010; Lehto and Alén, 2015; Lehto et al., 2015].

3.1 Kraft pulping

Excellent pulp strength, the capability of processing various fibrous materials, low energy consumption, short cooking time, and simple and effective chemical recovery, are the most significant reasons that make the kraft process superior to other pulping processes. However, the kraft process still contains numerous weaknesses, such as higher capital cost, low pulp yields (40-55 % of

wood), dark unbleached pulp color, high consumption of bleaching chemicals, and malodorous and toxic emissions [Kleppe, 1970; Sjöström, 1993; Uprichard and Walker, 1993; Alén, 2000b; Christopher, 2012]. In conventional kraft pulping, delignification is accomplished using aqueous white liquor (cooking liquor) containing the active cooking chemicals, sodium hydroxide and sodium sulfide, in addition to some sodium carbonate and sodium salts of oxidized sulfur-containing anions. In general, kraft cooking is performed at 155-175 °C for 1-3 hours, where the hydrogen sulfide ions (HS$^-$) and hydroxide ions (HO$^-$) react with lignin polymer and degrade it into smaller and alkali soluble fragments. The kraft process can be carried out in a batch or in a continuous digester [Grace and Malcom, 1989; Biermann, 1993; Sjöström, 1993; Uprichard and Walker, 1993; Chakar and Ragauskas, 2004; Sixta et al., 2006a]. After cooking, the pulp is separated from BL and screened before bleaching. The resulting BL, containing lignin (85-95 % of lignin originally present in wood) along with carbohydrate degraded products and minor amounts of extractives, is concentrated to 65-85 % of the solid content by evaporation and burned in the recovery furnace to recover cooking chemicals and generate energy [Sjöström, 1993; Alén, 2011b]. Currently, the kraft pulp mill has the potential to generate both power and heat. The inorganic smelt, mainly consisting of sodium carbonate and sodium sulfide, is dissolved in water to obtain green liquor. The green liquor reacts with calcium hydroxide (slaked lime) in the causticizing process in which sodium carbonate is converted into sodium hydroxide, which then can be reused as the cooking liquor [Adams, 1997; Sixta, 2006; van Heiningen, 2006; Alén, 2011b].

3.2   Soda-anthraquinone pulping

In wood pulping, the conventional soda process has almost completely been replaced by the kraft process [Sjöström, 1993]. However, compared to the kraft process, the soda process is sulfur free, which facilitates easier recovery of cooking chemicals and eliminates the emissions of malodorous sulfur [Finell and Nilsson, 2004]. On the other hand, in soda pulping, sodium hydroxide is the only active cooking chemical, and the pulping process is slower, resulting in lower yield and weaker pulp as carbohydrate reactions are only affected by the presence of HO$^-$ [Uprichard and Walker, 1993; Sixta, 2006; Alén, 2011b]. The alkali-catalyzed polysaccharide peeling reactions in alkali pulping can be avoided by reducing or oxidizing the reducing aldehyde end groups of the polysaccharide chains. Further, to improve the soda process, anthraquinone (AQ) is used as catalyst (0.1-0.5 % on dry wood) to increase the rate of delignification and reduce the polysaccharide peeling reactions by the oxidation of the reducing end groups of carbohydrate chains to alkali-stable aldonic end groups [Uprichard and Walker, 1993; Alén, 2011b]. The soda-AQ method is more effective in pulping hardwoods compared to softwoods [Kanungo et al., 2009]. Currently, soda-AQ pulping is economically viable for

non-wood raw materials, such as reed canary grass, straw, bagasse, and other agricultural residues [Ali et al., 2001; Feng and Alén, 2001; Bhardwaj et al., 2005; Khristova et al., 2006; Jiménez et al., 2009]. Pulps obtained from the soda-AQ process have strength properties comparable to those of kraft pulps. However, soda-AQ pulps are more difficult to bleach and the process requires higher sodium hydroxide content for cooking, which therefore, increases the causticity in the recovery of the cooking chemical [Uprichard and Walker, 1993; Bose et al., 2009].

3.3   Oxygen-alkali delignification

Oxygen-alkali delignification is the process in which a substantial amount of residual lignin is removed from unbleached pulp prior to bleaching by the use of oxygen and alkali [Malinen, 1974; Salmela et al., 2008]. The process seems to be important in modern pulp technologies, mainly due to economic, energy, and environmental related benefits. The use of oxygen-alkali delignification before bleaching in the pulp industry can decrease the use of bleaching chemicals, such as chlorine, chlorine dioxide, and hypochlorite [Hsu and Hsieh, 1988]. About 5 kg of oxygen can substitute about 3 kg of chlorine dioxide; the use of oxygen in delignification will reduce the chemical cost by about one-eight than that of using chlorine dioxide [Sixta et al., 2006b]. On the other hand, decreasing the use of chlorine and chlorine dioxide can reduce the bleach plant effluent chemical oxygen demand (COD) by 50 % and biological oxygen demand (BOD) by 25-50 % [Hsu and Hsieh, 1988; McDonough, 1996]. Unlike the bleach effluent, the dissolved material present in oxygen-alkali delignification process is free from chloride ions and can be burned in a recovery furnace instead of being a pollutant [McDonough, 1996].

However, the major drawback associated with oxygen-alkali delignification is that it is less selective than typical chlorine-compound-based bleaching. The delignification is limited to about 50 % of residual lignin removal, and beyond this it will result in excessive cellulose damage, leading to decrease in viscosity and loss of pulp strength [Sjöström, 1993; Sixta et al., 2006b]. In addition to lignin, the spent liquor from oxygen-alkali delignification contains hydroxy carboxylic acids, formic and acetic acids, hemicellulose residues, methanol, and carbon dioxide [Salmela et al., 2008]. Oxygen-alkali delignification is carried out at an elevated temperature (90-110 °C) for 30-60 minutes, in mainly medium consistency reactors [Hsu and Hsieh, 1988; McDonough, 1996; Sixta et al., 2006b]. Additional small amounts of magnesium carbonate can be used to improve the process selectivity. The oxygen-alkali delignification is practiced commercially using both single- and two-stage technologies [Yang et al., 2003]. Recent interest has been directed especially towards two-stage oxygen-alkali pulping systems in order to increase selectivity and treatment efficiency [Sixta et al., 2006b]. It should be noted that the oxygen-alkali pulping has also been studied as the main sulfur-

free delignification method for chemical pulps [Kleppe et al., 1972; Samuelson and Sjöberg, 1972; Abrahamsson and Samuelson, 1973].

4 POTENTIAL BY-PRODUCTS OF ALKALINE BLACK LIQUOR

4.1 Lignin

Lignin is the second most abundant biopolymer available on earth, next to cellulose and it is typically present in the cell walls of plants [Christopher, 2012]. Lignin plays a significant role in giving mechanical strength to plants by chemically or physically linking with carbohydrates [Iiyama et al., 1994; Hendriks and Zeeman, 2009; Alén, 2011a]. In general, softwoods have lignin content of 25-35 % of their dry mass, whereas hardwoods have 20-25 % [Gellerstedt et al., 2012]. Lignin is an amorphous heteropolymer with complex chemical structure, consisting of phenylpropanoid monomers containing both aromatic and aliphatic parts. Three types of phenylpropanoid monomers (monolignols or lignin precursors in its biosynthesis) have been identified: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These monomers are polymerized by enzymatic dehydrogenation, leading to the formation of a lignin heteropolymer. The phenylpropane units are linked together by ether linkages (e.g., β-*O*-4 and α-*O*-4) and carbon-carbon bonds (e.g., β-5 and 5-5'). The ether type linkages are dominant, in which the β-*O*-4 linkage is found to be most prominent in the woods (Figure 1) [Sarkanen and Ludwig, 1971; Glasser and Sarkanen, 1989; Lisperguer et al., 2009; Alén, 2011a; Christopher, 2012; Santos et al., 2013; Wen et al., 2013; Tolbert et al., 2014].

In alkali pulping, almost 90-95 % of the original lignin in the raw material fed to the process is degraded and solubilized in BL. The chemical composition of the dissolved lignin present in BL is complex, and it differs depending on the feedstock and pulping conditions.

Successive cooking yields a heterogeneous lignin biopolymer covering a wide MM distribution range of compounds. As a result, the dissolved lignin fractions have relatively high degrees of polydispersity with the presence of LMM monomeric phenols as well as of HMM lignin fragments linked to carbohydrate residues [Brodin et al., 2009; Gellerstedt et al., 2012].
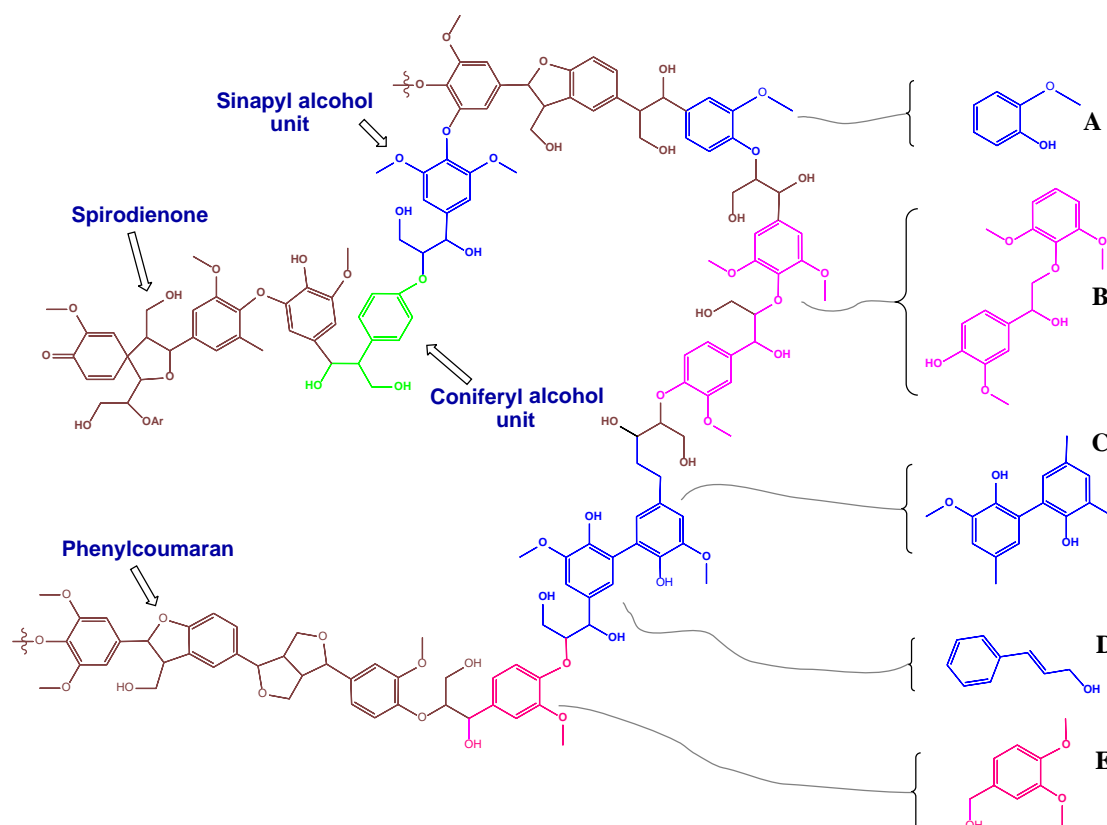
FIGURE 1 Schematic structure of lignin, showing various linkages and lignin model compounds to model (A) phenol and methoxy functionality, (B) β-*O*-4 linkages, (C) 5-5′ linkages, (D) propyl side chain, and (E) benzylic groups [Dutta et al., 2014].

4.1.1 Reactions in alkaline pulping

The chemical reactions occurring during kraft and soda cooking are complicated and not totally understood. The hydroxide and hydrosulfide anions are the main active chemical agents present in the kraft cooking liquor. In general, it is well known that the hydrogen sulfide ions play a significant role in delignification by reacting with lignin, whereas the reactions in carbohydrates are only affected by alkalinity [Sixta, 2006; Alén, 2011b].

The main objective of pulping is the selective removal of lignin without extensive degradation of the carbohydrates. During this operation, the macromolecule structure of lignin is degraded and solubilized to a major extent (i.e., cleavage of the inter-lignin linkages and dissolution of the fragments in the pulping liquor) [Sixta, 2006; Alén, 2011b]. In conventional kraft pulping, the dissolution of lignin occurs in three distinct kinetic phases as follows: 1) initial or extraction phase, 2) bulk delignification phase, and 3) residual delignification stage. The selectivity of delignification is rather low in the initial phase, resulting in the removal of lignin up to 15-25 %, but the loss of hemicelluloses is high (up to 40 %) under these conditions. In the bulk delignification phase, delignification is accelerated as the cooking temperature increases, above 140 °C. The rate of delignification remains high during this phase until about 90 % of the initial lignin is dissolved. The rate of

delignification proceeds slowly, whereas the loss of carbohydrates is significantly increased in the final delignification phase (residual delignification) [Alén, 2011b].

The reactivity of different lignin fragments towards cooking chemicals and cooking conditions is greatly dependent on the chemical structure of these fractions. Besides, the essential aspect in the delignification is the different behavior and stability of the linkages between the phenylpropane units in lignin [Sixta, 2006; Alén, 2011b]. Depolymerization of lignin occurs usually due to the cleavage of the different ether linkages and demethylation.

The principal types of linkages (50–70 %) present in both softwood and hardwood lignin are α- and β-aryl ether linkages (α-*O*-4 and β-*O*-4, respectively). These ether linkages in free phenolic structures are easily cleaved, and this increases the hydrophilicity of the lignin due to liberation of phenolic hydroxy groups. Thus, it enhances the dissolution of these depolymerized fragments into the cooking liquor as sodium phenolates [Sjöström, 1993]. Furthermore, some condensation reactions of lignin fragments are taking place [Alén, 2011b].

4.1.2 Recovery and utilization

Currently, the predominant source of wood lignin is in BLs from kraft pulping. Approximately half of the total organics present in BLs is lignin, with the residual being various carbohydrate degradation products and extractives [Gellerstedt et al., 2012]. In general, separation of lignin from BL has been carried out by precipitation. This can be done by reducing the pH of BL from about 13 to less than 10 [Huang and Ramaswamy, 2013; Alén, 2015]. Precipitation is done by carbonation (passing CO_2 under reduced pressure) or with possible addition of strong mineral acids [Merewether, 1962; Nikitin, 1963; Basu, 1971; Alén, et al., 1979; 1985c; Kim et al., 1987; Uloth and Wearing, 1989a; 1989b; Christopher, 2012]. This type of precipitation is most common and has a long history of application in various spent cooking liquors. Recently, the most effective industrial-scale process for a partial recovery of lignin by carbonation is known as the "LignoBoost process" [Wallmo, 2008; Tomani, 2010]. The new process enables the fast and effective recovery of high quality lignin from kraft BL [Bajpai, 2013; Alén, 2015]. Additionally, lignin particles can also be recovered by ultrafiltration, while the selection of membrane material needs to be considered to avoid problems with fouling and plugging [Alén, 2015].

Lignin is a renewable material and potential source for biorefineries. In principle, lignin can be treated under various conditions from thermochemical to chemical processes to obtain a wide range of products, such as solid and liquid fuels, carbon fiber, polymer modifiers, adhesives and resins, aromatic chemicals, and many other straightforward applications, for example, binders, emulsifiers, surface or dispersing agents, and sequestrants [Alén, 2015]. However, the most obvious use of the bulk production of the lignin is as a biofuel in the form of power, pellets, or mixed with other fuels. In such cases,

lignin can be used as fuel or syngas by gasification within the pulp mill or selling it to external customers interested in biofuel alternatives to fossil fuel [Olivares et al., 1988; Goldstein, 1981; Glasser and Sarkanen, 1989; Sarkar and Adhikari, 2000; Kadla et al., 2002; Sridhar et al., 2005; Brodin et al., 2009; Bajpai, 2013; Huang and Ramaswamy, 2013; Alén, 2015]. Moreover, it should be pointed out that kraft lignin contains some chemically bound sulfur; thus, the combustion plants need to be equipped with a flue gas treatment system for the sulfur emissions [Alén, 2015].

4.2   Aliphatic carboxylic acids

Besides lignin, large amounts of aliphatic carboxylic acids also exist in the alkaline BLs [Alén, 2011b; 2015]. These acids are present in the form of sodium carboxylates and generally formed as a result of degradation reactions of the carbohydrates (hemicelluloses and cellulose) [Sjöström, 1993; Alén, 2000a]. The acids in BL can be divided into volatile and non-volatile hydroxy carboxylic acids. Acetic and formic acid belongs to volatile acids, and non-volatile acids comprise several hydroxy monocarboxylic and hydroxy dicarboxylic acids together with minor amounts of di- and tricarboxylic acids. The non-volatile hydroxy monocarboxylic acids can also be divided into LMM hydroxy acids with 2-4 carbon atoms (glycolic, lactic, and 2-hydroxybutanoic acids) and HMM hydroxy acids with 5 and 6 carbon atoms (3,4-dideoxy-pentonic acid, 3-deoxy-pentonic acid, XISA and GISA). In general, almost 100 hydroxy carboxylic acids have been identified from BLs [Niemelä, 1990; Niemelä and Alén, 1999; Alén, 2011b]. Of the numerous aliphatic carboxylic acids, the most dominant ones are formic acid, acetic acid, glycolic acid, lactic acid, 2-hydroxybutanoic acid, 3,4-dideoxy-pentonic acid, XISA, and GISA [Alén et al., 1985b; Alén, 2015].

4.2.1   Polysaccharide reactions in alkaline pulping

In the conventional alkaline pulping process, the most important degradation reactions of feedstock polysaccharides (cellulose and hemicelluloses) are peeling and alkaline hydrolysis [Fengel and Wegener, 1989; Sjöström, 1993; Alén, 2000b]. The peeling reaction (primary peeling) of polysaccharides is a stepwise alkaline depolymerization of polymer beginning at the reducing end group (hemiacetal group) by eliminating monosaccharide units one by one with a simultaneous formation of various carboxylic acids (about 1.5 equivalents of acids are formed from one monosaccharide unit). However, most carbohydrate loss occurs (i.e., the most effective formation of acids) during the heating up period up to about 170 °C in the conventional kraft pulping. The peeling reaction intensively occurs already at 100 °C. Due to the high crystalline nature and high degree of the polymerization, cellulose undergoes fewer losses than those of hemicelluloses. The peeling starts with

the isomerization of the reducing end group to a ketose intermediate in the polysaccharide chain followed by the β-alkoxy elimination reaction, leading to a soluble monosaccharide unit and a new reducing end group. Finally, the eliminated end group is tautomerized to a carbonyl compound (2,3-diulose structure) from which either α- and β-GISA (from cellulose and gluco-mannans) [Alén and Sjöström, 1985; 1991] or XISA (from xylan) is formed via benzylic acid rearrangement (Figure 2). In addition, several other possible routes exist mainly resulting in the formation of 2-hydroxybutanoic acid (from xylan), 3,4-dideoxy-pentonic acid (from cellulose and glucomannans), lactic acid, and 3-deoxy-pentonic acid [Sjöström, 1993; Alén, 2011b].

A whole polysaccharide chain may be degraded by peeling reaction, until the dominant stopping reaction takes place, thus terminating the degradation. In cellulose, almost 50-65 glucose units are expected to be cleaved on an average before the competing stopping reaction occurs [Biermann, 1993; Alén, 2011b]. The stopping reaction is initiated by the β-hydroxy elimination (i.e., cleavage of the hydroxy group from the monosaccharide end unit) from reducing end of the polysaccharide without proceeding isomerization. The resulting dicarbonyl intermediate (1,2-diulose structure) attached to the polysaccharide chain is converted to the meta-saccharinic acid end unit through benzilic acid rearrangement. Other possible different end groups are also formed. Thus, the formation of the alkali-stable carboxylic acid group (present as carboxylate) in the end units of the polysaccharide chain prevents all peeling reactions based on the isomerization of the reducing end group [Sjöström, 1993; Alén, 2011b].
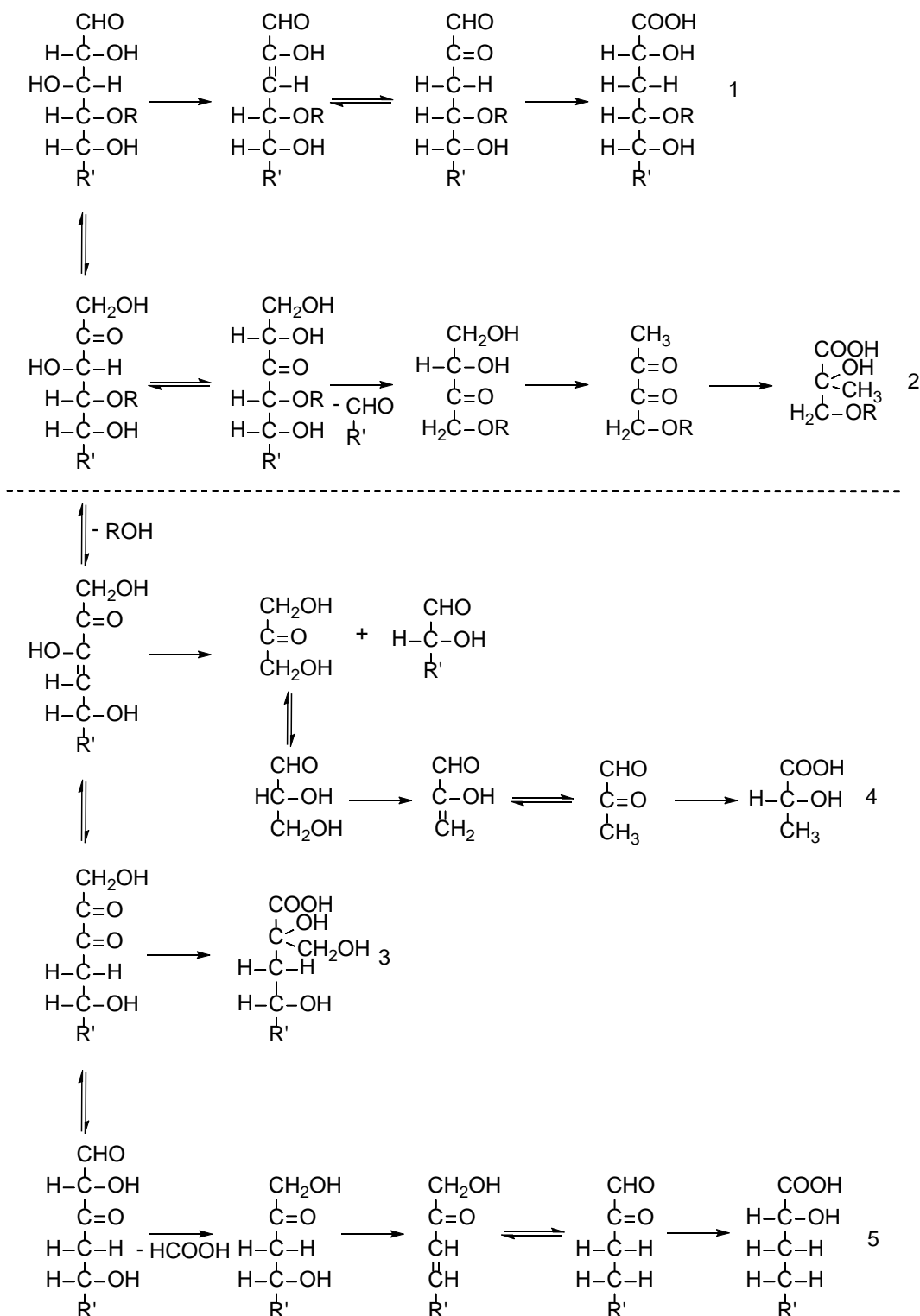
FIGURE 2 Peeling and stopping reactions of polysaccharides [Sjöström, 1977]. R = polysaccharide chain and R′ = CH₂OH (cellulose and glucomannans) or H (xylan). Cellulose and glucomannans (R′ = CH₂OH): (1) 3-deoxy-hexonic acid end groups (metasaccharinic acid), (2) 2-C-methylglyceric acid end groups, (3) 3-deoxy-2-C-hydroxymethylpentonic acid (glucoisosaccharinic acid), (4) 2-hydroxypropanoic acid (lactic acid), and (5) 3,4-dideoxy-pentonic acid (2,5-dihydroxypentanoic acid). Xylan (R′ = H): (3) refers to 3-deoxy-2-C-hydroxymethyltetronic acid (xyloisosaccharinic acid), (4) 2-hydroxypropanoic acid (lactic acid), and (5) 2-hydroxybutanoic acid.

In addition to peeling reactions, alkaline hydrolysis at elevated temperatures (160-170 °C) becomes important; it is initiated by the random cleavage of the glycosidic bonds present in the polysaccharides, resulting in the formation of new reducing groups [Alén, 2000b; 2011a]. Therefore, the polysaccharide chain can be susceptible to further degradation reactions (secondary peeling) leading to the formation of carboxylic acids.

4.2.2 Recovery and utilization

Since large amounts of aliphatic carboxylic acids are formed annually in the pulping industry, at least a partial recovery of these acids from BL has been an interesting alternative instead of using them as a fuel [Alén and Sjöström, 1985; Alén et al., 1986; 2011a]. The basic idea behind this approach is that these carboxylic acids have relatively low heating value in comparison to that of lignin, and their withdrawal from BL reduces its heat content less than expected [van Heiningen, 2006; Alén, 2011b].

Aliphatic carboxylic acids represent a potentially interesting group of compounds, since it can be used as single components, or as more or less purified mixtures in many applications. Of this group, formic, acetic, lactic, and glycolic acids are commercially important chemicals and are now being produced by alternative methods [Alén and Sjöström, 1980a; 1985; Alén, 2000b; Datta and Henry, 2006; Viikari and Alén, 2011]. So far, the utilization of the uncommon hydroxy acids, such as 2-hydroxybutanoic acid, 3,4-dideoxy-pentonic acid, XISA, and GISA has been studied only to some extent. Hydroxy acids can be converted into corresponding derivatives (Figure 3), such as polycarboxylic acids by oxidation, polyalcohol by reduction, production of emulsifying agents by esterification, or unsaturated reactive intermediate through dehydration (e.g., synthesis of acrylic-type resins made from hydroxy acid intermediate shown in Figure 4). These reaction products can be used as sequestering agents, tensides, and emulsifying agents, additives in plastics, surface treatment agents, and potential raw materials for the synthesis of chemicals [Sjöström, 1991; Alén, 2015].

The recovery of aliphatic acids presents several separation problems and has, so far, only been carried out on a laboratory scale [Alén and Sjöström, 1980b; Alén, 2011b]. The main obstacle is the lack of simple methods for separation of carboxylic acids from lignin and other components, along with the recovery of inorganic cooking chemicals. To overcome the separation problem, process streams containing less lignin than is present in BL has been recommended for use; for example, withdrawal of the pulping liquor from the digester at the early stages of the cook because the most extensive degradation of carbohydrates takes place during the heating-up period [Alén, et al., 1986]. In addition, the alternative approach is the pretreatment of the wood chips with NaOH alone prior to delignification [Alén et al., 1984b]. However, only a minor portion of aliphatic acids can be utilized as their sodium salts. Consequently, the aliphatic acids are liberated from sodium by acidification with carbon dioxide or by strong mineral acid (H_2SO_4) and simultaneous

precipitation of the lignin. After recovery of volatile acids by evaporation, a crude fraction composed mainly of free hydroxy carboxylic acids is obtained [Alén and Sjöström, 1980b; Alén et al., 1986; Alén, 2011b]. On the other hand, the purification of hydroxy carboxylic acids is rather problematic [Sixta and Schild, 2009], and yet to be solved satisfactorily [Alén, 2000b]. The recovery and utilization of hydroxy acids from BL can be accomplished, only if feasible methods of separation exist and the products can be marketed [Sjöström, 1991; Alén, 2015].
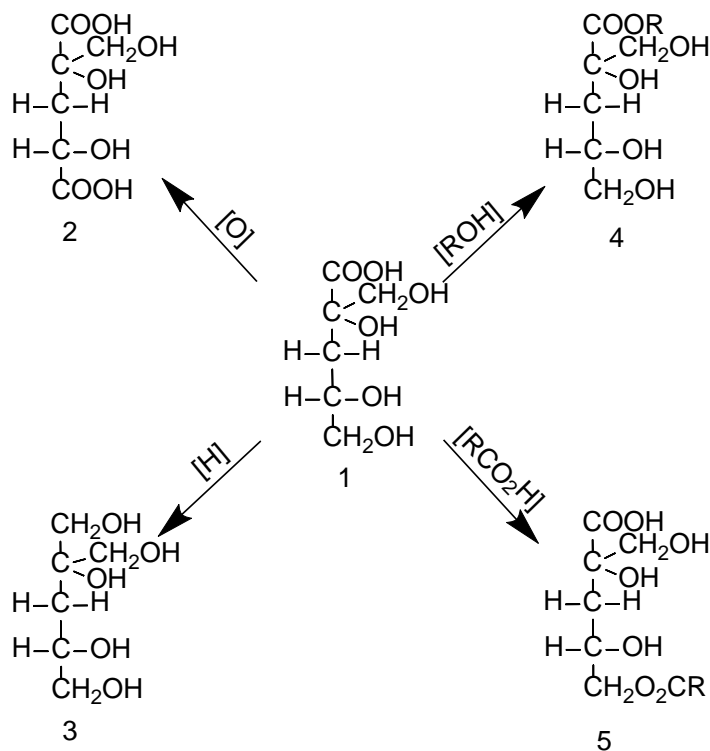

FIGURE 3 Conversion of glucoisosaccharinic acid (1) to a dicarboxylic acid (2) through oxidation, a polyalcohol (3) through reduction, esters (4) through a reaction with alcohols, and esters (5) through a reaction with fatty acids [Sjöström, 1991].
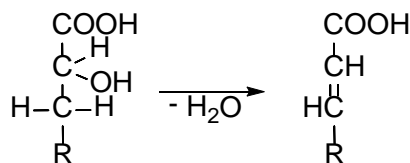

FIGURE 4 Formation of acrylic-type acids from α-hydroxy monocarboxylic acids through dehydration [Sjöström, 1991].

4.3 Extractives

The crude sulfate turpentine (volatile fraction) and the crude tall oil soap (CTOS) (non-volatile fraction) are the other two main by-products of softwood kraft pulping [Back and Allen, 2000]. The turpentine is distilled and collected from the digester relief after it condenses during the kraft pulping process [Alén, 2011b]. TOS is composed of sodium salts of resin acids and FAs, together with some non-saponfiable substances. The amount of these by-products varies significantly depending on the wood raw material used for pulping, the method and time of sorting wood logs and chips and finally, the growth conditions of the trees [Alén, 2015].

4.3.1 Behavior of extractives during pulping

The volatile turpentine components are chemically stable during kraft pulping whereas, the FA esters of the native wood are hydrolyzed completely. During pulping under alkaline conditions, the unsaturated FAs and resin acids are partly isomerized [Alén, 2011b]. Several new FA and resin components are formed via isomerization. For example, the dienoic and trienoic acids are isomerized to acids with conjugated double bonds having a *cis-trans* configuration. These products are mainly formed from linolenic and pinolenic acids [Holmbom and Ekman, 1978]. Similarly, resin acids also undergo double bond isomerization. The most common resin acid, levopimaric acid, is partially isomerized to abietic acid and other common resin acids are basically stable during kraft pulping [Holmbom and Ekman, 1978; Alén, 2011b]. In general, extractives are mostly removed during very early stage of the pulping [Alén, 2011b].

4.3.2 Recovery and utilization

The crude turpentine is purified by distillation process to remove impurities, such as methyl mercarptan, dimethyl sulfide, and other higher compounds. The average yield of crude turpentine is ranging from 5-10 kg/ton of pulp (pine species) [Alén, 2011b]. The major fractions are a monoterpene fraction, consisting mainly of *a*-pinene (50-80 % of all compounds), *β*-pinene, and *Δ³*-carene and pine oil fraction, consisting mainly of hydroxylated monoterpenes. Traditionally, turpentine (monoterpene) is used in manufacturing paint thinner, varnishes, and lacquers, or as rubber solvents and reclaiming agent [Alén, 2011b]. Today, it is widely used for manufacturing aroma chemicals, which can be used as flavoring agents in food and as fragrance chemicals in perfumes and cosmetics [Holmbom, 2011]. Pine oil is used when solvents with good emulsifying and dispersing properties and the flotation of minerals are needed [Alén, 2011b; 2015].

TOS is recovered during BL evaporation process as skimming, and the organic fractions (fatty and resin acids) are liberated by adding sulfuric acid to

yield CTO (the average yield is in the range of 30-50 kg/ton of pulp) [Lappi and Alén, 2012; Alén, 2015]. In this study, the CTO is then purified and fractionated by vacuum distillation to obtain various fractions, the main fractions, together with their mass proportions and main application are as follows: light oil (10-15 %; industrial oils, combustion and rust protection), FAs (20-40 %; surfactants, soaps, foam inhibition, printing inks, lubricants and greases, industrial oils, and flotation agents), resin acids (rosin, 25-35 %; printing inks, emulsifiers, soaps, alkyd resins, adhesives, coatings, paint and lacquer vehicles, and soaps), and pitch residue (20-30 %; combustion, rust protection, printing ink pitch, asphalt additive, and oil-well drilling muds) [Alén, 2011b; Holmbom, 2011]. Globally, 1.6 million metric tons of CTO are produced annually, and about two thirds of the FA supply to the chemical industry is derived from CTO. In recent years, there has been an increasing interest in using CTO for petrochemical applications, especially in Northern European countries, like in Finland, where CTO production reaches 100 000 metric tons annually. The companies in Finland, such as UPM (UPM BioVerno®) and Neste Oil (NExBTL®), have started producing biofuels (renewable diesel) from CTO by hydrogenation [Anthonykutty et al., 2015].

5 SEPARATION TECHNOLOGIES OF ORGANICS IN BLACK LIQUOR

5.1 General aspects

In general, BL is the most significant by-product of chemical pulping [Cardoso et al., 2009]. After recovery of the extractives-based compounds, the residual BL primarily contains organic material mainly composed of degraded products of lignin, carbohydrates, and minor fraction of extractives along with inorganic substances that are burned in the recovery furnace to recover energy and cooking chemicals [Adams, 1997; Louhelainen and Alén, 2009; Alén, 2015]. Currently, there is no feasible process available to recover and employ organic solids in BL for non-fuel applications. However, the major obstacle in the recovery of organic material from BL depends on numerous factors, such as the lack of a techno-economic separation process, potential industrial applications, and market [Alén et al., 1986; Chambost et al., 2009].

At present, turpentine and tall oil are the most significant commercial by products obtained from BL [Alén and Sjöström, 1980b]. On the other hand, the partial recovery of lignin and aliphatic carboxylic acids appears to be attractive in the future [Alén, 2015]. Modern kraft mills have surplus energy generated from burning BL [Wallberg et al., 2003; Wallberg and Jönsson, 2006]. In practice, if about 15 % of the dissolved organic material is withdrawn from kraft mills producing 500 000 tons of unbleached pulp annually, the amount of lignin, aliphatic carboxylic acids, and extractives would be about 25 000-34 000, 30 000-40 000, and 12 000 tons, respectively. Consequently, 20-27 % of the heating content may decrease in BL due this partial recovery of organics [Alén, 2011b]. Several commercial techniques are available for the recovery and the purification of the lignin from kraft BL [Lin, 1992; Hellstén et al., 2013b]. However, separation and purification of hydroxy acids from lignin and other impurities of kraft BL is challenging [Alén and Sjöström, 1980b; Hellstén et al., 2013a]. Various techniques have been suggested concerning the separation of hydroxy acids after the removal of lignin and inorganics from BL

[Alén and Sjöström, 1980c; Niemi et al., 2011; Hellstén et al., 2013a]. On the other hand, apart from a mill-scale process developed for recovery of volatile acids [Biggs et al., 1961; Weaver and Biggs, 1961], no industrial process exists for the separation of other hydroxy acids from BL [Alén and Sjöström, 1980b].

5.2 Membrane technologies

Membrane filtration technology is one of the most significant industrial processes in the pulp and paper industry [Olsen, 1980]. In recent years, there has been an increasing interest in membrane applications in industries due to its advantages, such as low energy and chemical requirements. Separation is simply controlled by membrane pore size, process streams, and operating parameters, and process streams can be treated directly without any further pretreatments [Jönsson and Wimmerstedt, 1985; Jönsson and Wallberg, 2009; Jönsson, 2013]. Typically, microfiltration (MF) (0.1-10 µm), ultrafiltration (UF) (1-20 nm), and nanofiltration (NF) (<2 nm) are three membrane filtration techniques widely implemented in the industry to separate molecules with different MMs. However, UF and NF are most commonly used in pulp industries [Huang and Ramaswamy, 2013; Jönsson, 2013]. Moreover, given the growing demand to protect and improve the environment, the exploitation level of the process of recovery and purification of valuable products are the two main reasons for the application of membrane processes in pulp industries [Kallioinen et al., 2013]. In the kraft pulp industry, the membrane processes are mainly applied to fractionation and purification of lignin from BL and purification of bleach effluent [Olsen, 1980; Al Manasrah et al., 2012]. Membrane technology allows the separation of specific MM lignin from BL for the synthesis of several high-value-added products [Toledano et al., 2010].

5.2.1 Ultrafiltration

UF is a pressure driven membrane process used to retain the macromolecules in the range of 1-20 nm [Cheryan, 1998; Bhattacharya and Misra, 2004]. A UF membrane is asymmetrically microporous and is usually made up of ceramics, polysulfone, polypropylene, nylon, polytetrafluoroethylene (PTFE), and poly-vinyl chloride (PVC) or acrylic copolymer material [Toledano et al., 2010]. UF is used to obtain specific molecules with different MM cut-offs in the range of 1-1000 kDa, with a driving force ranging from 1-10 bar [Jönsson, 2013]. In pulp industries, UF has so far been employed mainly for the separation of lignin from LMM compounds and fractionation of HMM lignin [Hill and Fricke, 1984; Wallberg et al., 2003; 2005; Bhattacharjee and Bhattacharya, 2006; Wallberg and Jönsson, 2006]. Most full-scale UF processes are used for the isolation of lignosulfonates from spent sulfite liquor [Jönsson, 2013]. In recent decades, interest has been shifted towards UF of kraft BL [Wallberg et al., 2003]. UF has been widely studied to concentrate kraft BL [Holmqvist et al.,

2005; Bhattacharjee and Bhattacharya, 1992; 2006]. In general, lignin obtained from the UF of kraft BL has been utilized as external biofuel. However, an advanced method based on the UF of kraft BL was developed to produce HMM lignin for manufacturing plywoods. More recently, UF has been further developed to yield high quality lignin, free from inorganic impurities and carbohydrates to make vanillin, carbon fibers, adhesives, and phenol-based polymers [Žabková et al., 2007; Brodin et al., 2009; Silva et al., 2009; Jönsson, 2013]. In addition, several studies on UF have been conducted to recover lignin from kraft BL [Kirkman et al., 1986; Rojas et al., 2006; Arkell et al., 2014]. However, data on the separation of hydroxy acids from BL are still very limited [Mänttäri et al., 2015].

5.2.2 Nanofiltration

NF is a comparatively new, pressure-driven membrane process to separate molecules from liquids [Cheryan, 1998; Mänttäri et al., 2013]. An NF membrane is thin, charged film with a pore size less than 2 nm, usually made up of cellulosic acetate and aromatic polyamide [Toledano et al., 2010]. NF is used to separate the molecules with different MM cut-offs in the range of 0.2-1 kDa, with a driving force ranging from 10-30 bar. Essentially, NF can be utilized to separate small organic molecules from water into retentate or from bigger organic solutes into permeate [Mänttäri et al., 2013]. NF can also be utilized to separate dissociated forms of a compound from the undissociated form [Cheryan, 1998]. In principle, NF is sufficient on its own for the recovery of lignin from kraft BL, but normally UF is used as pretreatment before NF [De and Bhattacharya, 1996; Dafinov et al., 2005; Jönsson et al., 2008; Arkell et al., 2014]. Hybrid UF/NF of BL is a suitable method to get pure lignin free from hemicelluloses and provides higher flux during NF [Jönsson et al., 2008]. However, NF of BL without pretreatment by UF seems to be a cost-efficient alternative to recover lignin compared to that of hybrid UF/NF [Arkell et al., 2014]. Currently, there has been an increasing interest in the recovery of hydroxy acids from BL. NF has been studied to purify the BL from lignin, followed by acidification and crystallization to recover the hydroxy acids [Niemi et al., 2011]. More recently, NF has been employed to purify residual liquor after lignin precipitation and cooling crystallization. The NF permeate solution achieved 80 % organic acid purity of the total dissolved solids [Mänttäri et al., 2015].

5.3 Acidification methods

During alkaline pulping, lignin is partly dissolved in the alkaline solution. The dissolved lignin usually interacts with sodium ions in the liquor and consequently behaves as a polyelectrolyte [Helander et al., 2013]. Precipitation by acidification using carbon dioxide or mineral acid can be applied to extract

lignin from alkali BL [Alén et al., 1979; Uloth and Wearing, 1989a; 1989b]. By lowering the pH of the BL, lignin is precipitated due to protonation of its ionized phenolic hydroxy groups. The protonation mainly depends on the pKa value of the lignin molecules and precipitates according to those conditions [Zhu and Theliander, 2015]. Kraft lignin is a complex molecule consisting of many functional structures with different pKa values. For example, the phenolic hydroxy groups and carboxylic groups present in softwood kraft lignin have a pKa value of around 10 and 4.4, respectively [Helander et al., 2013]. On the other hand, the pKa value of lignin can also be influenced by temperature, ionic strength, and type of solvent [Norgren and Lindström, 2000; Ragnar et al., 2000]. In general, the rate of lignin precipitation mainly depends on the concentration and pH of the BL [Lin, 1992].

5.3.1 Carbonation

Precipitation of lignin from BL by carbonation has been studied for a long time [Alén et al., 1979; 1985c] and recently various industrial processes has been developed [Tomani, 2010; Kouisni et al., 2012; Stoklosa et al., 2013; Velez and Thies, 2013]. In carbonation, BL with a solids content of 25-50 % is acidified to a pH of about 8.5 with carbon dioxide under reduced pressure [Sjöström, 1993; Alén, 2011b; Gellerstedt et al., 2012]. The process conditions are varied for different wood species. Basically, almost 75-80 % of the lignin can be precipitated from BL by a suitable carbonation process. The liquor is usually heated (60-80 °C) to improve the filterability of the gelatinous lignin precipitate. The carbonation of BL prior to acid acidification seems to be economically attractive. As carbonation, can be efficiently carried out as a two-stage process in which flue (stack) gas can be partly used in the first stage, followed by the use of pure carbon dioxide, whereas the precipitation yield is increased significantly in the presence of pure carbon dioxide [Alén, et al., 1979; Sjöström, 1993; Alén, 2011b]. On the other, hand carbonation cannot be used to liberate the carboxylic acid groups of lignin, as it is not possible to reach pH below 8.5 [Sjöström, 1993; Gilarranz et al., 1998; Alén, 2011b].

5.3.2 Use of mineral acids

Acidification with mineral acids, such as sulfuric acid, can be applied directly [Sun and Tomkinson, 2001; Ibrahim et al., 2004; García et al., 2009] or in combination with carbonation to precipitate lignin from BL [Gilarranz et al., 1998; Kouisni et al., 2012]. The lignin fraction can be precipitated more or less completely by acidification of BL (pH to about 2). In general, acidification of BL to a pH of about 2 liberates carboxylic groups in addition to phenolic hydroxy groups, in kraft lignin, resulting in precipitation of more lignin. Almost 90 % of the initial lignin can be precipitated at pH 2, simultaneously liberating aliphatic carboxylic acids completely [Alén et al., 1984b; Alén, 2011b]. In contrast, the highly water soluble lignin monomers (about 10 % of the total kraft lignin) cannot be precipitated, and there is also the difficulty of

finding a suitable way of handling a huge amount of sodium sulfate formed as a by-product from the acidification of BL at low pH [Sjöström, 1993; Alén, 2011b].

5.3.3   Electrodialysis

ED is a unit operation where ions are transported through an ion-selective membrane with an electrical driving force [Yang and Lu, 2013]. The cation selective membrane (CSM), anion selective membrane (ASM), and bipolar membrane (BPM) are the three types of membranes that can be applied in ED separately or in combination. Both CSM and ASM hinder the passage of co-ions (anion and cation, respectively), and the special BPM is the combination of both the CSM and ASM. This membrane has a distinct function compared to those of mono-polar membranes, where they can dissociate solvents; for example, water (H_2O) is split into H^+ and HO^- [Huang et al., 2007].

At first, ED was applied to remove ions in the desalination process of sea-water and brackish water [Boniardi et al., 1997; Tado et al., 2016]. The last two decades have seen a growing trend towards the application of ED in the separation and purification of organic acids from their fermentation broths [Huang and Ramaswamy, 2013]. ED is most commonly used to separate organic acids, such as acetic [Jones et al., 2015]; butyric [Lopez and Hestekin, 2013]; citric [Novalic et al., 1996; Pinacci and Radaelli, 2002; Tongwen and Weihua, 2002]; formic [Luo et al., 2002]; gluconic, itaconic, and lactic [Boyaval et al., 1987; Kim and Moon, 2001]; malic [Sridhar, 1988]; propionic [Boyaval et al., 1993]; and tartaric acids [Andres et al., 1997].

In the pulp industry, ED has been identified as potentially being able to recover pulping chemicals from acid sulfite and alkaline BL [Radhamonan and Basu, 1980; Mishra and Bhattacharya, 1984; 1987; Arulanantham and Shanthini, 1997; Patil et al., 2016; Haddad et al., 2016]. The past fifty years have seen an increasing number of studies regarding the removal of organic material from BL by ED. In addition to liberation of carboxylic acids from sodium, importance has also been given towards the removal of lignin, which precipitates due to a decline in the pH of the liquor [Prabhu and Basu, 1980]. However, despite its potential applications, ED poses some major drawbacks, including low current efficiency as well as fouling of membranes [Mishra and Bhattacharya, 1987; Yang and Lu, 2013; Xie et al., 2016].

5.4   Purification methods of crude fractions

Lignin usually needs to be purified before application. The purification technique may be based on the contamination of lignin and its application. In general, acidified lignin from kraft BL retains a substantial amount of mother liquor impurities, such as degraded carbohydrates and inorganic salts [Lin, 1992; Gilarranz et al., 1998]. There are several industrial processes to purify

lignin. The purification of lignin can be carried out by repeated washing with water or an acidic aqueous solution (pH 2) until the ash content of the lignin is reduced (<2 %) [Silva et al., 2009; Zhu and Theliander, 2015]. On the other hand, dialysis, UF or ion exchange techniques are carried out for small-scale process of lignin purification [Gilarranz et al., 1998]. The hydroxy acids obtained from kraft BL seem to have potential applications, such as production of biodegradable films and plastics, tissue engineering, and cosmetics. However, high purity of hydroxy acids is required for such application, since impurities may cause some serious adverse effects in the synthesis of valuable products from these acids. The purification of the hydroxy acids obtained from BL is very challenging, especially in the purification of acids from inorganic salts and LMM lignin [Hellstén et al., 2013b].

5.4.1 Ion-exclusion chromatography

Ion-exclusion chromatography is a technique widely used for separating relatively small organic and inorganic acids especially those of a hydrophilic nature [Tanaka and Fritz, 1986; Glód, 1997; Weiss, 2004]. The technique basically involves the use of strong cation or anion exchange resins for the separation of ionic solutes from weakly ionized or neutral solutes. In general, aliphatic carboxylic acids are usually separated on a column filled with strongly acidic sulfonated polystyrene cation exchange resins (normally used in H^+ form) cross linked with divinylbenzene [Alén et al., 1990; Fritz, 1991; Tanaka et al., 2002; Haddad and Jackson, 2003; Helaleh et al., 2003]. Since, due to the Donnan effect, the ionic material is rejected by resin and passes through quickly, but the neutral substances are impeded and pass through more slowly [Alén et al., 1990; Fritz and Gjerde, 2009]. Recently, there has been renewed interest in the separation of aliphatic carboxylic acids using ion-exclusion chromatography [Tanaka and Fritz, 1986; Ohta et al., 1996; Tanaka et al., 2002; Helaleh et al., 2003]. Industrial ion-exclusion chromatography processes have been extensively employed in sugar industries [Springfield and Hester, 1999] and small-scale pilot-plant experiments in the separation of sulfite spent liquors from pulp industries [Alén, 2015]. The ion-exclusion chromatography has also been applied in the purification of aliphatic carboxylic acids from other constituents in the alkaline pulping liquors [Alén et al., 1990; Alén, 2015]. Consequently, to apply ion-exclusion chromatography, the hydroxy acids present in the BL must be liberated by using strong mineral acids [Alén et al., 1990; Stoklosa and Hodge, 2014]. On the other hand, ion-exclusion chromatography seems to be promising, as both volatile and hydroxy acids have been almost completely purified from the inorganic fraction, although further studies are required to develop the process [Alén et al., 1990].

5.4.2 Vacuum distillation

Vacuum distillation or distillation at reduced pressure is a technique extensively used for compounds that have high boiling points (>200 °C). Typically, vacuum distillation utilizes reduced pressure to distill a high boiling point liquid at low temperatures. Vacuum distillation is employed for heat sensitive liquids or compounds that degrade at their boiling point [Pavia et al., 2005; Ledgard, 2006]. The vacuum distillation has been most widely used in petroleum refineries [Favennec and Baker, 2001; Speight, 2010], cosmetics [Jouhar and Poucher, 2012], and food industries [Pennarun et al., 2001]. Vacuum distillation is most commonly used to distill volatile carboxylic acids [Pigman, 1957]. The carboxylic acids present in BL after their liberation from sodium salts can be purified completely by vacuum distillation [Alén, 2015].

Full-scale purification of hydroxy carboxylic acids along with their individual fractionation could be accomplished by vacuum distillation under reduced pressure (0.067-0.173 kPa) [Alén and Sjöström, 1981]. The initial fraction obtained at 0.053 kPa (<110 °C) consists of glycolic, lactic, and 2-hydroxybutanoic acids. In another main fraction (110-175 °C, 0.040 kPa), the distillate consists mainly of XISA, about 73 %, and small amounts of other acids. Following the increase in temperature to 210 °C, distillate consists of approximately 50 % GISA and residual comprising mainly XISA and 3-deoxy-pentonic acids. However, the individual separation of the LMM acids with close boiling points can be separated with an effective fractionating technique [Alén and Sjöström, 1981]. On the other hand, far too little attention has been paid to the recovery of carboxylic acids by distillation, and further studies are required to optimize the process [Alén and Sjöström, 1980b; 1980c; 1981].

5.4.3 Esterification and distillation

The Fischer esterification process can be best described as the reaction of carboxylic acid with alcohol in the presence of an acid catalyst to obtain their corresponding carboxylic esters with simultaneous removal of water [Dewan and Singh, 2003; Houston et al., 2004]. The esters of carboxylic acids have high boiling points, but lower than their corresponding acids, and they can be easily distilled without any decomposition [Emanuel, 1965]. Currently, the esterification reaction has been well established because of its extensive applications in the chemical and pharmaceutical industries [Yang et al., 2008]. The esterification technique is the most effective purification technique in the recovery of lactic acid from fermentation broth [Sun et al., 2006; Kumar and Mahajani, 2007; Zhao et al., 2009]. Esterification can also be the simplest route to recover selected carboxylic acids from BL. In this case, the acidified and concentrated BL can be simply esterified with alcohol in the presence of a catalyst to the corresponding esters [Weaver and Biggs, 1961; Alén, 2015], which can be further distilled to obtain individual fractions of carboxylic acids based on their relative volatilities [Alén, 1981]. However, the direct

esterification of carboxylic acids is limited to LMM acids, since the HMM acids exist in the form of their lactones. On the other hand, the HMM carboxylic acids, especially GISA, can be esterified with long chain FAs present in CTO to obtain surfactants [Sjöström, 1991]. Up to now, very little attention has been paid towards the esterification of carboxylic acids present in BL [Alén, 2015].

6   EXPERIMENTAL

6.1   Black liquor samples

Conventional laboratory scale soda-AQ cooking was conducted in an 18-L rotating stainless steel cooking digester. The birch (*Betula pendula*) chips used for pulping were laboratory-screened according to standard SCAN-CM 40:1 [2001], and those with a thickness of over 7 mm and below 13 mm were accepted. Irregular sized chips, shives, knots, and bark were eliminated. Data on cooking condition are presented in Table 1. BL was then separated from the pulp/liquor mixture by pressing it into a nylon-woven fabric bag and was stored at -18 °C prior to further analyses and experiments [I-V].

TABLE 1 Soda-AQ cooking data

Parameter	Birch
Alkali [% on o.d. feedstock]	20
AQ [% on o.d. feedstock]	0.1
Liquor-to-wood ratio [L/kg]	4.5
Maximum cooking temperature [°C]	162
Heating-up ratio [°C/min]*	2.4
H-factor total	650

* From room temperature to the maximum cooking temperature.

CBL was prepared by treating the initial BL with carbon dioxide (pH to about 8.5) in a 0.8 L pressurized stainless steel reactor at 80 °C (pressure about 1.5 bar) for 40 min (Figure 5). The precipitates were separated from the liquid phase by centrifugation at 3000 rpm for 30 min. At this point, the supernatant (CBL) was carefully decanted, pipetted out, and stored at -18 °C prior to further analysis and experiments.
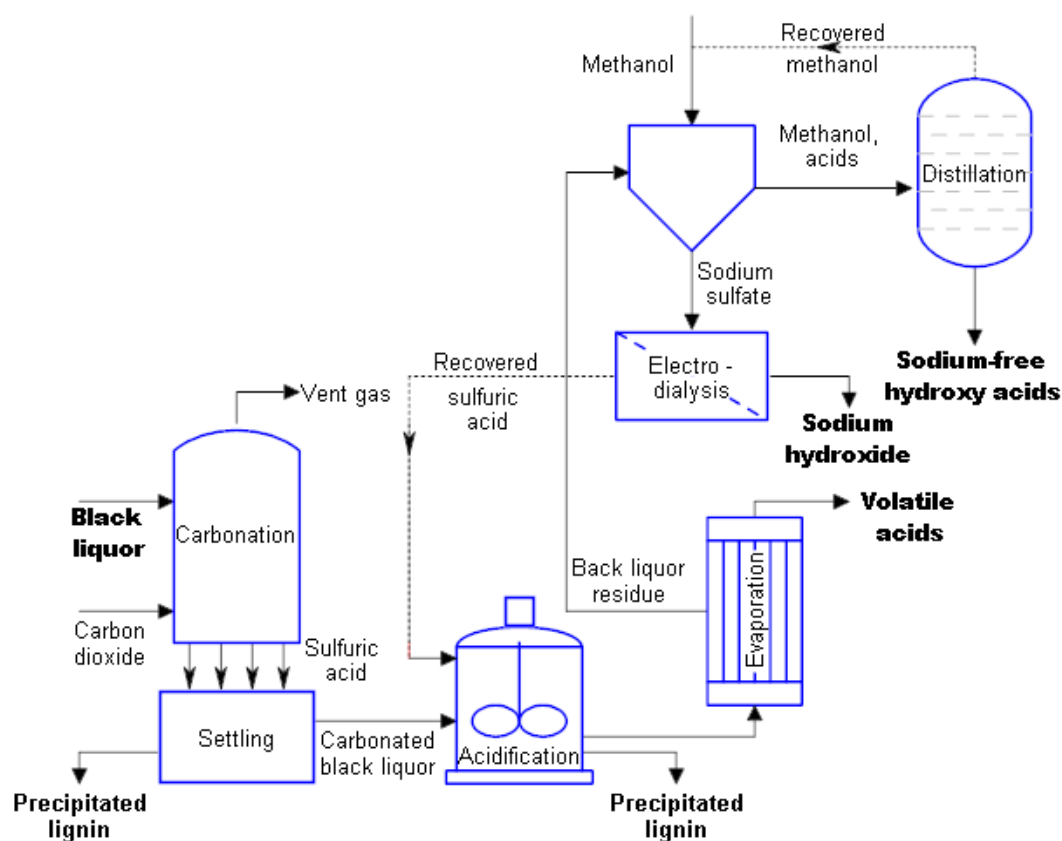
FIGURE 5 Schematic representation of recovering NaOH and sodium-free aliphatic carboxylic acids from CBL when carboxylic acids are first liberated by H_2SO_4 and the Na_2SO_4 formed is then separated by precipitation and electrodialyzed [I].

6.2 Recovery of aliphatic carboxylic acids and sodium

6.2.1 Acidification with mineral acids

In order to liberate aliphatic carboxylic acids from sodium and to precipitate more lignin, the CBL was acidified with 2 M H_2SO_4 to a pH of about 2. After acidification, the free volatile acids were evaporated followed by precipitation of Na_2SO_4 with methanol (1:1 v/v). Further, precipitated Na_2SO_4 was treated by ED to recover NaOH and H_2SO_4 (Figure 5).

6.2.2 Electrodialysis

Four different ED experiments were carried out by the ED equipment shown in Figure 6. In the first and second set of experiments, CBL (1:5 diluted with water) was directly ED to recover NaOH and free hydroxy acids with a total volume of 1 L and 5 L, respectively. In the third and fourth set of experiments, the precipitated Na_2SO_4 from CBL and commercial model compound (MC) Na_2SO_4 (reference material) were ED separately to recover NaOH and H_2SO_4.

All the experiments were carried out for 5 h, at a constant rate of 20 V and a constant flow rate of 10 L/h [I]. The membrane configuration used for the treatment of CBL is given in Figure 7.
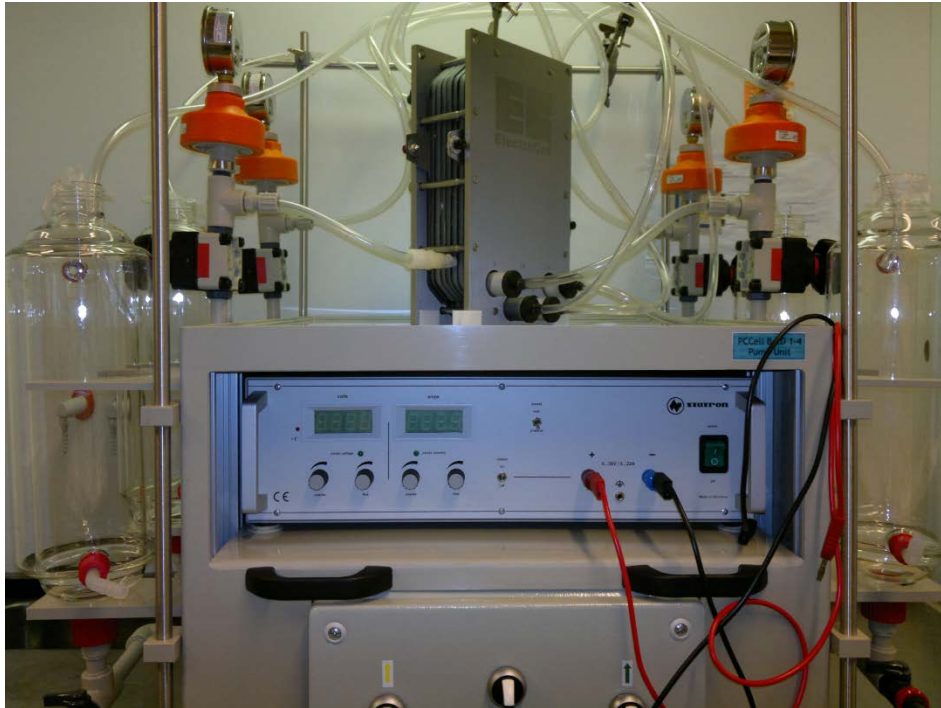

FIGURE 6 Electrodialysis equipment with membrane stack.
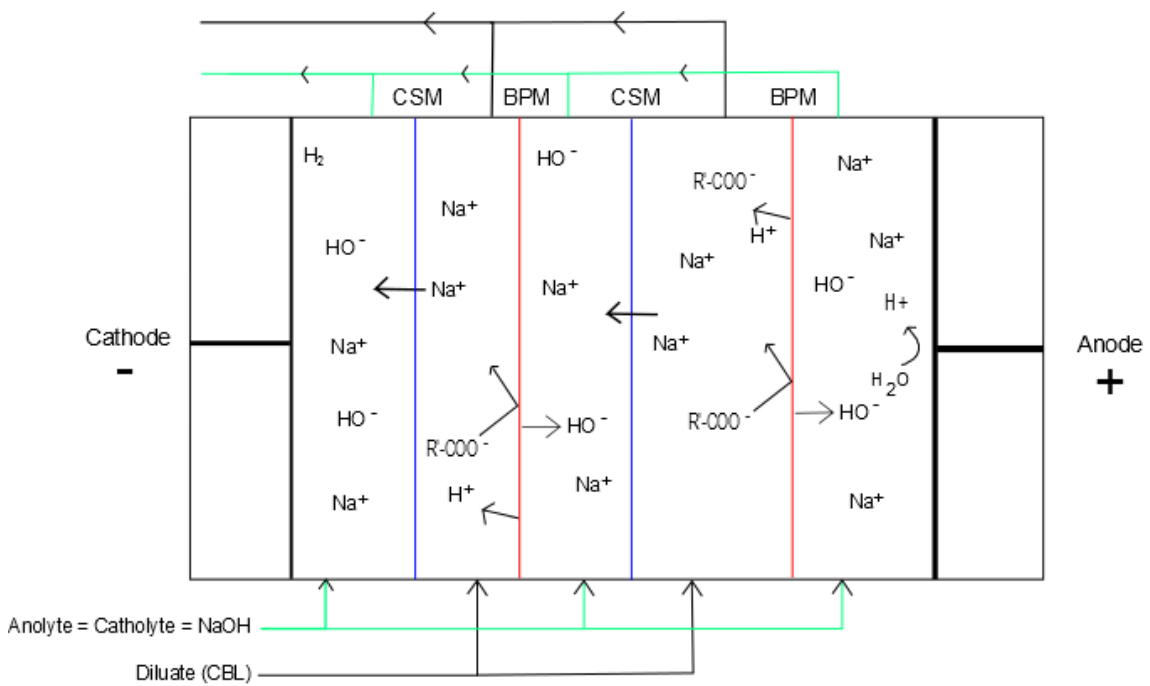

FIGURE 7 Schematic representation of the ED system used for the treatment of CBL (1:5) [I].

6.3 Conversion of valuable products from black liquor

6.3.1 Low-molar-mass carboxylic acid esters

After precipitation of the sodium sulfate, the liquid phase consisting of crude hydroxy acids was esterified directly in a 1 L round bottom flask fitted with a dean stark condenser. The reaction was carried out at 70 °C in the presence of an acid catalyst Amberlyst 15 (0.2 wt %), and the content was refluxed for 4 h, 8 h, 12 h, and 16 h (Figure 8). In each case, the crude reaction product was collected for further analyses [II]. Then, the LMM esters were recovered by dissolution of the reaction mixture into toluene (unreacted residual phase mostly consisting of HMM acids were separated by decanting).
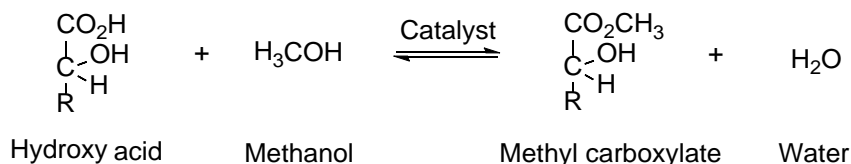

FIGURE 8 Esterification of low-molar-mass hydroxy acids with methanol. Acids: glycolic (R = H), lactic (R = CH$_3$), and 2-hydroxybutanoic (R = CH$_2$CH$_3$).

6.3.2 High-molar-mass carboxylic acids

α-Glucoisosaccharinic acid lactone (3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone, α-GISAL) was prepared from lactose [Whistler and BeMiller, 1963]. FA esters of α-GISAL were directly prepared using a microwave-assisted batch reactor (10 mL) in the presence of *p*-toluenesulfonic acid (*p*TSA) catalyst (Figure 9). Almost 1:3 moles of lauric acid with α-GISAL (added in four portions at an interval of 20 min) were esterified with a *p*TSA catalyst (0.03 mmol) at 100 °C under magnetic stirring for 6 h. Similarly, oleic acid and TOFAs were separately esterified at 70 °C for 24 h. In each case, the crude reaction product was collected for further analyses.
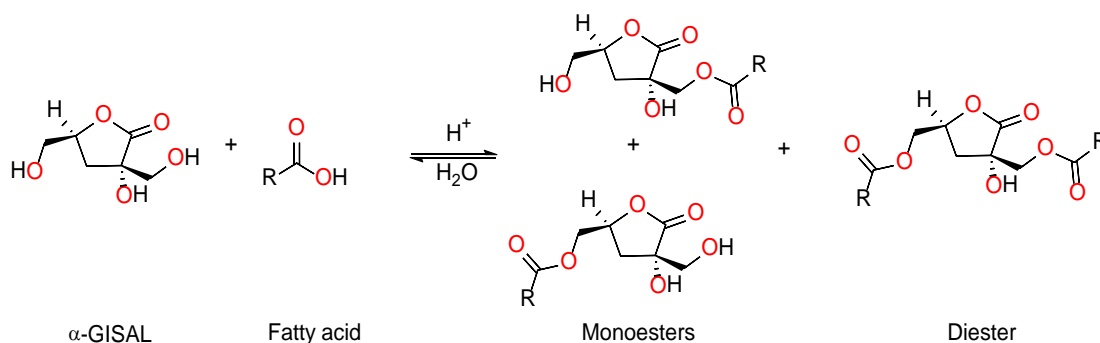

FIGURE 9 Principal products of the catalytical esterification of α-GISAL with a fatty acid.

Similarly, the residual phase after separating the LMM esters, mostly consisting of HMM acids, was directly esterified with TOFAs (molar ratio 1:2) in the presence of pTSA catalyst (0.03 mmol) at 100 °C in an oil bath under magnetic stirring for 4 hours (inert condition). The unreacted carboxylic acids were analyzed from the reaction mixture for calculating the overall conversion yield.

6.3.3   Esterification of tall oil fatty acids — Lignin-based catalyst

The freeze dried acidified lignin was dissolved in distilled water. The phenol formaldehyde condensation reaction was carried out by adding formaldehyde and hydrochloric acid and stirring the chemicals for 5 h at 90 °C. The reaction mixture was filtered out and dried at 105 °C for 4 h. The final sulfonation reaction was carried out by adding 10 mL of concentrated H_2SO_4 to the dried reaction mixture, and the suspension was stirred at 150 °C for 2 h. The final product (lignin catalyst) was completely washed and dried.

The activity of lignin-based acid catalyst was tested by simple microwave esterification of TOFAs with methanol. About 1 mole of TOFA with 3 moles of methanol was esterified with 5 wt% of lignin catalyst at 100 °C for 10 min to 60 min in a microwave reactor. Similarly, the esterification reaction was carried out using an Amberlyst 15 acid catalyst for comparison. The final FAME product was washed and collected for further analysis.

6.4   Chemical analysis

6.4.1   Carboxylic acids

Volatile acids were determined as their benzyl esters by gas chromatography/flame ionization detection (GC/FID) [Alén et al., 1985a]. Before GC, acids were liberated from their sodium salts with a strongly acidic cation exchange resin, and crotonic acid was used as an internal standard (IS).

Hydroxy mono- and polycarboxylic acids were determined as their per(trimethylsilyl)ated (TMS) derivatives by GC/FID [Alén et al., 1984a] and they were identified by using GC/MSD (mass selective detection). An aqueous solution of xylitol was used as an IS.   For the quantitative calculations, the mass-based response factors between xylitol and the peaks derived from the acids studied were based on the data given in the literature [Alén et al., 1984a].

6.4.2   Sodium

The concentration of sodium was determined with an inductively coupled plasma optical emission spectrometer (ICP/OES), PerkinElmer Optima 4300

DV. The results were studied with WinLab32 (version 3.4.0.9253, PerkinElmer) software.

6.4.3 Lignin

The amount of dissolved lignin in various liquors was determined by a UV/Vis (ultraviolet/visible) spectrophotometer (280 nm in 0.1 M NaOH) using an absorptivity value of 20.9 L/(gcm) according to [Alén and Hartus, 1988]. Similarly, a comparative study of lignin dissolved in various liquors was measured in the absorbance range of 205 nm to 300 nm.

The lignin obtained from acidification of BL with carbon dioxide, and acidification of the CBL with H_2SO_4 or direct acidification of BL with H_2SO_4, was analyzed using Fourier transform infrared (FTIR) spectrometry. The spectra were taken as an average of 32 scans in the wavenumber between 400 cm^{-1} and 4,000 cm^{-1} and with a resolution of 4 cm^{-1}.

The molar weight distribution (MWD) of the lignins was determined by gel permeation chromatography (GPC) using a high performance liquid chromatography (HPLC) system equipped with a column (460 mm × 10 mm I.D.) filled with Superdex 75 gel (Pharmacia) [Pakkanen and Alén, 2012]. The flow-rate of the eluent was 0.3 mL/min at room temperature. Detection was conducted by a Waters 996 photodiode array detector (PDA) within a wavelength range of 240–400 nm, and 280 nm was used for the determination of MMs. Calibration of the GPC system was accomplished with a commercial set of protein standards and several lignin-like monomer/oligomer model substances.

Qualitative ^{13}C nuclear magnetic resonance (NMR) spectroscopy was carried out in deuterated dimethyl sulfoxide (DMSO-d_6) at a sample concentration of 100 mg/0.6 mL using a 30° pulse angle with a recycle delay time of 2 s. The acquisition time of 1.82 s and an observed pulse of 6.5 μs were used for 75 MHz spectrometer (acidified lignins), and for 101 MHz spectrometer (carbonated lignin) they were 1.48 s and 6.0 μs, respectively. The spectra were analyzed with Topspin and the peaks were assigned the chemical shift w. r. to 39.51 (for (CD$_3$)$_2$SO) [Gottlieb et al., 1997] and all the analyses includes a decoupling mode to reduce the Nuclear Overhauser Enhancement (NOE).

The molar amount of -SO$_3$H per gram of lignin-based catalyst (indicated as M-SO$_3$H) was determined by acid-based titration that was modified from the literature [Zhang et al., 2013]. In this determination, the aqueous 2 M sodium chloride solution (20 mL) and the lignin catalyst (0.1 g) were mixed in an Erlenmeyer flask, and the mixture was sonicated for 1 h and filtered. The solution was then titrated with the standardized 0.1 M sodium hydroxide solution using phenolphthalein as an indicator. The total molar amount of acid groups -SO$_3$H, -CO$_2$H, and -OH (i.e., the sum of M-SO$_3$H, M-CO$_2$H, and M-OH) was determined by acid-based titration described in the literature [Lee, 2013]. In this determination, about 0.1 g of lignin catalyst was added to 40 mL 0.1 M NaOH, and the solution was then shaken for 4 h and filtered. The

solution was back titrated with the standard 0.1 M HCl solution using a pH meter; thus, the amount of the NaOH consumed corresponded to the total amount of acid groups. In the third determination, about 0.1 g of lignin catalyst was added to 25 mL of 0.08 M $NaHCO_3$ solution, which was sonicated for 2 h and filtered. The solution was then titrated with 0.1 M HCl to pH 3.9, resulting in the total molar amount of acid groups $-SO_3H$ and $-CO_2H$ (i.e., the sum of $M-SO_3H$ and $M-CO_2H$), which was obtained from the $NaHCO_3$ consumed. Finally, M-OH was obtained by subtracting $\sum M-SO_3H+M-CO_2H$ from $\sum M-SO_3H+M-CO_2H+M-OH$.

6.4.4 Tall oil fatty acids

The TOFAs were diluted in acetone and derivatized with a mixture of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (99:1, respectively). The quantitative analysis was performed by GC/FID. The relative mass-based response factors in relation to that of the ISs, heneicosanoic acid and betulinol, and those of compounds were equal to 1.

6.4.5 Esters

The methyl esters of LMM carboxylic acids present in BL were analyzed by GC/FID. The relative mass-based response factors used between the GC peak areas derived from IS, 1-heptanol, and those of compounds were equal to 1. The formation of esters was also separately followed by thin-layer chromatography (TLC) and an FTIR spectrometer.

The FA esters of α-GISAL were determined by GC/FID. The compounds were diluted in toluene and derivatized with a mixture of BSTFA and TMCS (99:1, respectively). The relative mass-based response factors in relation to that of the IS (1.0) were determined by the separately-purified esters of mono- and dilaurate α-GISAL, and they were 3.5 and 3.7, respectively. These values were also used for the quantitative determination of other FA mono- and diesters. The formation of esters was also followed by TLC. The high resolution mass spectrometric (HRMS) data were obtained in the positive mode using a mass spectrometer. The accurate sample masses were measured in relation to IS [for monolaurate aspartame, for dilaurate and dioleate erythromycin, and for monooleate 2-(4-hydroxyphenylazo)benzoic acid]. The ^{1}H NMR spectra were recorded in $CDCl_3$. The chemical shifts were reported in ppm relative to the residual $CHCl_3$ (δ 7.26)

The quantitative analysis of FA methyl esters (FAMEs) was also determined by GC/FID. The FAMEs were dissolved in hexane, and methyl heptadeconate was used as an IS.

7 RESULTS AND DISCUSSION

7.1 Lignin

7.1.1 Precipitation

Lignin was initially precipitated from BL by acidification with carbon dioxide (pH to about 8.5), and about 59 % of lignin was removed. Further decrease in pH (to about 2) either by the acidification of CBL with 2 M H_2SO_4 [I; II; IV; V] or by ED of diluted CBL (1:5) resulted in a lignin removal of 76 % and 66 %, respectively (Table 2).

TABLE 2 Concentration of lignin in various BL samples (g/L)* [I]

Liquor sample	pH	Lignin
BL	13.5	82.1
CBL	8.5	34.0
CBL (1:5)	8.2	6.2
Acidified CBL	2.0	8.3
Electrodialyzed CBL (1:5)	2.3	2.1

*BL refers to black liquor and CBL refers to carbonated black liquor.

Lignin was obtained from acidification of BL with carbon dioxide, acidification of the CBL with H_2SO_4, or direct acidification of BL with H_2SO_4. The UV absorption spectra of the three lignin samples are shown in Figure 10. It has been well-known that the aromatic compounds and other chromophoric structural elements present in the lignin fractions absorb intensely in the UV range of the spectrum [Alén and Hartus, 1988]. The spectra show the maximum absorbance at 220 nm. The absorptivity increased in the following order: carbonated lignin > directly acidified lignin > acidified lignin. A lower absorptivity for acidified lignin could be due to the presence of co-

precipitation of non-lignin material, such as carbohydrate degradation products, ash, and salts at pH 2 [Sun and Tomkinson, 2001; IV].
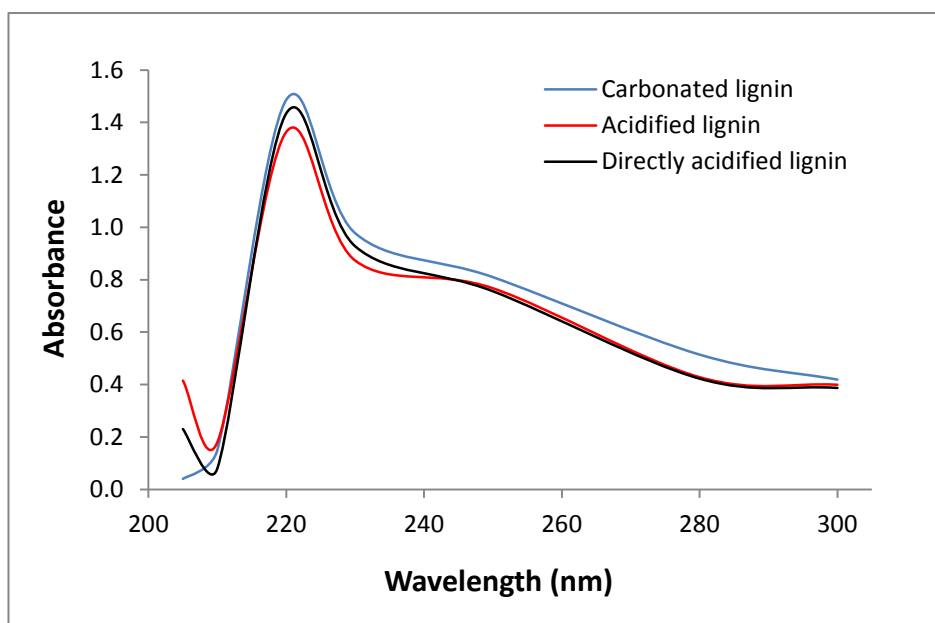

FIGURE 10 UV spectra of lignins precipitated from birch soda-AQ black liquor [IV].

The normalized MWDs of lignin precipitated from carbonation and acidifications of BL are shown in Figure 11. In general, the MW of the lignin precipitated from carbonation was noticeably higher than that of lignin precipitated through acidification. Table 3 gives the weight-average (M_w) and number-average (M_n) MM and polydispersity (M_w/M_n) of the lignin fractions. The results also indicate that the M_w of carbonated lignin was higher than that of the acidified lignin samples. The C-C bonds of lignin are the most important feature when considering their MW, as these bonds are not cleaved during the wood pulping due to their higher stability [Sun and Tomkinson, 2001; Tejado et al., 2007]. The lignin samples showed no significant difference in their M_n, whereas the polydispersity and M_w were observed to be higher for the carbonated lignin as compared to that of acidified lignins; moreover, there were no significant variations observed between the lignin precipitated from carbonation and directly via acidification [IV].
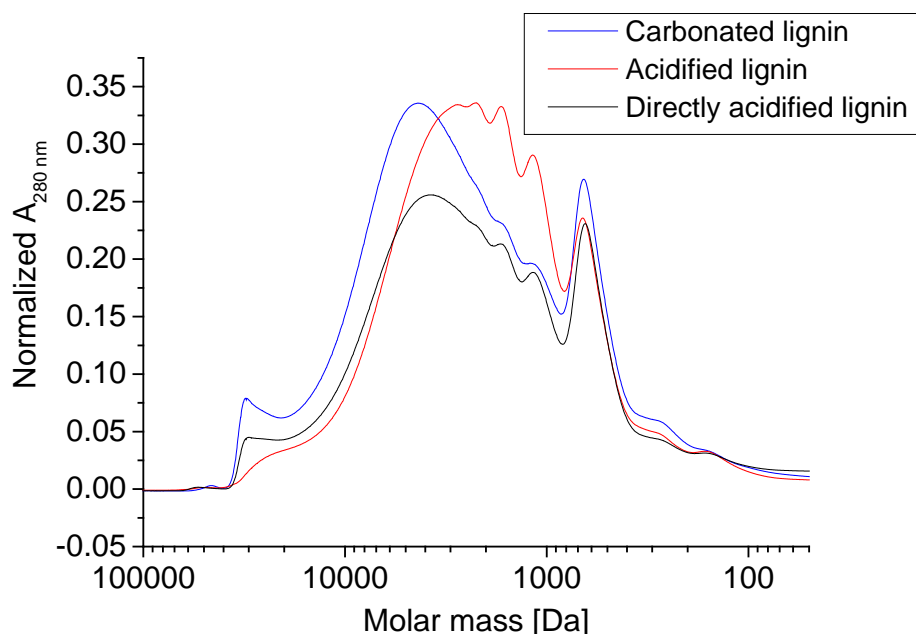
FIGURE 11 Normalized MWDs of lignin precipitated birch soda-AQ black liquor [IV].

TABLE 3 Weight-average (M_w) and number-average (M_n) molar masses, and poly-dispersity (M_w/M_n) of lignins precipitated from birch soda-AQ black liquor [IV]

Lignin sample	M_w	M_n	M_w/M_n
Carbonated	4728	781	6.0
Acidified	3373	862	3.9
Directly acidified	4253	801	5.3

It was apparent from the ^{13}C-NMR spectra shown in Figure 12 that there was no significant difference in the structure of the lignin precipitated by carbonation and acidification, due to the presence of similar structural constituents in these lignins. The weak peaks in the chemical shift ranging from 170 ppm to 130 ppm corresponded to the aromatic carbons attached to oxygen atoms (=C-O-); strong peaks from 130 ppm to 100 ppm corresponded to the secondary aromatic protons (=CH-C); weak peaks from 130 ppm to 100 ppm corresponded to the tertiary aromatic protons (=C-C); strong peaks in the range 80 ppm to 50 ppm corresponded to the (OCH_3) carbons and aliphatic carbons attached to oxygen atoms; and the peaks in the range 40 ppm to 0 ppm corresponded to the aliphatic carbons [Stoklosa et al., 2013].
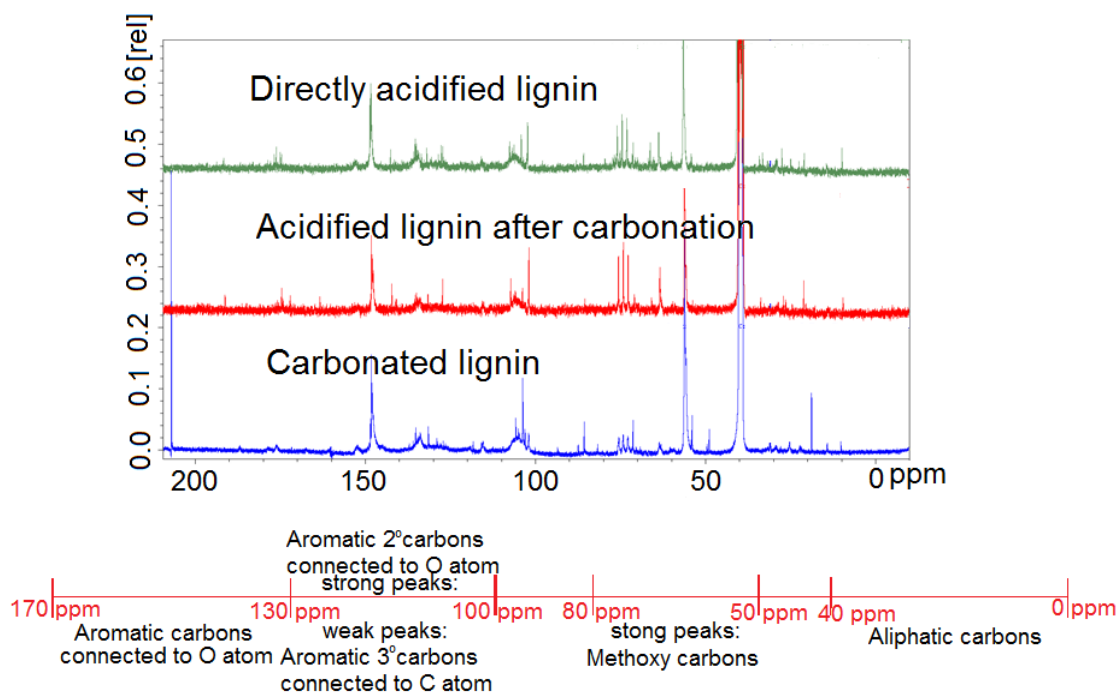
FIGURE 12 ^{13}C-NMR spectra of lignins precipitated from birch soda-AQ black liquor [IV].

7.1.2 Lignin catalyst

The lignin catalyst was successfully prepared. The total density of acid groups for lignin catalyst and recycled lignin catalyst was observed to be about 3.1 mmol/g and 2.7 mmol/g, respectively. In the FTIR spectrum, the vibration bands at 1030 cm^{-1} (SO$_3$ stretching) and 1149 cm^{-1} (S-O-S is stretching in SO$_3$H) indicated the presence of -SO$_3$H groups [Zhang et al., 2013]. The vibration bands existed at 1557 cm^{-1} and 1698 cm^{-1}, which could be due to -OH in the plane deformation and C=O stretching of -COOH groups, respectively [Liang et al., 2013]. The elemental analysis of lignin catalyst and recycled lignin catalyst is shown in Table 4 [V].

TABLE 4 Density of acid groups in the catalysts (mmol/g) [V]

Samples	–SO$_3$H	–COOH	–OH
Lignin catalyst	1.4±0.2	0.9±0.2	0.8±0.1
Recycled lignin catalyst	1.2±0.2	0.7±0.2	0.7±0.1
Amberlyst 15	4.2±0.1	-	-

7.2   Recovery of sodium by electrodialysis

7.2.1   Carbonated black liquor (1:5)

Sodium hydroxide could be easily recovered from CBL (1:5) using ED. During the first 3 h, the rate of sodium recovery was rather high (0.065 mol Na/h), and almost 80 % sodium was recovered with an energy consumption and a current efficiency of 0.4 kWh/mol Na and 45 %, respectively. After the treatment time of 5 h, almost 90 % of sodium was recovered, with an average recovery rate of sodium and energy consumption of 0.044 mol Na/h and 1.76 kWh/mol Na, respectively. The increase in the energy consumption during the final stage of the experiment was mainly due to a deposition of lignin on the anionic side of the BPM, thus hindering the passage of ions. This was mainly due to decrease in the sodium concentration of the diluate, causing gradual liberation of sodium from hydroxy and carboxylic acid groups of the lignin [I].

The recovery of sodium hydroxide was improved for the ED experiment conducted with the diluate solution containing 5 L of CBL (1:5) (Figure 13). The energy consumption was 0.2 kWh/mol with a relative high recovery rate of sodium (35 %), 0.138 mol Na/h during the first 3 h, reaching a maximum of around 70 % after 10 h.
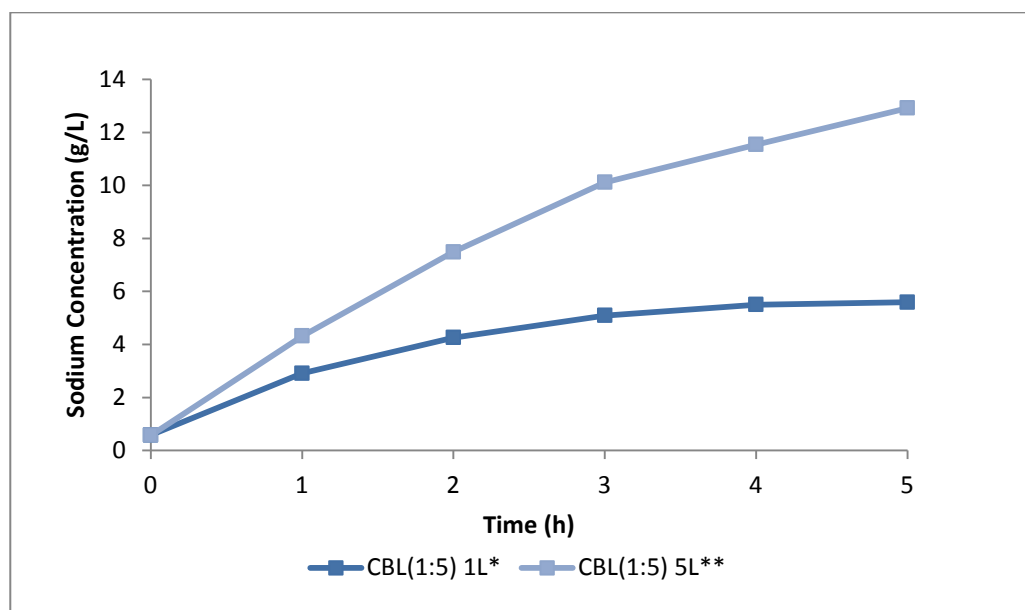
FIGURE 13 Sodium (present in NaOH) in concentrates from ED experiment with *CBL(1:5) 1 L diluate and ** CBL(1:5) with 5 L diluate [I].

The current efficiency was observed to gradually decrease for the first 5 h and was found to be 54 % and reduced to 39 % after 10 h. Similarly, the energy consumption was constant in the beginning and started to increase as the sodium concentrate of the diluate declined. The decrease in the recovery was

mostly due to inadequate membrane area for the sample containing 5 L of the diluate sample, as deposition of more lignin on the anionic side of the membrane occurred [I].

7.2.2 Sodium sulfate

The behavior of the both MC Na_2SO_4 and the precipitated Na_2SO_4 (contained some BL impurities) was observed to be almost similar during the ED experiments (Figure 14). In both cases, almost 90 % of sodium was recovered with an average sodium recovery rate of 0.110 mol Na/h and 0.104 mol Na/h, respectively. The recovery of sodium was increased in the final stage of the experiment, which was mainly due to liberation of Na^+ and SO_4^{2-} from the $NaHSO_4$ (formed in the initial phase). The overall energy consumption in the ED experiments was observed to be 0.38 kWh/mol Na and 0.43 KWh/mol Na for MC and precipitated Na_2SO_4 CBL, respectively. Furthermore, during these experiments, energy consumption started to increase during the final stage mainly due to an increasing flux of H^+ through the CSM as the concertation of SO_4^{2-} started to decrease in the diluate solution [I].

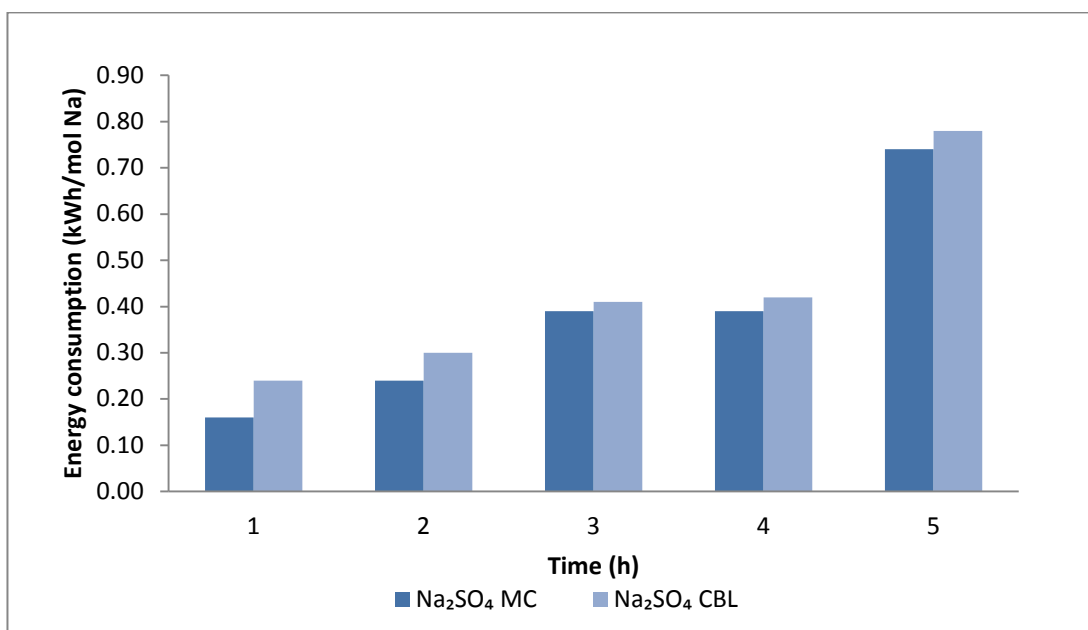**FIGURE 14** Energy consumption in the recovery of sodium from Na_2SO_4 preparations [I].

7.3 Carboxylic acids

The acidification of BL by H_2SO_4 and CBL by H_2SO_4 or ED (pH to about 2) process led to liberation of aliphatic carboxylic acids from their sodium salts. There was no significant decrease in the individual acid component. The composition of aliphatic carboxylic acids in various BLs is shown in Table 5.

The differences in their final concentrations were due to difference in liquor volume. It has been observed that some decrease in liquor volume during carbonation [Alén et al., 1979] and increase in the liquor volume during acidification with H_2SO_4 may take place [I; II; IV].

TABLE 5 The aliphatic carboxylic acids in various black liquor samples (g/L) [I; IV]

Acid component	BL	CBL	Acidified CBL	ED CBL(1:5)	Acidified BL
Formic	6.2	6.0	4.8	1.0	3.6
Acetic	17.3	15.6	13.0	2.7	12.0
Glycolic	2.0	1.9	1.3	0.3	1.3
Lactic	2.3	2.1	1.6	0.4	1.5
2-Hydroxybutanoic	3.2	3.0	2.4	0.5	2.1
3,4-Dideoxy-pentonic	1.3	1.2	0.7	0.2	0.5
3-Deoxy-pentonic	1.5	1.4	1.0	0.2	0.8
Xyloisosaccharinic	3.0	3.3	2.7	0.4	2.0
Glucoisosaccharinic	2.9	3.1	2.4	0.4	1.7
Miscellaneous	4.1	4.4	2.7	0.8	1.8
Total	43.8	42.2	32.6	6.9	27.3

7.4 Tall oil fatty acids

The fraction of TOFAs contained 92.4 % fatty and 3.2 % resin acids (Table 6). These composition data were slightly different from those (97.0 % and 1.7 %, respectively) reported by the manufacturer. This was probably partly due to the "inaccuracies in compound quantification" (i.e., no specific relative response factors between the GC peak areas derived from the IS and the individual compounds were used), and the amount of "unidentified compounds" (about 4 %). The main FA components analyzed were linoleic ($C_{18:2}$), oleic ($C_{18:1}$), and linolenic ($C_{18:3}$) acids, which, respectively, comprised about 50 %, 25 %, and 9 % of the total FAs [III].

TABLE 6 Weight percentages of fatty acids in the TOFAs [III]

Compound		Content
Fatty acids		92.4
Stearic acid	$C_{18:0}$	3.5
Oleic acid	$C_{18:1}$	25.0
Linoleic acid	$C_{18:2}$	45.4
$C_{18:2}$ (conjugated)		1.0
$C_{18:2}$ (conjugated)		1.6
$C_{18:2}$ (conjugated)		2.2
Linolenic acid	$C_{18:3}$	8.5
$C_{18:3}$ (conjugated)		1.0
10-Nonadecenoic acid	$C_{19:1}$	1.2
Eicosatrienoic acid	$C_{20:3}$	1.0
Others*		2.0
Resin acids		3.2
Pimaric acid		1.1
8,15-Isopimaridien-18-oic acid		2.1
Miscellaneous		4.4

*Fatty acids which are present in lower concentrations.

7.5 Ester derivatives

7.5.1 Esters of fatty acids with glucoisosaccharinic acid (lactone)

FA esters of α-GISAL could be successfully prepared. The catalytic micro-wave-assisted esterification yield of α-GISAL with lauric acid (i.e., saturated FA) was observed to be about 62 % in specific conditions. On the other hand, corresponding yields of oleic acid and TOFA esters were about 60 % and 40 %, respectively, even with a prolonged reaction time. The microwave-assisted reactions were separately optimized, and the highest yields for unsaturated and saturated FAs were obtained at 70 °C and 100 °C. Furthermore, it should be pointed out that at a temperature above 70 °C, the unsaturated FAs were self-polymerized and resulted in lower ester yield.

The esterification of FAs with α-GISAL results in the formation of monoester and diester products. The HRMS (ESI+) data mass to charge ratio (m/z) calculated for $[C_{18}H_{32}O_6Na]^+$ was 367.2091 (found as 367.2094), which corresponded to monolaurate, and m/z calculated for $[C_{30}H_{54}O_7Na]^+$ was 549.3762 (found as 549.3778), representing dilaurate. Similarly, the m/z data on mono- and dioleate were, respectively, the following: 449.2874 (calculated

for $[C_{24}H_{42}O_6Na]^+$) and 449.2853 (found) and 713.5327 (calculated for $[C_{42}H_{74}O_7Na]^+$) and 713.5313 (found).

The formation of esters was followed by ^1H NMR. The esterification had a significant impact on the chemical shifts of H_4 proton due to the deshielding effect caused by the ester functional groups; thus, it was used as a characteristic peak to identify the corresponding monoesterification products. Without any difficulty, a multiplet observed at 4.88 ppm for H_4 proton suggested a diester product (Figure 15a). Esterification of a hydroxymethyl group attached either to C_4 or C_2 caused the respective downfield and upfield chemical shifts as shown in Figures 15b and 15c. The electron withdrawing nature of the ester functional group at C_4 could be accounted for the downfield chemical shift observed in Figure 15b. On the other hand, the esterification at C_2 group had the long-range deactivation effect on H_4 proton, thus resulting in the upfield chemical shift as shown in Figure 15c [III].

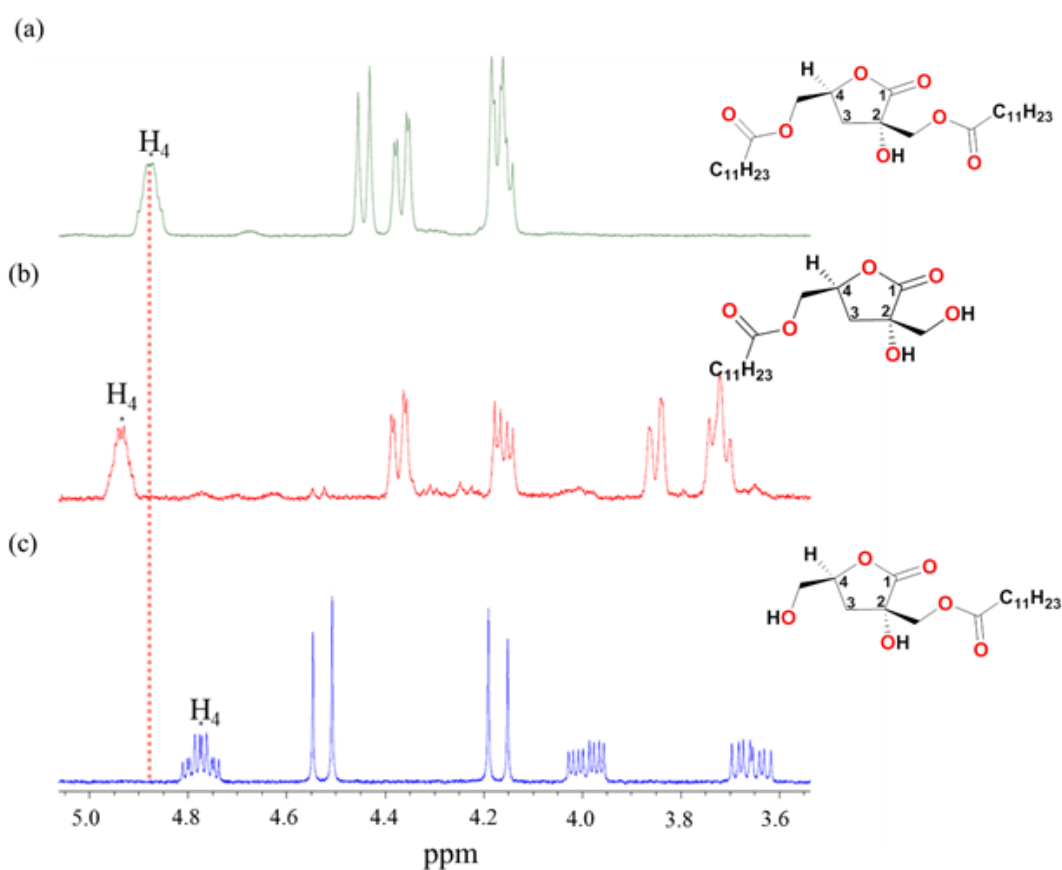

FIGURE 15 Partial ^1H NMR spectra of lauric acid diester (a) and monoester (b and c) with α-GISAL [III].

7.5.2 Esters of LMM carboxylic acids from black liquor

The methyl esters of lactic, glycolic, and 2-hydroxybutanoic acids (LMM) present in BL were synthesized. It was observed that the almost 50 % yields of these LMM methyl esters could be produced by refluxing the mixture of free

hydroxy acids with methanol for approximately 8 h. After this point, the rate of reaction gradually decreased, and higher yield levels of approximately 70 % were obtained after 16 h (Figure 16).
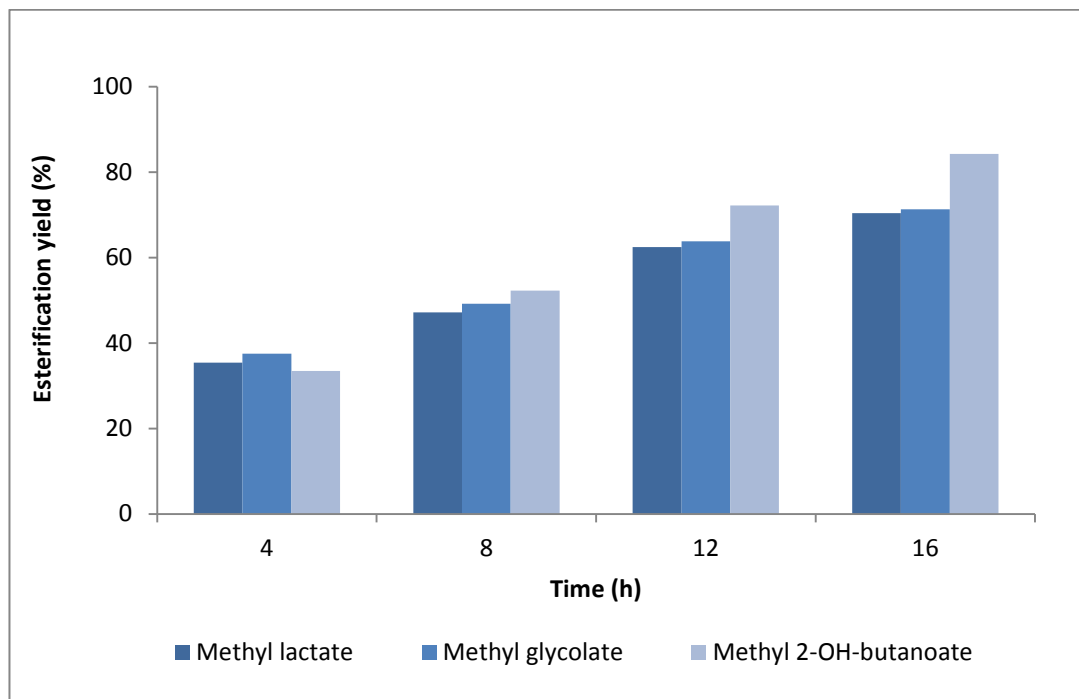

FIGURE 16 Esterification yields for glycolic, lactic, and 2-hydroxybutanoic acids in CBL with methanol at 70 °C [II].

Esterification reactions were followed by FTIR and TLC. The FTIR spectra methyl esters were compared with a mixture of hydroxy acids (as their sodium salts). The spectrum of hydroxy acids had two adsorption bands: characteristics of antisymmetric (at 1650–1550 cm^{-1}) and symmetric (1440–1360 cm^{-1}) CO_2 stretch vibrations [Günzler and Gremlich, 2002; Larkin, 2011]. The main adsorption bands in the spectrum of esters were due to a strong C=O stretch vibration at 1750–1700 cm^{-1} and to a C-O stretch vibration at 1300–1100 cm^{-1} (Figure 17) [II].
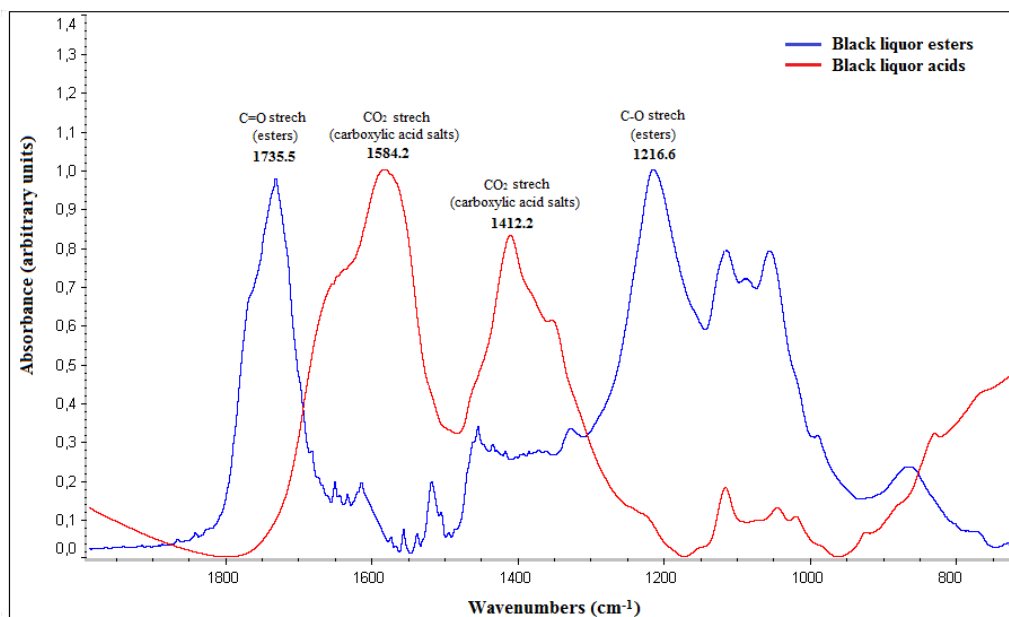
FIGURE 17 FTIR spectra of carboxylic acids and carboxylic esters in black liquor before and after esterification [II].

7.5.3   Esters of HMM carboxylic acids from black liquor

The TOFA esters of HMM acids were synthesized. A conversion yield of about 70 % (based on GC data) HMM acids was achieved. The corresponding conversion yield of major HMM acids, such as, 3-deoxy-pentonic acid, XISA, and GISA were, respectively, about 70, 68, and 60.5 % for 4 h at 100 °C. The increase in reaction temperature or prolonged reaction time led to the degradation of the compounds.

7.5.4   Fatty acid methyl esters of tall oil fatty acids

The lignin-based acid catalyst seemed to be suitable for the synthesis of methyl esters of TOFA. This lignin-based catalyst was compared with different catalysts for the microwave-assisted esterification of TOFA. The reactions showed good yield for catalytic reactions compared to that of non-catalytic reactions. The reactions gave a higher FAME yield for lignin catalyst (88 %) compared to that of Amberlyst 15 (80 %) for 1 h (Figure 18). On the other hand, the maximum FAME yield of 93 % was achieved for *p*TSA and the lowest yield of 20 % for the non-catalytic reaction. Likewise, the reaction showed no significant decrease in the reusability of lignin catalyst. It should be pointed out that in using lignin catalyst; the maximum FAME yield of 67 % was achieved for a short reaction time of 10 min. However, the esterification yields also depended on the composition of the TOFAs. The monounsaturated and diunsaturated FAs showed a higher rate of conversion in the catalytic esterification in comparison with other unsaturated FAs (Figure 19) [V].
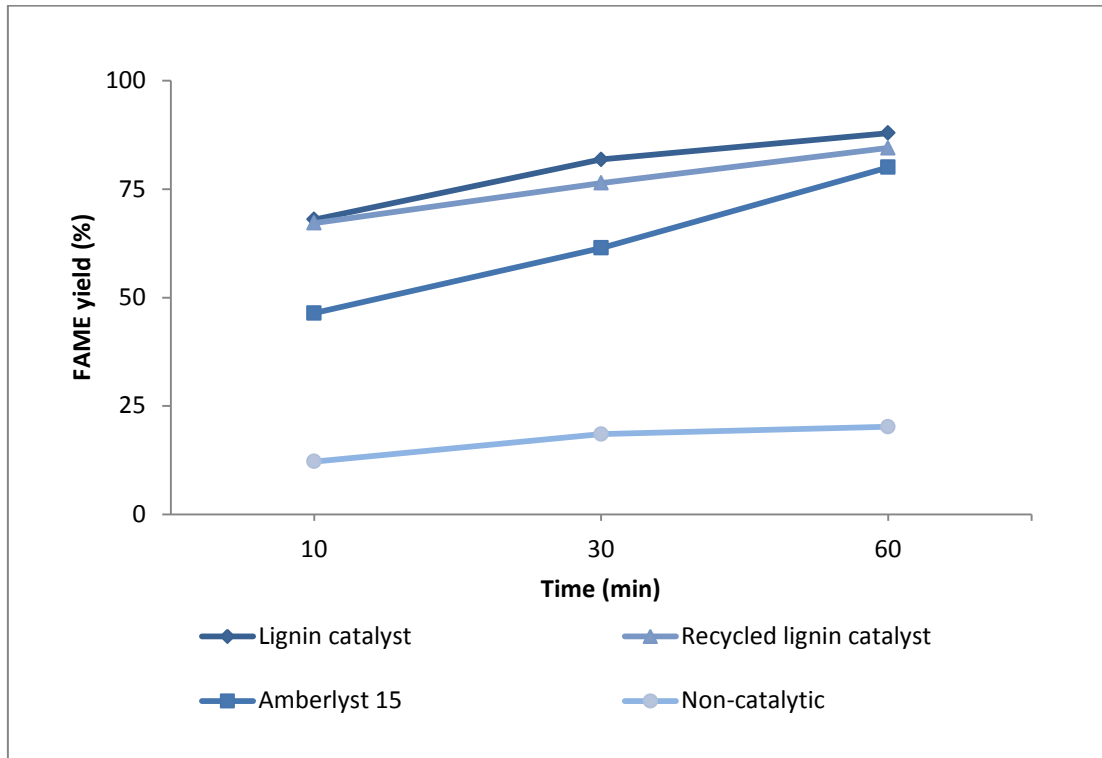
FIGURE 18 Esterification yields of fatty acids with methanol at various reaction times at 100 °C and with heterogeneous catalysts [V].
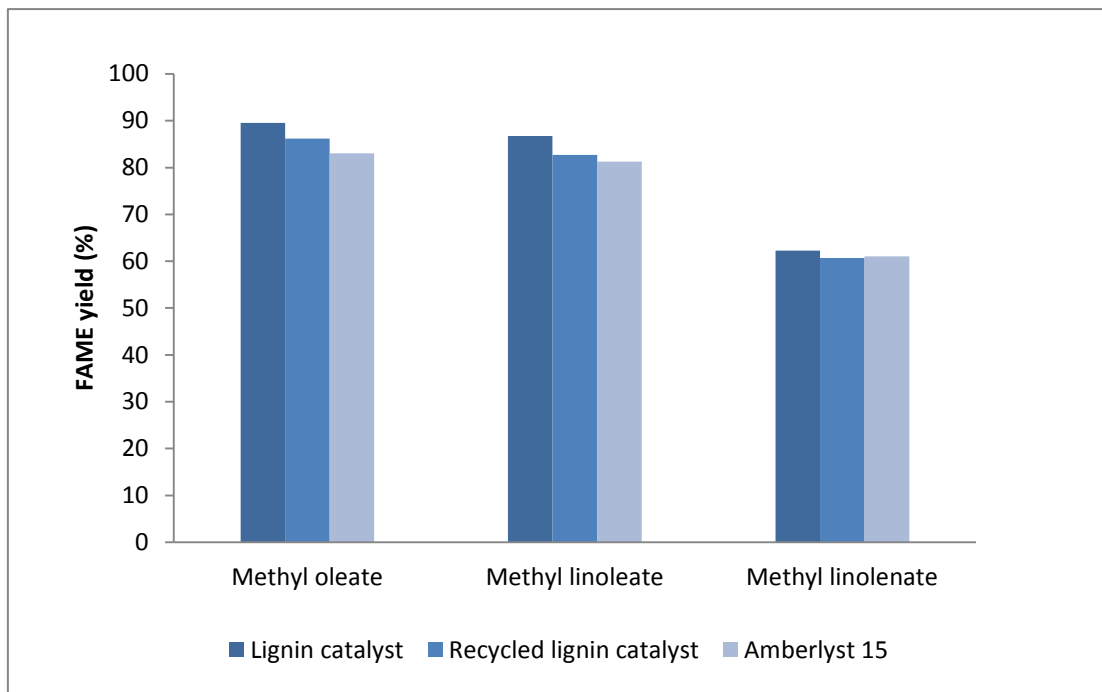

FIGURE 19 Esterification yields of oleic, linoleic, and linolenic acids with methanol at various reaction times and at 100 °C with heterogeneous catalysts [V].

7.6 Total recovery of organics from soda-AQ black liquor

Almost 90 % of the lignin was removed from BL by carbonation followed by acidification with H_2SO_4. After separation of Na_2SO_4 from the acidified liquor, approximately 70 % of volatile acids could be recovered by evaporation. The LMM acids (about 70 %) from the crude hydroxy fractions could then be directly esterified with methanol. The LMM esters were separated by direct distillation or by liquid-liquid extraction. The HMM acids (about 60 %) were recovered by direct esterification with TOFAs for the synthesis of non-ionic surfactants. The residual phase mostly contained 20-25 % of aliphatic acids and 5–10 % of the initial lignin. Figure 20 illustrates the typical material balances of organics in the recovery process of valuable chemicals from soda-AQ BL.
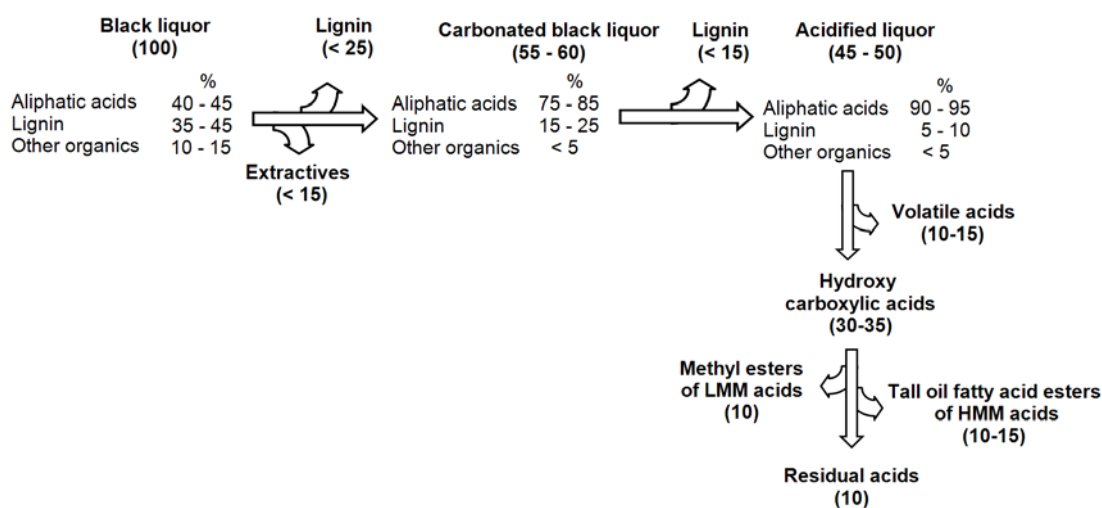

FIGURE 20 Typical material balance of soda-AQ black liquor organics for the synthesis of low-molar-mass (LMM) and high-molar-mass (HMM) esters.

8 CONCLUDING REMARKS

8.1 Main findings

The findings of this study suggested that it is possible to develop potential techniques to separate and utilize organic and inorganic materials present in alkaline BL. The results indicated that the effective separation of lignin from BL is possible by carbonation, followed by acidification with H_2SO_4 or by direct acidification with H_2SO_4. ED offered an attractive technique to recover NaOH from Na_2SO_4, with the simultaneous formation of H_2SO_4 for recycling. After precipitation of most lignin by acidification, almost two thirds of the volatile acetic and formic acids could be easily recovered by straightforward evaporation. In addition, the recovery of the LMM hydroxy acids (about 70 %) was also possible by direct catalytic esterification with methanol, followed by evaporation. The most obvious finding of this study was that the esterification of α-GISAL with FAs leads to the formation of two different forms of monoesters and diesters. Similarly, the residual HMM hydroxy acids from BL can be esterified with TOFAs for the synthesis of non-ionic surfactants, thereby potentially utilizing both side-stream by-products.

The three fractions of lignin from birch soda-AQ were characterized to promote the utilization of hardwood alkali lignins. The fractions originated from carbonation (pH to about 8.5) or acidification (pH to about 2) with H_2SO_4 after carbonation or directly, showed only a small difference between them; thus, their similar chemical utilization seemed possible. Furthermore, the lignin-based heterogeneous catalyst containing $-SO_3H$, $-CO_2H$, and $-OH$ functional groups was produced from acid-precipitated alkali lignin by phenol formaldehyde condensation and sulfonation reaction. This lignin catalyst exhibited a high conversion rate in the acid-catalyzed esterification of TOFAs with methanol in microwave-assisted reaction. Compared to other commercial catalysts (Amberlyst 15 and *p*TSA), the lignin-based catalyst showed good activity, and it could be easily recycled.

8.2   Suggestion for the future research

The main aim of this study was to explore new technologies towards the recovery and utilization of the valuable by-products from alkaline pulping. This study offered attractive possibilities to manufacture various chemicals (LMM hydroxy acid esters, volatile acids, non-ionic surfactants and lignin-based acid catalyst) and biofuels (biodiesel) from alkaline pulping in addition to traditional chemical pulping.

The separation technologies developed in this study can be further modified and employed in other suitable industrial applications. Although significant research in this field has been conducted on a laboratory scale, in forthcoming studies, special attention must be given towards the scale up of this recovery process. Moreover, these methods need to be simplified and detailed cost analysis studies must be carried out that deal with each unit operation of the process. This appears challenging but will ultimately determine the most optimal recovery processes.

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