

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 206

**COMBUSTION BEHAVIOR OF BLACK LIQUORS – DROPLET
SWELLING AND INFLUENCE OF LIQUOR COMPOSITION**

BY

CHENGCONG CHEN

Academic Dissertation for the Degree of
Doctor of Philosophy

*To be presented, by permission of the Faculty of Mathematics and Science of the
University of Jyväskylä, for public examination in Auditorium KEM4,
on December 1st, 2017 at 12 noon*



UNIVERSITY OF JYVÄSKYLÄ

Copyright © 2017
University of Jyväskylä
Jyväskylä, Finland
ISBN 978-951-39-7246-2
ISSN 0357-346X

Author's address

Chengcong Chen, M.Eng.
Laboratory of Applied Chemistry
Department of Chemistry
Survontie 9A
FI-40500 Jyväskylä
Finland

Supervisor

Raimo Alén, Professor
Laboratory of Applied Chemistry
Department of Chemistry
University of Jyväskylä
Finland

Reviewers

Mika Järvinen, Associate Professor
Department of Mechanical Engineering
Aalto University
Finland

Keijo Salmenoja, PhD
Technology Director, Recovery Boilers
ANDRITZ Oy
Finland

Opponent

Esa Vakkilainen, Professor
School of Energy Systems
Lappeenranta University of Technology
Finland

ABSTRACT

Chen, Chengcong

Combustion Behavior of Black Liquors – Droplet Swelling and Influence of Liquor Composition

Jyväskylä: University of Jyväskylä, 2017, 39 p.

Department of Chemistry, University of Jyväskylä, Research Report No. 206

ISSN 0357-346X

ISBN 978-951-39-7246-2

The combustion of black liquor (BL) in a recovery boiler is a central process in a kraft pulp mill for recovering the cooking chemicals and for producing heat and power. This work explored the most important combustion behavior of BL, the swelling of in-flight droplets, from the viewpoint of liquor composition. It also studied the combustion behavior of BL droplets obtained from two biorefining subprocesses (carbonation and hot-water pretreatment, HWP) and sulfur-free pulping alternatives (soda-anthraquinone (AQ) and oxygen-alkali pulping).

The formation of a plastic state essential for the swelling of BL droplet was found to result from the melting of an array of carbohydrate-derived aliphatic carboxylic acids (sodium salts) and NaOH. Another two necessary conditions for swelling were: (i) the release of volatiles by the decomposition lignin and other organics for expanding the plastic mass and (ii) the formation of a rigid char surface with the organic carbons mainly from the pyrolysis of lignin.

Biorefining subprocess using carbonation to partially separate lignin from the BL had a significant impact on the swelling behavior of the resulting BL droplets. The reduced lignin content and the increased Na₂CO₃ content led to lower maximum swelling of the droplet but did not influence the combustion times. The content of lignin seemed to affect the degree of swelling greater than its molar mass distribution. Further experiments indicated that the medium molar mass lignin (i.e., the 5-10 kDa fraction) pyrolyzed in mixture with organic acids swelled more than other fractions (i.e., the 1-5 kDa and >10 kDa fractions).

The HWP of feedstock prior to chemical pulping was another biorefining subprocess that influenced the combustion behavior of the BLs by altering the delignification behavior and thus the liquor composition. Generally, the HWP reduced the amount of acetic acid but increased the amount of hydroxy acids and lignin for almost all BLs. Consequently, the maximum swelling of BL droplets from chips increased but for most of the BLs from sawdust it decreased after the HWP. The sulfur-free BL droplets, especially the soda-AQ droplets, typically swelled less and burned slower than the kraft droplets. The mass ratio lignin-to-organic acids was found to correlate with the swelling of BL droplets.

Keywords: aliphatic carboxylic acids, black liquor, combustion behavior, kraft pulping, lignin, plastic state, pyrolysis, recovery boiler, swelling

LIST OF PUBLICATIONS

This thesis is based on the following original research articles referred to in the text by their Roman numerals (Papers I-V).

- I Chen, C.; Alén, R.; Lehtimäki, E.; Louhelainen, J. 2017, A salt-induced mechanism for the swelling of black liquor droplet during devolatilization, *Fuel* 202: 338-344.
- II Chen, C.; Pakkanen, H.; Alén, R. 2017, Role of lignin and sodium carbonate on the swelling behavior of black liquor droplets during combustion, *Holzforschung*, DOI: <https://doi.org/10.1515/hf-2017-0092>
- III Chen, C.; Alén, R.; Lehto, J.; Pakkanen, H. 2016, Combustion behavior of kraft black liquor droplets from hot water pretreated hardwood and softwood chips, *TAPPI Journal* 15(11): 685-691.
- IV Chen, C.; Alén, R.; Lehto, J.; Pakkanen, H. 2016, Combustion properties of birch (*Betula pendula*) black liquors from sulfur-free pulping, *Journal of Wood Chemistry and Technology* 36(6): 401-411.
- V Chen, C.; Alén, R.; Lehto, J.; Pakkanen, H. 2016, Combustion properties of spruce black liquor droplets: Sulfur-free pulping and influence of hot-water pretreatment, *Nordic Pulp and Paper Research Journal* 31(4): 532-540.

The author was responsible for the study concept and literature research, experimental design and execution, data analyses and interpretation, and manuscript preparation in Papers I and II. The manuscripts for Papers III, IV, and V were prepared by the author together with Raimo Alén. Jarmo Louhelainen performed the swelling test in Paper I. Hannu Pakkanen conducted the gel permeation chromatographic (GPC) analyses for the molar mass distribution of lignin in Papers II, III, IV, and V. Joni Lehto carried out most of the chemical pulping and aliphatic carboxylic acids analyses. Esa Lehtimäki made the thermogravimetric (TG) analyses for all the compounds in Paper I. Marja Salo performed other analyses on the aliphatic carboxylic acids. Raimo Alén supervised all studies and gave feedback on the manuscripts.

PREFACE

My journey to Finland started when I got a letter confirming my acceptance to PaPSaT graduate school on 25th October, 2011. Then, Jyväskylä became my second hometown after 5 years of living there. I began my first day at work with playing snow on my way to the office, without any idea of black liquor combustion properties. “Welcome to Finland”, Prof. Raimo Alén shook my hand and said by the printing machine in front of his office. It was a privilege to research on this subject with his guidance and great share of knowledge. I appreciate the opportunity to develop my independence and collaboration skills in this group.

At Soveltavan Kemia Osasto, Arja Mäkelä kindly helped me with different practical issues and introduced me to Finnish language and so on. Marja Salo always helped me with acids analyses and delivered excellent results. It was lovely to listen to her stories in Finnish. Hannu Pakkanen is an amazing partner with proven expertise in chromatography analytics, who is always responsible and responsive to my request for help. Thanks Jarmo Louhelainen for having established a good system for combustion test and some floorball games. Joni Lehto is so nice an office neighbor that I could always knock his door for help. Jukka Pekka Isoaho and Hannu Salo always helped me with all kinds of problems, but I should always start with all kinds of jokes before they agreed to help me. Piia Valto shared a lot of daily life stories that were so culturally educating to me. I have learned a lot from my international fellows Hemanathan Kumar, Maryam Ghalibaf and Saleem Ullah by sharing each other’s stories, unique cultural experiences, and even difficulties. I would like to say “kiitos kaikille” to my nice colleagues of applied chemistry for being together in the past 5-6 years.

The financial support from PaPSaT allowed me to do my doctoral study in Finland. Dr. Elias Retulainen, Dr. Jiri Basta, Ismo Mäkinen, and Prof. Shiyu Fu have offered generous help, and Prof. Raimo Alén’s support was vital. It is so great that we still keep in touch after these years. I would like to thank external reviewers Mika Jarvinen and Keijo Salmenoja for their valuable input to my thesis and Prof. Esa Vakkilainen for agreeing to take the job as my opponent.

It has been lucky to have a close and friendly Chinese community around in Jyväskylä. I’ve had many happy times with them in gatherings, doing sports, short-distance excursions, hiking and picking mushrooms in the forest, spontaneous meet-ups, etc. I am also very happy to have met so many lovely Finns in different social occasions, being friends, someone you know, or even strangers.

Thanks to my parents for being my first best friends. Your constant encouragement and love are sources of my happiness. I am thankful for the enjoyable childhood moments with my brother. I appreciate very much my parents-in-law for being so kind to me. I want to dedicate this thesis to my best friend, sweet loving wife, Li-Tang, who is so considerate, supportive, kind, I am so grateful that another sweet, joyful member (our son) joined us on 18th June, 2015, from whom we get a lot of inspiration, motivation and happiness.

Odense, Denmark 06.11.2017

Chengcong Chen

CONTENTS

ABSTRACT	i
LIST OF PUBLICATIONS.....	ii
PREFACE	iii
CONTENTS	v
ABBREVIATIONS.....	vi
1 INTRODUCTION.....	1
1.1 Kraft process	1
1.1.1 Pulping.....	2
1.1.2 Recovery of cooking chemicals.....	4
1.1.3 Recovery boiler	5
1.2 Combustion of black liquor	6
1.2.1 Black liquor chemical characteristics.....	7
1.2.2 Combustion behavior of black liquor droplet.....	8
1.2.3 Single particle reactors.....	10
1.3 Objectives of the study	12
2 EXPERIMENTAL.....	13
2.1 Raw materials	13
2.2 Kraft and sulfur-free pulping.....	14
2.3 Carbonation of black liquor.....	16
2.4 Droplet combustion	16
2.5 Pyrolysis	16
2.6 Analytical determinations.....	17
2.6.1 Aliphatic carboxylic acids	17
2.6.2 Dissolved lignin.....	17
2.6.3 Carbohydrates.....	18
3 RESULTS AND DISCUSSION.....	19
3.1 Mechanism for the swelling of black liquor droplets	19
3.2 Role of lignin and sodium carbonate on droplet swelling.....	23
3.3 Combustion behavior of kraft and sulfur-free black liquors	29
3.3.1 Influence of HWP on liquor composition.....	29
3.3.2 Combustion behavior of black liquor droplet.....	31
4 CONCLUDING REMARKS.....	34
REFERENCES.....	36

ABBREVIATIONS

α -GISA	α -Glucoisosaccharinic acid
AHQ	Anthrahydroquinone
AQ	Anthraquinone
BB	Boiler bank
BL	Black liquor
DME	Dimethyl ether
FD	Forced draft
FID	Flame-ionized detector
fps	Frames per second
GC	Gas chromatography
GISA	Glucoisosaccharinic acid
GPC	Gel permeation chromatography
HMM	High molar mass
HPLC	High performance liquid chromatography
HWP	Hot-water pretreatment
ID	Induced draft
IS	Internal standard
LMM	Low molar mass
MM	Molar mass
MMD	Molar mass distribution
MMM	Medium molar mass
MS	Mass spectrometry
o.d.	Oven-dry
RB	Recovery boiler
SCAN	Scandinavian Pulp, Paper and Board Testing Committee
SHs	Superheaters
TAPPI	Technical Association for Pulp and Paper Industry
TBA	Tetra- <i>n</i> -butyl ammonium
TG	Thermogravimetric
TMS	Trimethylsilylated
UV-Vis	Ultraviolet-visible

1 INTRODUCTION

A kraft pulp mill is an integrated forest biorefinery (van Heiningen 2006) that converts wood into cellulosic fiber materials that can be used for, for example, paper, board, and dissolving pulp for textile and hygiene products (Kumar and Christopher 2017). It also generates several gaseous, liquid, and solid waste streams that need proper management. This chapter briefly introduces the main kraft pulp mill processes relevant to this study and defines the main research questions investigated.

1.1 Kraft process

A kraft pulp mill normally includes a fiberline that converts wood feedstock into desired pulp products and a chemical recovery cycle that regenerates the inorganic cooking chemicals for pulping and produces heat and power for different mill processes (Fig. 1) (Rydholm 1965). A fiberline consists of a series of chemical and mechanical processes in a strategic sequence (including pulping,

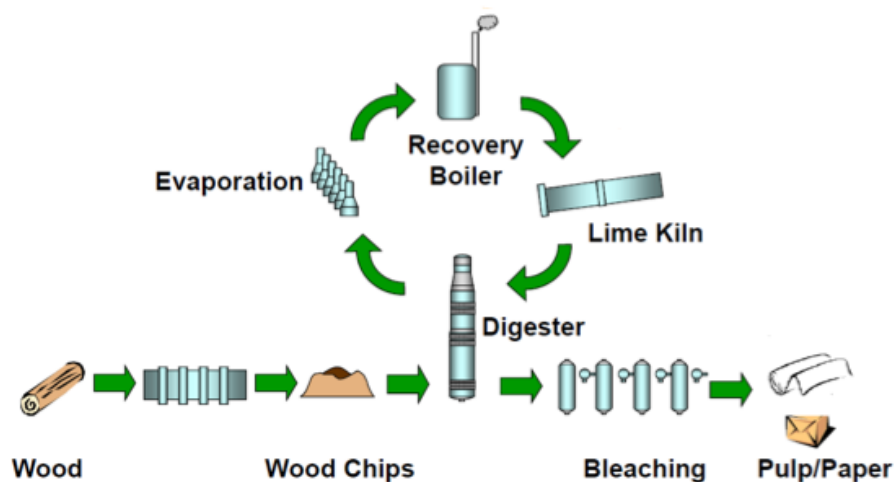


FIGURE 1 Kraft pulp mill main processes (Courtesy of Valmet).

oxygen delignification, and bleaching) to optimize the removal of most of the non-cellulosic materials and minimize the loss of cellulosic materials from fiber. It generates two major streams of waste liquors: the spent cooking liquor (i.e., black liquor, BL) and the bleaching effluent (Rydholm 1965, Sjöström 1993, Sjöström and Alén 1999). The BL enters the chemical recovery system, and the bleaching effluent is treated separately in a wastewater plant. The chemical recovery makes a chemical pulp mill economically viable and environmentally friendly.

Kraft pulping (or sulfate pulping) is the most popular chemical process for the manufacture of chemical pulp. About 130 million tons/year kraft pulp are produced globally, accounting for two-thirds of the world's virgin pulp production and for over 90% of chemical pulp (Tran and Vakkilainen 2007). It treats the feedstock at elevated temperature in a pressurized vessel (digester) with white liquor containing mainly sodium hydroxide (NaOH) and sodium sulfide (Na₂S), which is capable of handling various types of feedstocks and produces strong fibers for papermaking (Fig. 2) (Alén 2000). About 50% of the initial wood feedstock is dissolved in the cooking liquor after pulping. These materials, together with the inorganic cooking chemicals, account for 15-20% of the BL dry solids. Each year, 1.3 billion tons of BL and more than 200 million tons of BL dry solids are produced (Tran and Vakkilainen 2007). However, kraft pulping has an inherent drawback of emitting sulfur-containing odors.

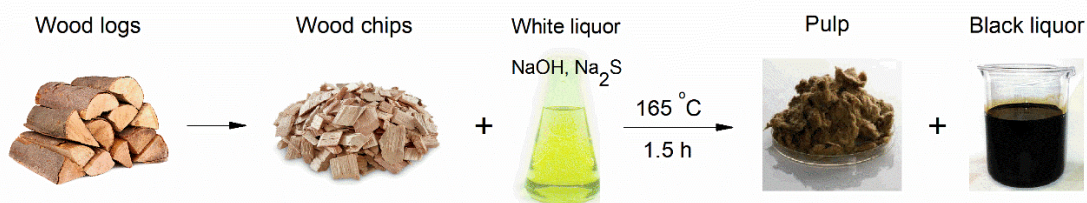


FIGURE 2 Kraft pulping.

1.1.1 Pulping

The primary purpose of pulping is to remove the non-cellulosic “glue-like” lignin holding the fibers together. Removal of lignin is mainly achieved by the cleavage of the aryl alkyl ether structures (>50% of the native lignin linkages) and the increase of the solubility of lignin fragments in the cooking liquor (Sjöström 1993). Under alkaline conditions, the nucleophilic hydroxide anions initiate the formation of a quinone methide and subsequently break the phenolic α - and β -aryl ether bonds, while nonphenolic β -aryl ether bonds are cleaved primarily by the formation of an oxirane intermediate. If sodium sulfide is present (kraft pulping), the even stronger nucleophilic hydrogen sulfide anions greatly facilitate the cleavage of β -aryl ether structures via the formation of a thiirane structure. Sometimes, AQ is added (kraft-AQ pulping), which not only preserves the carbohydrates by oxidizing the reducing end groups, but also aids the dissociation of β -aryl ether linkages with the reduced AQ (i.e., anthrahydroquinone, AHQ). In the case of oxygen delignification, the alkali-

induced reactive oxygen species target only the free phenolic structures of lignin presumably by radical reactions (Rydholm 1965, Adler 1977, Sjöström 1993).

Part of the carbohydrates is unselectively removed during pulping, particularly the hemicelluloses whose chemical structure is amenable to alkaline degradation. For example, at the initial stage of alkaline pulping, the degradation of hemicelluloses could be as much as 40%, and only part of xylan (typical in hardwood) and glucomannan (typical in softwood) maintains initial integrity. The loss of carbohydrates starts with the so-called peeling reaction at the reducing end of the polymer, which generates a monosaccharide-based compound that undergoes a benzilic acid rearrangement to form an isosaccharinic acid. The reaction forms a new reducing end for the polymer that can undergo further peeling reactions. The saccharides lost in the peeling reaction are converted into various hydroxy acids that are neutralized by alkali. The neutralization of acetyl groups and other acids formed during the alkaline degradation of polysaccharides consumes a large proportion of the alkali charged for pulping. The peeling reaction continues until the introduction of a carboxyl group at the reducing end on the carbohydrates (i.e., stopping reaction), preventing the carbohydrates from further decomposition. In the stopping reaction, a diketone intermediate rearranges via a benzilic acid rearrangement for the creation of a carboxylic acid group on the terminal end. However, a hydrolysis reaction can randomly cut the carbohydrate structure, leading to the creation of a new reducing end. Compared to hemicelluloses, the loss of cellulose is minor because the highly crystallized structure prevents itself from hydrolysis and severe peeling-off (Sjöström 1993, Alén 2000).

From a biorefining point of view, many hemicellulose-derived materials are potential feedstock for valuable chemical products (Kamm et al. 2007). It seems promising to integrate a chemical extraction stage, for example, a hot-water or alkali pretreatment (Lehto and Alén 2013, 2015) or others, prior to chemical pulping for recovering part of the hemicelluloses which otherwise ends up in the BL and is burned as low-value fuel (van Heiningen 2006, Tunc and van Heiningen 2008, Agbor et al. 2011, Alén 2011). Hot-water pretreatment (HWP, also known as autohydrolysis or prehydrolysis) has been shown to be capable of extracting certain valuable wood organic constituents, such as hemicelluloses, lignin, and extractives in an environmental-friendly way (Tunc and van Heiningen 2011, Lehto and Alén 2012). It helps to increase the accessibility of cooking chemicals to the wood matrix and influences the delignification behavior during the cooking phase. An ideal strategy for partial extraction of hemicelluloses from feedstock may be reached by optimally fine-tuning the pretreatment and pulping conditions.

Lignin extracted from BL is becoming more and more profitable for other value-added applications. One commercial technology for the separation of lignin is carbonation that introduces a stream of flue gas (CO_2) to the BL in a separate unit by lowering the pH to precipitate part of the lignin (Alén et al. 1979, Tomani 2010), during which Na_2CO_3 is also formed as CO_2 reacts with the residual NaOH in the BL. The precipitated lignin is filtered and washed (Wallmo 2008). And the filtrate is remixed with the main BL stream in the evaporators.

1.1.2 Recovery of cooking chemicals

A significant amount of cooking chemicals is charged for kraft pulping, which should be recovered (Rydholm 1965). This recovery is achieved through the chemical recovery system which includes several major unit operations: the evaporation of BL, the combustion of BL in a recovery boiler (RB), the causticizing of sodium carbonate (Na_2CO_3) to NaOH by $\text{Ca}(\text{OH})_2$, and the regeneration of active lime (CaO from CaCO_3) in a lime kiln (Fig. 3). Weak BL (15-20% dryness) from the cooking and brown stock washing is concentrated in multi-effect evaporators to 65-85% dryness (strong BL), so that it can be burned effectively in the RB. The strong BL is combusted as sprayed droplets and finally, in the bottom of the furnace, it forms a smelt bed consisting of mostly Na_2S and Na_2CO_3 . The smelt is discharged and dissolved in a dissolving tank to form green liquor. This green liquor is sent to the causticizing plant, where CaO ($\text{Ca}(\text{OH})_2$ after dissolution in water) is added to convert Na_2CO_3 into NaOH ($\text{CaO} + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3 = 2\text{NaOH} + \text{CaCO}_3$), while Na_2S passes the process unchanged. The causticized green liquor (now white liquor with mainly Na_2S and NaOH) returns to the digester for cooking. The precipitated lime (CaCO_3) is burned in a lime kiln at a high temperature to regenerate CaO (Adams et al. 1997, Vakkilainen 2005). Therefore, chemical recovery is like the heart of a kraft pulp mill: the BL from the fiberline enters the recovery cycle and returns as white liquor for cooking in the digester.

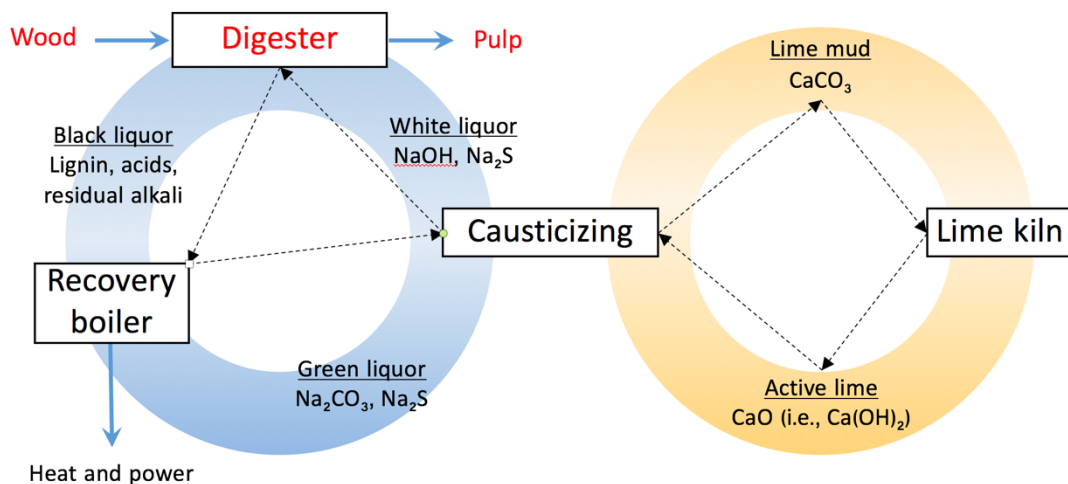


FIGURE 3 Chemical recovery of a kraft pulp mill.

Combustion of BL in the RB not only reclaims the inorganic cooking chemicals as smelt, but also produces superheated steam for heat and power generation. The superheated steam is high in pressure (90-105 bar) and temperature (480-515°C), which can be utilized to generate electricity in steam turbines (Adams et al. 1997, Vakkilainen 2005). Annually, over 200 million tons of BL dry solids are burnt in RBs to recycle about 50 million tons of inorganic cooking chemicals and to produce 700 million tons of superheated steam for power generation. This makes BL the fifth most important fuel worldwide, after coal, oil,

natural gas, and gasoline (Tran and Vakkilainen 2008). Since BL is derived from sustainable fiber feedstock, it is also the most important renewable bio-fuel today, particularly in Finland and Sweden.

1.1.3 Recovery boiler

The combustion of BL in a Tomlinson-type RB became popular since the 1930s. Nowadays, there are more than 1000 RBs operating in the world (Tran and Vakkilainen 2008). The general structure of a modern RB is shown in Fig. 4. In the upper furnace, there are heat exchangers, including a screen, superheaters (SHs), boiler bank (BB), and an economizer. In the middle furnace, there are combustion air inlets and nozzles for droplet spray. In the lower furnace, BL sprays in, combustion air blows, a char bed accumulates at the beginning and keeps at an optimally steady thickness, and a smelt bed forms and drains out of the furnace to the dissolving tank. The furnace is surrounded by pipes wherein water circulates and absorbs heat from combustion. Besides, there are other peripheral systems for the RB to function well, including flue gas air preheaters, fans to introduce combustion air, liquor guns with spray nozzles, auxiliary fuel burners for startup and shutdown and to assist unstable burning, a spout for smelt to run into the dissolving tank, a sootblower to clean the fouling from heat exchangers, and an electrostatic precipitator to remove particulates from the flue gas leaving the RB (Vakkilainen 2005).

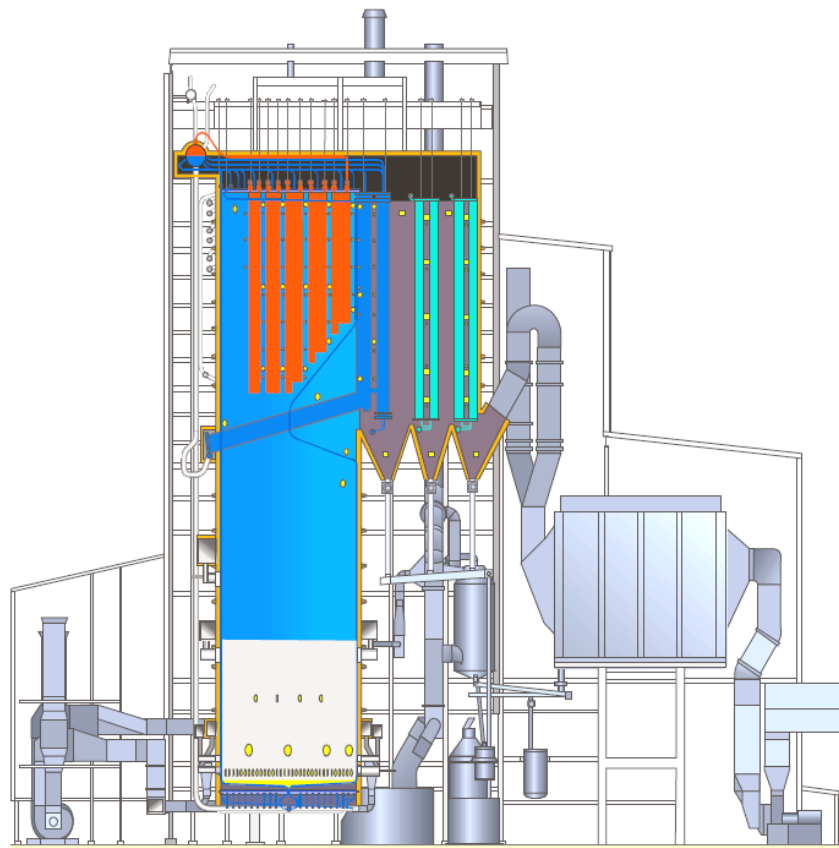


FIGURE 4 Recovery boiler (Courtesy of Valmet).

The RB is a chemical reactor that converts the BL organics into energy and transforms the inorganic chemicals into mainly Na_2CO_3 and Na_2S . Combustion of BL occurs in the lower furnace section. It requires the BL and combustion air to be intermixed thoroughly through the liquor sprays and the forced draft (FD) air system, while the upper furnace provides room and residence time for complete combustion. An induced draft (ID) fan draws the hot flue gas upwards through the SHs, BB, and economizer. The reduction of Na_2SO_4 to Na_2S in the char bed requires a reducing (oxygen deficient) environment, but an appropriate amount of oxygen is needed for the combustion of the gases to provide heat for reduction. However, it is inevitable to lose some Na_2SO_4 in flue gas, and there is incomplete reduction of Na_2SO_4 in the char bed. The extent of reducing sulfate to sulfide is measured as reduction efficiency (typically over 95%). The molten smelt containing mostly Na_2CO_3 and Na_2S is drained from the bottom through spouts down to the dissolving tank to form green liquor (Adams et al. 1997, Vakkilainen 2005).

The RB is also a steam boiler. Generation of superheated steam starts with feedwater entering the economizer for heat-up near to its boiling point. This heated-up water continues to the steam drum, and through the downcomers it is distributed to the BB and the waterwall to generate steam in the water flow. The steam-water mixture runs through the risertubes back to the steam drum where steam and water are separated. The saturated steam is further heated to a supercritical condition in the SHs. Modern RB generates high value steam with a temperature of up to 515°C and pressure up to 135 bar (most mills operate around 100 bar), which can be used to produce electricity in steam turbines. Lower pressure steams are also extracted from the turbines for uses in various mill processes, such as fiberline, evaporation plant, pulp drying, among others (Vakkilainen 2005). The generated electricity is used in, for instance, pump, lightning, ventilation, and motors.

It should be mentioned that new technologies for utilizing BL are emerging. Gasification of BL is being piloted to extract even more heat from the BL organics and to lower the size and cost of the equipment (Demirbaş 2002, Carlsson et al. 2010, Pettersson and Harvey 2010, Wiinikka et al. 2010, 2012). Besides, refining BL by various techniques of separation, thermal conversion, and biochemical modification are being researched extensively. The BL organics can be valorized into value-added fuels, chemicals, and biomaterials, for example, tall oil-based bio-diesel (Kumar 2016), dimethyl ether (DME) as a transport fuel (Naqvi et al. 2010a,b), turpentine, lignin (Stewart 2008, de Wild et al. 2009), and aliphatic carboxylic acids.

1.2 Combustion of black liquor

BL is a special fuel because it contains a substantial amount of inorganics and water, apart from the wood-based organics. It is combusted in a RB as sprayed droplets (through nozzles). Both the liquor and spraying properties and furnace operating conditions have a significant influence on BL combustion behavior.

1.2.1 Black liquor chemical characteristics

It is known that during alkaline pulping, in addition to a significant degradation and dissolution of lignin, a substantial amount of polysaccharides (mainly hemicelluloses) is converted into numerous aliphatic carboxylic acids via various alkali-catalyzed degradation reactions (Sjöström 1993, Alén 2000, 2011). BL is a complex mixture of numerous organic and inorganic compounds dissolved in water (Fig. 5). The organic materials include lignin, carbohydrate-derived products, and a few extractives. The inorganic compounds are residual cooking chemicals (NaOH and Na₂S) and accumulated process impurities, for example, Na₂SO₄, Na₂S₂O₃, Na₂CO₃, and NaCl (Sjöström and Alén 1999).

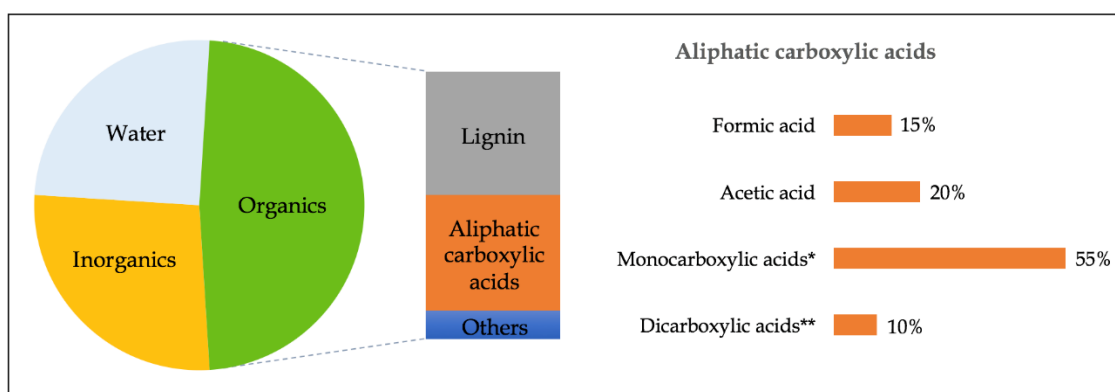


FIGURE 5 Composition of a concentrated BL droplet (75% dryness).

- * For example, glycolic acid, lactic acid, glyceric acid, 3-hydroxypropanoic acid, 2-C-methylglyceric acid, 2-hydroxybutanoic acid, 4-hydroxybutanoic acid, 2-deoxy-tetronic acid, 3-deoxy-tetronic acid, 2-hydroxy-2-methylbutanoic acid, 2-hydroxypentenoic acid, 3,4-dideoxy-pentonic acid, 3-deoxy-pentonic acid, xyloisosaccharinic acid, anhydroisosaccharinic acid, 3,6-dideoxy-hexonic acid, 3-deoxy-hexonic acid, glucoisosaccharinic acid.
- ** For example, oxalic acid, succinic acid, malic acid, methylsuccinic acid, 2-hydroxyglutaric acid, 3-deoxy-pentonic acid, 2-hydroxyadipic acid, 2,5-dihydroxyadipic acid, glucoisosaccharinaric acid.

Lignin is a class of cross-linked phenylpropanes having a range of molar mass distribution (MMD). Lignin is usually bound with carbohydrates, known as the lignin-carbohydrates complex. Hardwood lignin typically contains more carbohydrates and a higher amount of methoxyl groups in the phenylpropane structures than softwood lignin (Sjöström 1993). The chemical structure of dissolved lignin in BL is different from its native form in the fiber cell wall. The net heating value of BL is about 13 MJ/kg dry solids, which corresponds to about 3.5 kg superheated steam. Pure lignin itself has a heating value of about 24 MJ/kg dry solids, much higher than that of the carbohydrates fraction.

Carbohydrate-derived products include a series of aliphatic carboxylic acids containing one to six carbons and polysaccharides that are formed via hydrolysis, peeling, and oxidative reactions under alkaline condition. Hemicellu-

loses are the main source of these substances, because they are more amenable than the cellulose to alkali-catalyzed degradation due to its amorphous chemical structure and lower degree of polymerization. The aliphatic carboxylic acids are volatile formic and acetic acids and non-volatile hydroxy carboxylic acids. Non-wood BLs contain a substantial amount of polysaccharides (Alén 2011).

Extractives (about 5% wood dry mass) are hydrolyzed by alkali during the pulping process. The amount of extractives in BL is minor compared with other organics, but they are the most recovered valuable chemicals so far, for example, tall oil (including resin acids, fatty acids and alcohols, and sterols) and turpentine (including α -pinene, β -pinene, and 3-carene) (Sjöström 1993).

1.2.2 Combustion behavior of black liquor droplet

The combustion of BL occurs at the lower part of the RB (Fig. 6). It has been stated that knowledge about BL in-flight combustion behavior from nozzle to char bed is vital to achieving proper combustion and char bed burning control (Hupa 2014). The combustion behavior of BL droplet refers to the three sequential burning stages (i.e., drying, pyrolysis, and char burning) and the tendency to swell during the pyrolysis stage (Hupa et al. 1987). With a high-speed camera, the combustion process of a BL droplet can be observed in detail, and the time durations of different combustion stages and the degree of volumetric swelling can be measured quantitatively. The drying stage lasts on average 1–2 seconds with a droplet temperature of 150–300°C, during which the residual water of the droplet evaporates rapidly and some organics may have started decomposition already. At this stage the droplet expands slightly, with an expansion factor of about 1.5 in diameter. The appearance of a bright yellow flame marks the beginning of the pyrolysis stage. The flame spreads rapidly around the droplet, indicating the massive decomposition of the organic matters and the combustion of volatiles. It lasts 0.5–2 seconds for a typical liquor droplet size, and the temperature rises rapidly until it reaches the ambient temperature. At this period, the droplet swells significantly to a degree of more than 30 folds of its original size, appearing in an irregular spherical shape (Fig. 7), reaching its maximum swelling near the end of the pyrolysis stage, which is indicated by the disappearance of the bright yellow flame.

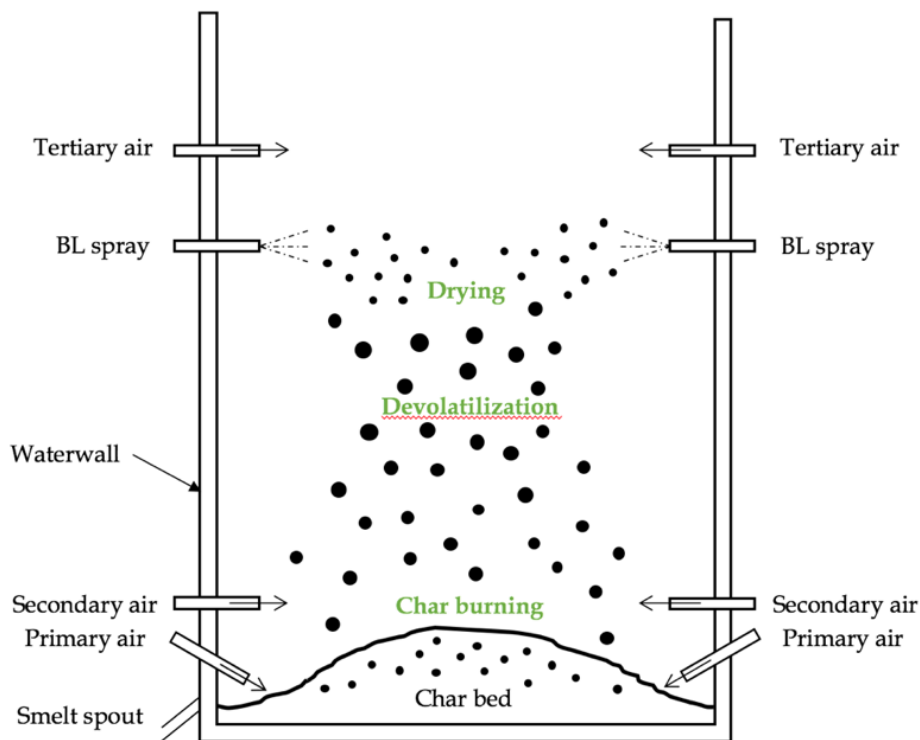


FIGURE 6 RB lower furnace processes.

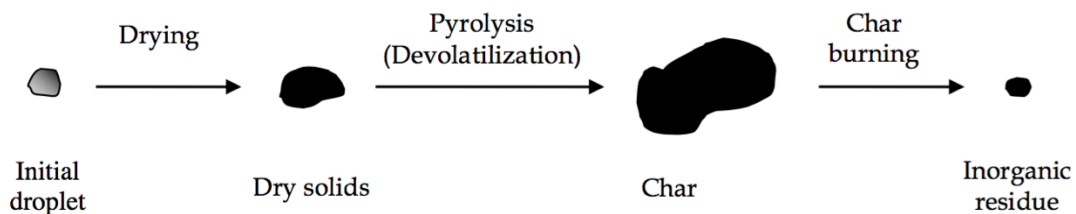


FIGURE 7 Droplet swelling process.

The char burning stage occurs during flight and at the char bed, which involves chemical interactions among, for example, the organic carbon, oxygen, steam, carbon oxides, nitrogen, sodium, and sulfur. In practice, chloride, potassium, and other non-process elements also participate in the char burning processes (Adams et al. 1997). The swollen droplet particle burns at its surface in contact with oxygen (O_2 , CO_2 , and H_2O are all oxygen sources), and it shrinks as the organic carbon burns away. The temperature of the droplet increases much higher than the ambient temperature. There is no visible flame but a glow in this period. The char burning stage is crucial for the reduction of sulfur (from sulfate to sulfide) through the oxidation of carbon. At the end of this stage, the droplet collapses to a molten bead consisting of mainly Na_2CO_3 and Na_2S . However, the presence of oxygen will undesirably oxidize the newly formed Na_2S back to Na_2SO_4 . Thus, it is of practical importance that the droplet reaches the char bed before the char burning stage ends and that the char bed should

maintain a certain thickness to prevent the oxidation of sulfide back to sulfate. However, it is also not ideal for the droplets to reach the char bed wet (e.g., still at the early pyrolysis stage) (Adams et al. 1997).

Swelling at the pyrolysis stage is a typical phenomenon for the BL droplet during combustion. The volumetric expansion of the droplet is of practical significance to its combustibility in the RB (Baklien 1960, Oye et al. 1977, Miller and Clay 1986, Frederick et al. 1991). Due to the aerodynamic environment (i.e., upward flue gas flow), the swollen BL droplet changes its flight path when flying from liquor gun to the char bed with an initial velocity of, for example, 15 m/s tilted 10-30° downwards. Highly swollen droplets tend to be entrained by flue gas, leading to increased fouling of the heat exchangers in upper furnace and increased load for the ESP; poor swollen droplets tend to reach the char bed too early at the drying or early pyrolysis stage (Frederick and Hupa 1997).

The mechanism for the swelling process has long been a puzzle (Baklien 1960, Oye et al. 1977, Hupa et al. 1987, Milanova 1988, Miller et al. 1989, Alén et al. 1995, Maček 1999). Lignin and sugar acids (i.e., aliphatic carboxylic acids) have been found to be two indispensable components for swelling, and other compositions (i.e., polysaccharides, extractives, and inorganics) influence the degree of swelling (Milanova 1988, Miller et al. 1989, Alén 1994). Furnace temperature, gas environment, and pressure are external factors governing the degree of swelling (Hupa et al. 1987, Frederick and Hupa 1994, Whitty et al. 2008). Higher temperature, oxygen concentration, and pressure all lead to decreased swelling. The most important aspect for the swelling of a BL droplet is the formation of a plastic state during pyrolysis (Baklien 1960, Hupa et al. 1987, Milanova 1988, Miller et al. 1989, Alén et al. 1995). Understanding the process of forming a plastic state is key to unraveling the mechanism for swelling.

1.2.3 Single particle reactors

It is difficult to study the combustion behavior of BL droplets on-site because of the harsh furnace condition of an operating RB. Several laboratory-scale single droplet techniques have been developed for researching the combustion behavior of BL droplets. The first documented application of the single droplet technique dates back to the 1960s, which was used to study the combustion behavior of spent sulfite liquors (Monaghan and Siddall 1963, Huldén 1968), and that for the study of kraft liquor was first reported during the 1980s (Hupa et al. 1987). The single droplet technique manipulates the furnace conditions analogous to the environment of a real RB and uses a camera to record the visual appearance of BL droplets during combustion. In recent years, the single droplet concept has been better equipped and used to study the combustion or gasification behavior of BL droplets. Some popular apparatuses are described as below.

The single droplet muffle furnace is a laboratory furnace operating under atmospheric pressure (Fig. 8). The droplet sample attached to a platinum wire is inserted through an opening from atop, and a quartz side window allows the observation of the burning process with a camera. There is a small air channel at the back of the furnace to allow natural air-flow so as to keep an atmospheric pressure. The stagnant air environment in the muffle furnace is different from

the aerodynamic environment with flue gas flowing upwards in a real RB. However, this is still a suitable technique for identifying and measuring the different combustion stages and the specific maximum swelling of a BL droplet.

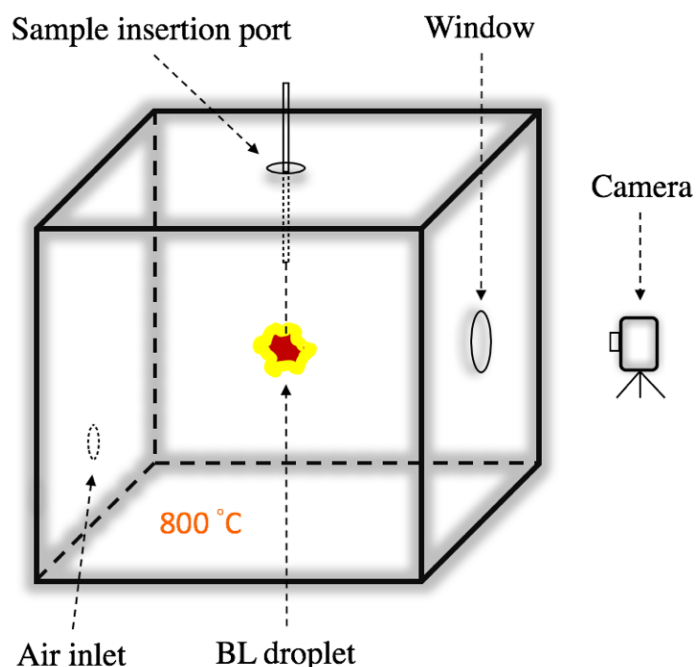


FIGURE 8 Model of the muffle furnace for combustion tests.

Several other single particle reactors have been used to study the pyrolysis and gasification behavior of BL dry solids (Whitty et al. 1997): i) The single droplet tube reactor is designed to pyrolyze the sample in an inert atmospheric condition. A quartz tube is positioned vertically and heated inside a furnace, and the sample is protected from heating before and after pyrolysis. It is a pyrolysis apparatus for determining volatile yield and volume of swelling. The result obtained is more relevant to the gasification of BL solids in an inert atmosphere. ii) The pressurized grid heater simulates the pyrolysis condition under elevated pressure. Heating is achieved by the application of an electric current through a fine wire net. The pressure, heating rate, final temperature, and holding time can all be controlled delicately. Volatiles yield and the degree of swelling can also be determined. iii) The pressurized TG reactor uses a microbalance to record the mass loss process during the pyrolysis and gasification of BL dry solids, which is able to study the reactivity of the pyrolyzed char and to measure the volatiles yield. Being able to operate at a pressurized condition is an advantage of this apparatus for the study of the pressurized gasification behavior of BL dry solids, which can be related to an industrial-scale gasifier.

1.3 Objectives of the study

The main objectives of this study were to answer the following questions:

1. What is the mechanism for BL droplet swelling during the devolatilization stage of combustion? (Paper I)
2. How does partial removal of lignin by carbonation of the BL extracted from the evaporation stream in a separate unit affect the swelling behavior of the remixed (carbonated and noncarbonated) BL droplets? (Paper II)
3. How does HWP of feedstock prior to chemical pulping affect the composition and combustion behavior of BL droplets? And how does sulfur-free BLs behave differently from kraft BLs (Papers III, IV, and V)

2 EXPERIMENTAL

2.1 Raw materials

The sodium salts of the BL aliphatic carboxylic acids, including formate, acetate, glycolate, lactate, 2-hydroxybutyrate, disodium malate, disodium oxalate, and disodium succinate, and wood-based polymers, such as lignin, lignosulfonates, xylan, and cellulose, were used for the pyrolysis studies. Different from these commercial model substances, the sodium salt of α -glucoisaccharinic acid, 3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone, was prepared by the neutralization (to pH 7 with 0.1M NaOH solution) of α -GISA obtained from lactose (Whistler & BeMiller 1963) (Paper I).

Three lignin fractions of different molar masses (MMs) were prepared by membrane ultrafiltration of an industrial birch BL using three membrane cut-offs: 1 kDa, 5 kDa, and 10 kDa. The fraction retained between the 1-5 kDa range was noted as low molar mass (LMM) lignin, between the 5-10 kDa as medium molar mass (MMM) lignin, and above the 10 kDa as high molar mass (HMM) lignin. Detailed process for the ultrafiltration refers to Paper II.

Softwood spruce (*Picea abies*) and hardwood birch (*Betula pendula*) in the form of either chips (Paper III) or sawdust (Papers IV and V) were the main feedstocks for the preparation of BLs. The HWP of wood chips was conducted at the University of Jyväskylä, while that of the sawdust was performed at LUKE and VTT. The conditions for the HWP are given in Tables 1 and 2, and the detailed procedures are described in Papers III, IV, and V.

TABLE 1 Pretreatment of chips (Paper III)

Parameter	Birch	Spruce
Temperature, °C	150	150
Treatment duration, min	60	60
Liquor-to-wood ratio, L/kg	4.5	4.5
Solid yield of HWP, %	83.0	90.7

TABLE 2 Pretreatment of sawdust (Papers IV and V)

Parameter	Birch	Spruce (batch)	Spruce (continuous)
Temperature, °C	170	160 + 170	180
Treatment duration, min	38	40 + 60	32
Liquor-to-wood ratio, L/kg	5	5	5
Solid yield of HWP, %	71.9	80.0	75.5

2.2 Kraft and sulfur-free pulping

Most BLs used in this study were prepared by kraft and sulfur-free pulping (soda-AQ and O₂-NaOH pulping) of the chips and sawdust feedstocks at the University of Jyväskylä with the same laboratory-scale autoclaves applied to the HWP of wood chips. The chips were cooked employing a kraft process, and the sawdust was cooked with all three different methods. The cooking conditions are shown in Tables 3 and 4. Pulp yields were calculated on the o.d. (oven dried) basis of the feedstock and pulp.

TABLE 3 Kraft cooking conditions for birch (B) and spruce (S) chips (Paper III)

Parameter	B65	HWP+B65	S85	HWP+S85
Effective alkali as NaOH, %	18	18	19	19
Sulfidity, %	35	35	35	35
Liquor-to-wood ratio, L/kg	4.5	4.5	4.5	4.5
Max. cooking temperature, °C	162	162	170	170
Cooking time, min	65	65	85	85
H factor	600	600	1,500	1,500
Pulping yield, %	55.6	49.8	51.2	48.0
Residual alkali, g/L	6.0	3.9	9.3	9.5

B65 refers to birch BL cooked for 65 min and S85 refers to spruce cooked for 85 min.

TABLE 4 Cooking conditions for birch (B) and spruce (S) sawdust (Papers IV and V)

Parameter	Soda-AQ	O ₂ -NaOH	Kraft
Effective alkali as NaOH, %	19 (B), 20 (S)	19	19
Sulfidity, %	-	-	35
AQ dose, %	0.1	-	-
Liquor-to-wood ratio, L/kg	5	5	5
Max. cooking temperature, °C	170	170	160
Cooking time, min	30, 60, 90, 120, and 150		

TABLE 5 Cooking yields for sawdust (mass % of the o.d. feedstock) (Papers IV and V)

Cooking time (min)	Soda-AQ						O ₂ -NaOH*						Kraft							
	Birch		Spruce		Birch		Spruce		Birch		Spruce		Birch		Spruce		Birch		Spruce	
	HWP	Ref	HWP-B	Ref	HWP	Ref	HWP-C	Ref	HWP	Ref	HWP	Ref	HWP	Ref	HWP	Ref	HWP	Ref	HWP-B	Ref
30	55.5	54.2	48.8	60.2	59.7	59.5	56.2	67.9	54.4	55.5	54.4	55.5	54.4	55.5	48.2	63.3	54.4	55.5	48.2	63.3
60	53.0	49.7	43.2	53.7	54.7	56.8	53.1	65.3	51.7	52.7	51.7	52.7	51.7	52.7	44.8	57.7	51.7	52.7	44.8	57.7
90	50.7	49.3	39.6	49.9	52.4	55.4	50.1	60.3	50.9	49.6	50.9	49.6	50.9	49.6	41.1	54.3	50.9	49.6	41.1	54.3
120	51.4	50.8	38.0	50.4	52.3	54.1	48.2	58.3	51.6	50.2	51.6	50.2	51.6	50.2	44.1	52.5	51.6	50.2	44.1	52.5
150	46.2	51.0	36.2	48.4	50.0	51.2	46.3	57.4	50.2	46.8	50.2	46.8	50.2	46.8	38.1	51.8	50.2	46.8	38.1	51.8

HWP refers to hot-water pretreatment and Ref to untreated feedstock.

HWP-B and HWP-C refer to hot-water pretreatment conducted in a batch process and a continuous process, respectively.

* Data are based on (Lehto et al. 2015).

2.3 Carbonation of black liquor

The partial removal of lignin from BL was carried out by carbonation using a pure CO₂ gas stream to bubble through the liquor until it reached the target pH values, and the precipitated lignin was subsequently removed by centrifugation. The progressive separation of lignin was conducted with an industrial birch BL by lowering the pH (initial value approximately 13) to different levels: 12, 11.5, 11, 10.5, 10, and 9 (Paper II).

2.4 Droplet combustion

Weak BLs (dryness ~15%) were concentrated to a dryness of typically 50-75% so that the droplet was viscous enough to be attached and held on a platinum wire, which was performed by evaporation under reduced pressure at 40°C with a laboratory Rotavapor. After evaporation, the flask containing the concentrated BL was filled with N₂ and stored in a cold room at 4°C. The BL dry solids content was determined according to TAPPI T650 om-09.

15-20 strong BL droplets approximately 9 mg in mass were combusted in a laboratory furnace at 800°C in stagnant air. The droplets were formed with a thin glass rod and were held on a platinum wire that is hang on a hook and mounted on a glass tube. The sample was inserted carefully into the preheated furnace from a small hole atop (Fig. 8). The droplet combustion process was filmed using a frequency of 50 fps (frames per second). Video editing software Virtualdub was used to obtain the pyrolysis and char burning times (s/mg) from the films. The swollen BL droplet was approximated as an ideal sphere so that the specific maximum swelling could be calculated as $S_{\max} = \frac{4}{3}A \sqrt{\frac{A}{\pi}}/m$, cm³/g, where A is the sectional area of the swollen particle measured from a selected frame of the video recording with software ImageJ and m is the dry solids of the droplet. The results were averaged from the 15-20 individual tests.

2.5 Pyrolysis

There were two pyrolysis experiments conducted with the BL model substances and the salt-polymer mixtures: (i) the non-oxidative pyrolysis with a TG device and (ii) the atmospheric pyrolysis with a laboratory furnace (Paper I). Some relatively abundant aliphatic carboxylates and wood-based polymers (see 2.1 Raw materials) were selected as model substances for the pyrolysis studies. In the TG analyses, the specimen (approximately 10 mg) was placed on a platinum crucible and pyrolyzed under an inert atmosphere (heating rate of 5°C/min,

maximum temperature of 700°C, and N₂ flow rate of 45 mL/min). Both the sample's mass loss and heat flow status were measured simultaneously, and the melting point was observed where heat was significantly absorbed without losing mass at the time. The moisture of the sample was removed by holding the analyzer at 110°C for 10 min. After each analysis the platinum crucible was carefully washed with concentrated HNO₃ solution and then calcined in a high-temperature butane-propane flame to remove any char residue. Char yield was calculated as the ratio of pyrolysis solid residue to initial dry mass of the sample, expressed as a percentage (Eq. 1), and the volatiles yield was the corresponding gaseous proportion released during pyrolysis (Eq. 2).

$$\text{Char yield} = \frac{\text{solid residue}}{\text{initial dry mass}} \times \% \quad (1)$$

$$\text{Volatiles yield} = \frac{\text{volatiles}}{\text{initial dry mass}} \times \% = 1 - \text{char yield} \quad (2)$$

The atmospheric pyrolysis was performed at 500°C in stagnant air. Each sample was placed on a porcelain crucible and heated for five minutes. 11-20 mg of acetate or NaOH and the polymer were mixed in a mass ratio of 1:1, forming eight salt-polymer composites: acetate-lignin, acetate-lignosulfonates, acetate-xylan, acetate-cellulose, NaOH-lignin, NaOH-lignosulfonates, NaOH-xylan, and NaOH-cellulose. A few drops of deionized water were added to the composite to enable homogeneous mixing while stirring with a tiny glass rod. Pictures were taken for the solid residues after pyrolysis, with a reference object of 13 mm in diameter alongside it.

2.6 Analytical determinations

2.6.1 Aliphatic carboxylic acids

Volatile acids (formic and acetic acids) were determined as their benzyl esters by gas chromatography (GC) equipped with a flame ionization detector (FID). In this analysis, the sodium salts of formic and acetic acids were liberated to their acid form, converted into tetra-*n*-butyl ammonium (TBA) salts, and then esterified to benzyl esters prior to GC/FID (Alén et al. 1985).

Hydroxy acids (mono- and dicarboxylic acids) were identified by GC equipped with a mass selective detector (MSD) and quantitatively determined by GC as their per(trimethylsilyl)ated (TMS) derivatives. This method involved the conversion of the sodium salts of these acids into their ammonium salts, which were then per(trimethylsilyl)ated prior to GC (Alén et al. 1984).

2.6.2 Dissolved lignin

After dilution with 0.1 M aqueous NaOH, the content of dissolved lignin in BL was estimated by a UV-Vis light spectrometry at 280 nm (Alén and Hartus 1988). A GPC system (a Waters HPLC equipped with a Superdex 75 gel column

using 0.1 M aqueous NaOH as the eluent) was applied to determine the MMD of lignin (Pakkanen and Alén 2012).

2.6.3 Carbohydrates

Acid hydrolysis was performed according to TAPPI T 249 cm-00, and the resulting monosaccharides were analyzed as per(trimethylsilyl)ated derivatives using a GC/FID system. Xylitol served as an internal standard (IS). For each monosaccharide, an IS was calibrated based on a separate run with the corresponding model monosaccharide: arabinose, xylose, galactose, glucose, and mannose. It was then possible to perform the peak identification and obtain the mass-based response factor between each monosaccharide and the corresponding IS (Paper IV).

3 RESULTS AND DISCUSSION

3.1 Mechanism for the swelling of black liquor droplets

The TG behavior of the BL model substances, including the aliphatic carboxylates and wood-based polymers, showed that most monocarboxylates and some dicarboxylates underwent a melting stage prior to decomposition (Fig. 9), and the rest of the substances studied decomposed without undergoing a melting stage, most of which were polymers. Therefore, the model substances were

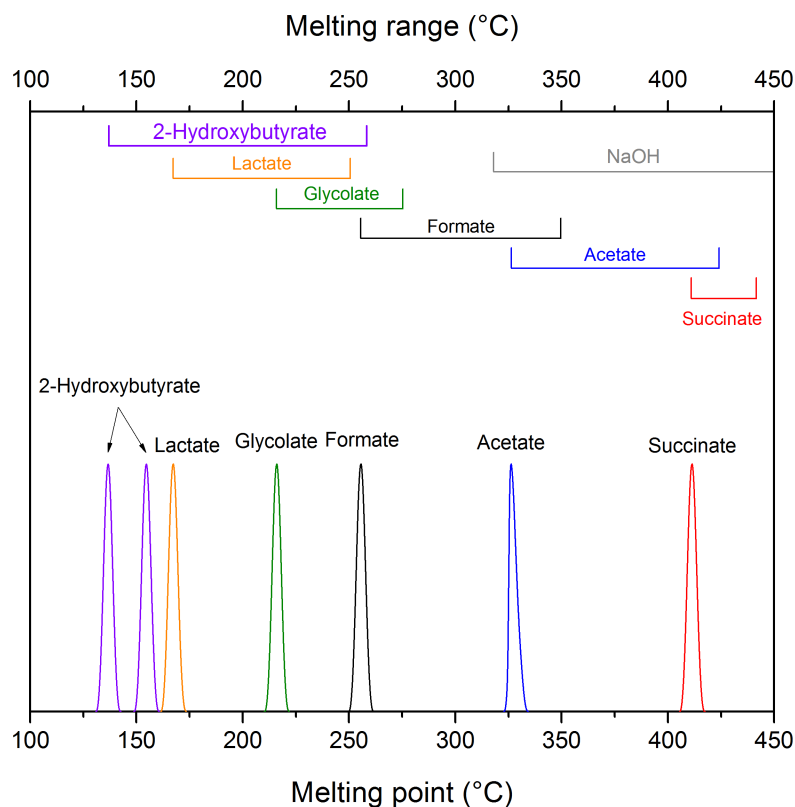


FIGURE 9 Melting point and overall melting range of sodium carboxylates and NaOH.

divided into two groups of substances: melting substances (i.e., formate, acetate, glycolate, lactate, 2-hydroxybutyrate, and succinate) and non-melting substances (malate, oxalate, and polymers). In fact, there should be numerous other carboxylic acids (sodium salts) in BL that belong to the group of melting substances, while others belong to the non-melting substances. The decomposition (mass loss) behavior of these substances was given in Figs. 10 and 11, and most of the substances degraded between 200-500°C.

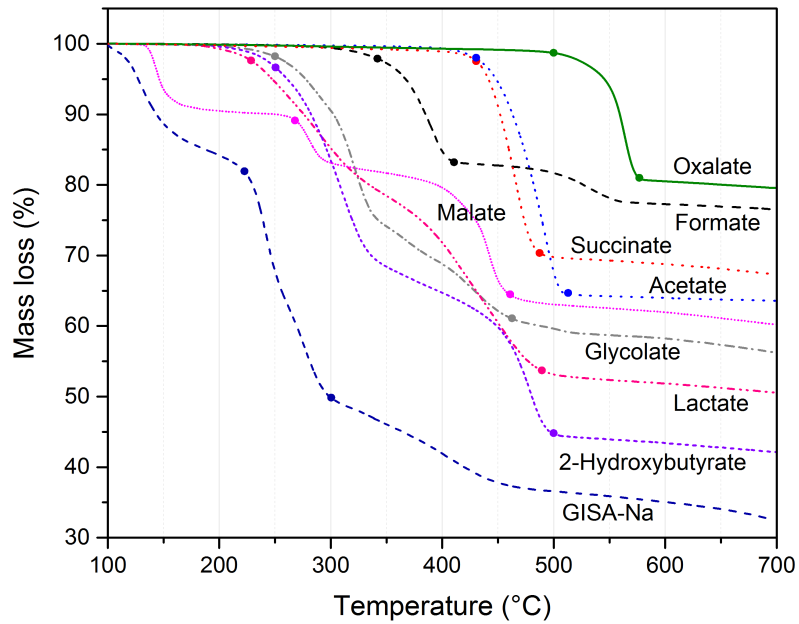


FIGURE 10 Combined decomposition of sodium carboxylates.

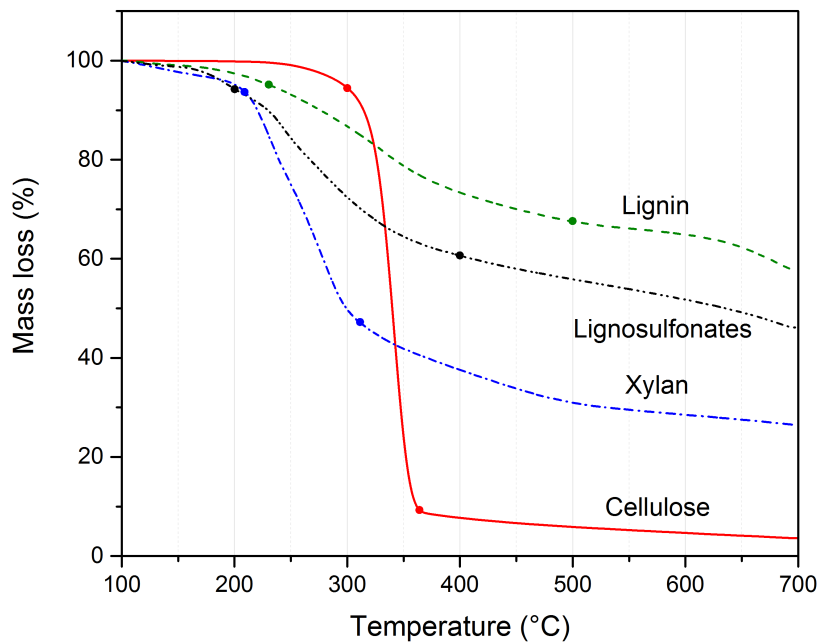


FIGURE 11 TG analysis of wood-based polymers.

It was postulated that melting of an array of carboxylates forming a liquid state would induce the development of a plastic state for the BL mass. To prove this hypothesis, the pyrolysis experiment was performed with individual polymer and salt-polymer mixtures to see if: (i) an addition of melting salt would induce the formation of a plastic state and (ii) the mixture of the melting carboxylate and the polymer would produce significant swelling. It was demonstrated that none of the polymer (lignin, lignosulfonates, xylan, and cellulose) swelled individually, but all the salt-polymer mixtures swelled significantly to a degree comparable to typical BL droplets (Fig. 12). This proved the hypothesis that the formation of a plastic state is induced by the melting of salts. NaOH was used because it is an abundant melting salt in BL and has a melting point close to that of sodium acetate.

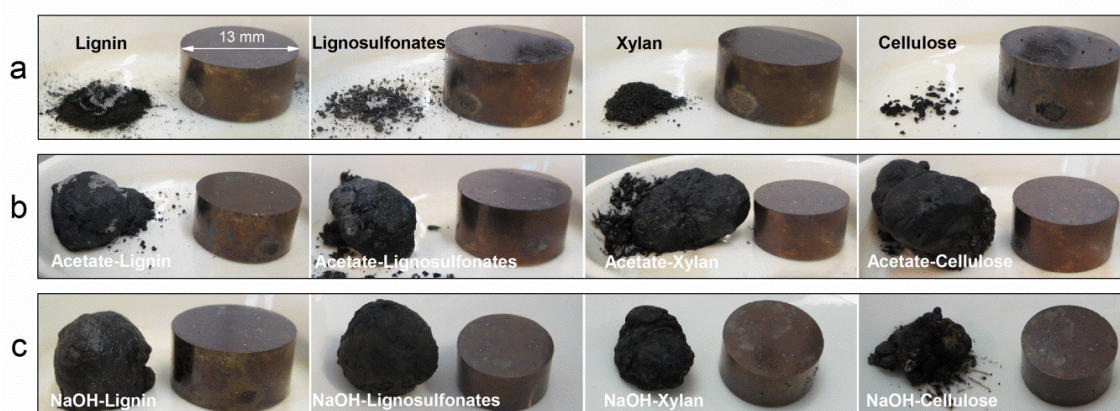


FIGURE 12 Pyrolysis of salt-polymer mixtures at 500°C in stagnant air for 5 minutes.

Considering both the melting ranges (the salt was at a liquid state, Fig. 9) and decomposition ranges (losing mass most rapidly, Figs. 10 and 11) for all the studied substances, it depicted the pyrolysis behavior of a synthetic BL. An array of sodium carboxylates as well as NaOH melted and decomposed consecutively and concurrently, creating the plastic state for the BL mass. Volatiles were needed for swelling at this state, and they were provided by the decomposition of the polymers and the aliphatic carboxylates (Figs. 13 and 14). The decomposition of lignin (230–500°C) and carbohydrates (e.g., xylan 220–450°C) occurred in a wider temperature range that covered the melting range for most melting salts (Fig. 11). NaOH (melting point of about 323°C) was the only BL inorganic salt that participated in the formation of the plastic state, while other inorganics were so high in melting point (e.g., Na_2S 1172°C, Na_2CO_3 856°C, and Na_2SO_4 884°C, see Table 6) that they principally did not melt below 800°C.

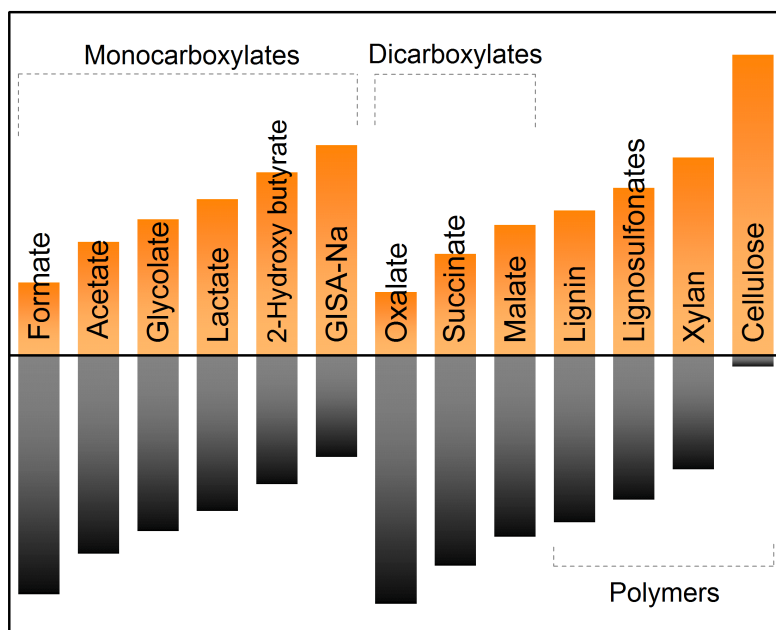


FIGURE 13 Proportion of volatiles (in orange) and char (in black) upon pyrolysis. TG analysis: N_2 45 mL/min, $5^\circ C/min$, $700^\circ C$.

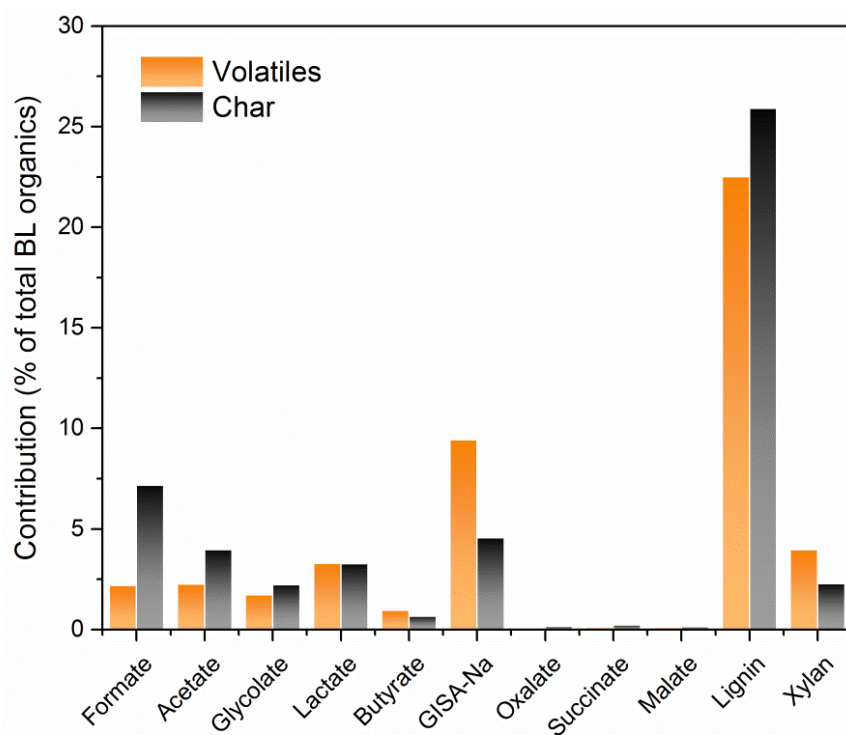


FIGURE 14 Estimated contributions of sodium carboxylates, lignin, and xylan to volatiles and char formation during pyrolysis of a hardwood BL droplet.

TABLE 5 Examples of the inorganic compounds in pine kraft BL

Composition	Amount (%)	Melting point (°C)
NaOH	6	323
Na ₂ S	17	1172
Na ₂ SO ₄	12	884
Na ₂ S ₂ O ₃	14	decomposes
Na ₂ SO ₃	7	911
Na ₂ CO ₃	32	856
Others	12	

Three basic processes are involved in the swelling of BL droplets: (i) the creation of a plastic state through the melting of an array of aliphatic carboxylates and NaOH over 230-500°C; (ii) the production of volatiles by the decomposition of lignin and other organics; and (iii) the formation of a rigid char surface with the fixed carbon mainly from pyrolysis of lignin. This newly derived mechanism was capable of explaining different swelling phenomena observed previously (Paper I). For example, softwood BLs often swell less than hardwood BLs (Noopila et al. 1991); acid or neutral sulfite liquor does not swell (Hupa et al. 1987); the lignin-sugar acids mixture with a ratio of 1:1 swell the most (Miller et al. 1989); higher temperature and oxygen concentration in air result in lower swelling (Frederick and Hupa 1994); acidification of a kraft liquor from its pH 13 down to 2 gradually deletes the swelling tendency (Hupa et al. 1987); and heat treatment of BL increases swelling (Louhelainen 2003).

3.2 Role of lignin and sodium carbonate on droplet swelling

The remixed BL is a lignin-lean BL with relatively lower lignin content than the original BL, depending on how much lignin is to be separated (Fig. 15). Paper II

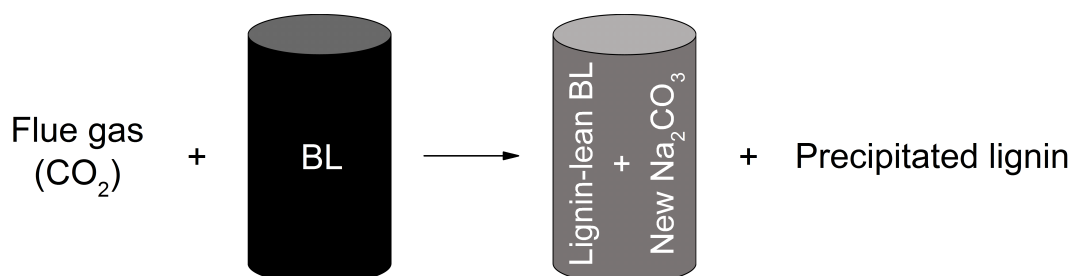


FIGURE 15 Carbonation of BL using flue gas (Paper II).

discusses the compositional factors that affect the swelling behavior of lignin-lean BL. For the hardwood lignin the threshold for precipitation was pH 11, and

that for the softwood lignin was pH 11.5, after which lignin started to precipitate rapidly (Fig. 16). The general chemical characteristic of the removed lignin was further analyzed directly and indirectly with respect to their MMD and carbohydrate content. The MMD of the carbonated BLs at different pH levels showed that the higher MM lignin tended to precipitate easier than the lower MM lignin during carbonation (Fig. 17). Table 7 calculated the changes in the different MM ranges of the hardwood lignin as an example, showing that the proportion of the higher MM lignin (>10 kDa) reduced significantly (from 43% down to 20%) while the relative proportion of other lower MM fractions (i.e., <10000 Da) slightly increased (by 4-14%). This confirmed that the separated lignin at different pH levels was predominantly the higher MM lignin. Analysis of the lignin fractions fractionated from the same hardwood BL found that the HMM lignin contained more carbohydrates than other fractions. Particularly, the hardwood lignin contained substantially more carbohydrates than the softwood lignin, except the LMM fraction which contained hardly any carbohydrates (Fig. 18).

TABLE 6 MMD of dissolved lignin in carbonated BLs

MM (kDa)	pH 13	pH 12	pH 11	pH 10.5	pH 10	pH 9
> 10	8	8	7	4	3	3
5-10	11	12	12	10	9	10
1-5	50	50	51	52	56	56
< 1	31	30	30	34	32	31

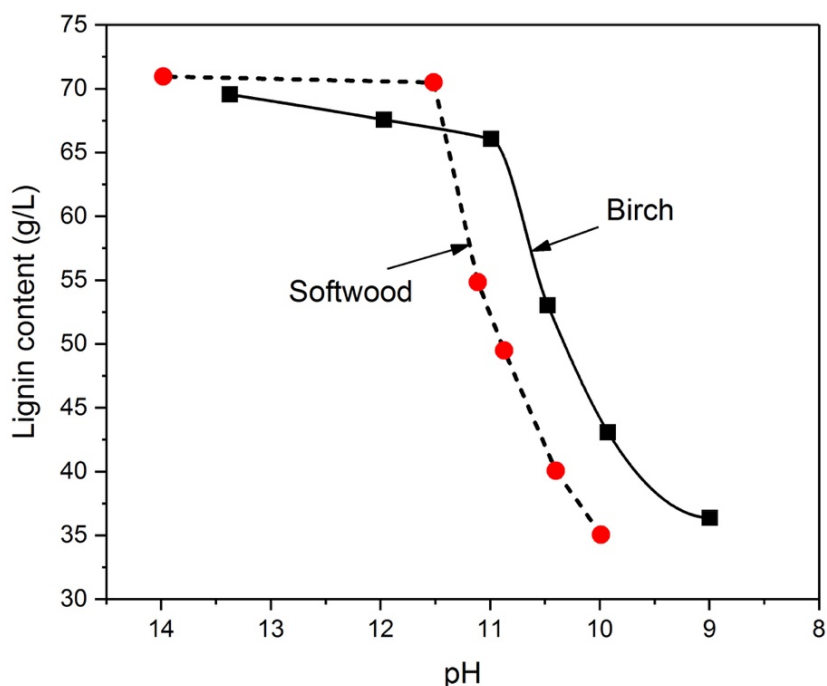


FIGURE 16 Dissolved lignin in the BL after stepwise carbonation.

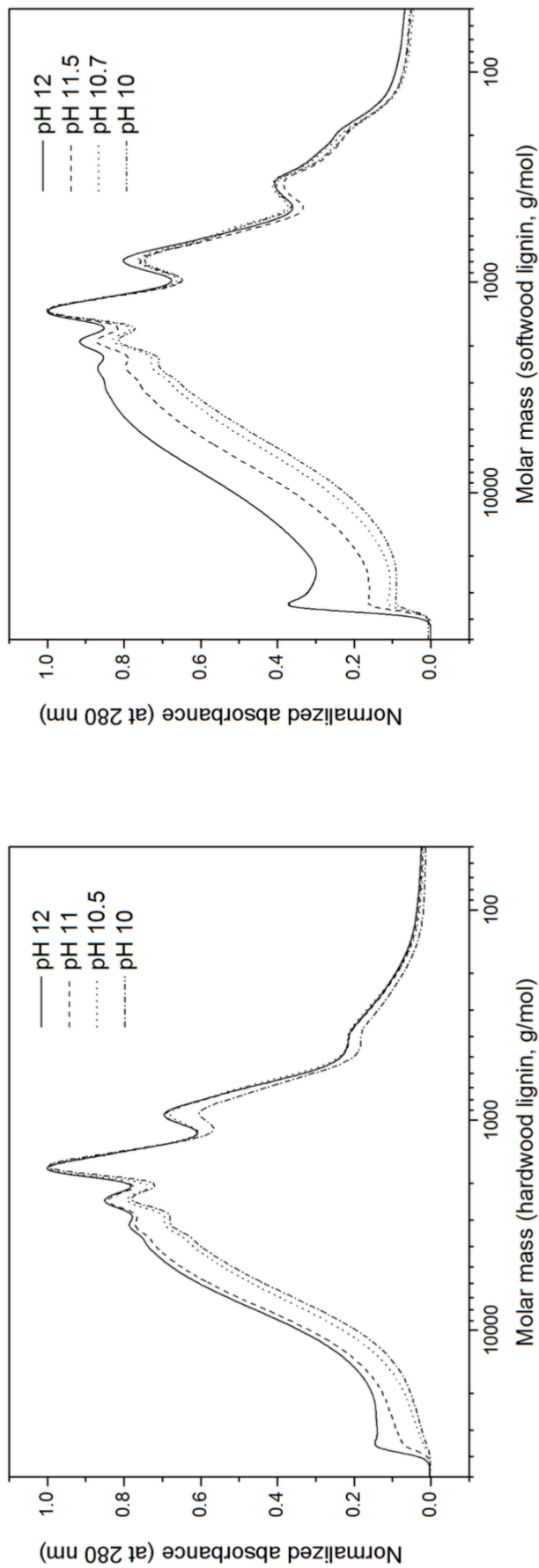


FIGURE 17 MMD of dissolved lignin in carbonated BLs.

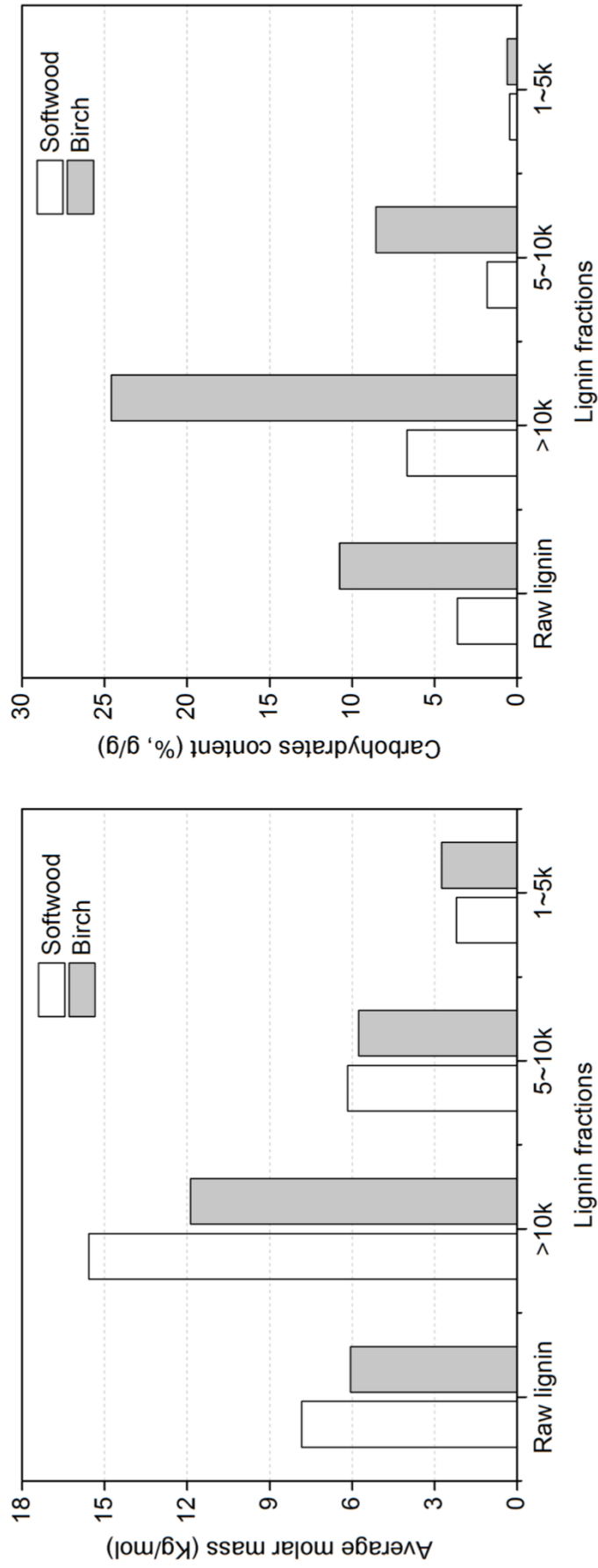


FIGURE 18 Average MM and carbohydrate content of different lignins.

The ratio of lignin to other BL ingredients is relatively lower after the separation process. Since lignin is the main source for producing organic carbons for building a swollen char structure during the pyrolysis stage (Paper I), a lower lignin proportion in this kind of BL is the main reason for a lower maximum swelling of the droplet (Vähä-Savo et al. 2014, Zhao et al. 2015). When different amounts of lignin separated from an industrial kraft BL (with H_2SO_4 until a pH value of 3 was reached) were added to the organic acids prepared from the same BL, the maximum swelling displayed a positive and linear relationship with the lignin content (Fig. 19). However, this was not generally applicable for predicting the maximum swelling of different BLs because other minor factors also influence the droplet swelling behavior, including carbohydrates, organic acids sodium salts, extractives, and major inactive cooking chemicals (e.g., Na_2CO_3 and Na_2SO_4).

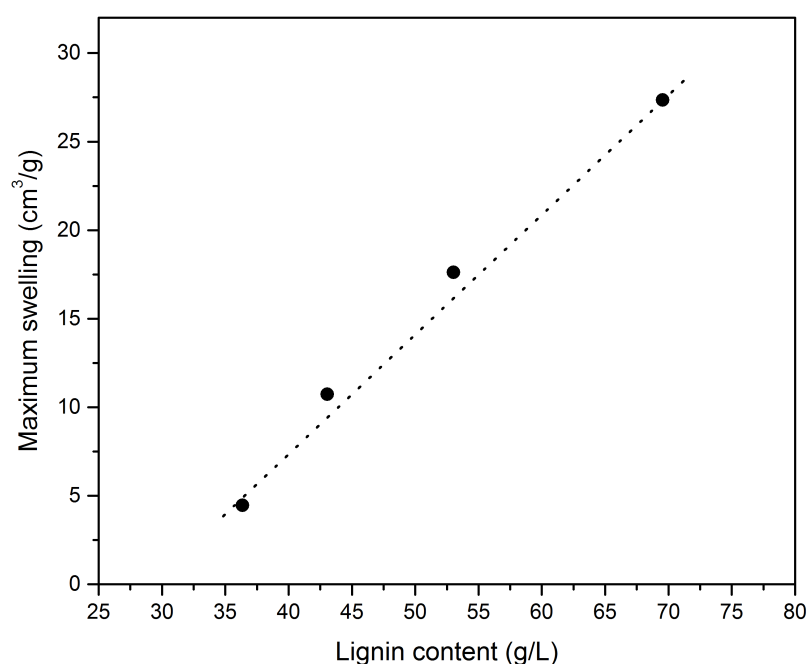


FIGURE 17 The influence of lignin content on droplet swelling.

So far, there are only limited data on the effect of lignin MM distribution on droplet swelling. Paper II studied the degree of swelling of the three lignin fractions (i.e., LMM lignin of 1-5 kDa, MMM lignin of 5-10 kDa, and HMM lignin of >10 kDa). It was found that the MMM lignin swelled the most compared to other fractions, and the hardwood MMM lignin swelled in a comparable degree to the original lignin (Fig. 20). This result was different from the previous studies which have reported that LMM lignin swelled more (Miller 1989) or that HMM (3500-5000 Da) was associated with higher swelling (Alén 1994). Though, this result seemed not to have a greater impact on swelling than the effect of lignin content.

Another important influence of carbonation on the BL swelling behavior is the introduction of Na_2CO_3 ; however, this factor seemed to have been previously ignored. The amount of Na_2CO_3 introduced varies depending on how much

BL is subjected to carbonation and how much lignin is to be separated. It was investigated how increased Na_2CO_3 content affected the degree of swelling (Paper II). As can be seen from Fig. 21, the more Na_2CO_3 in the BL, the lower the maximum swelling. It led to a 25% decrease in the maximum swelling even only 5% of Na_2CO_3 was added.

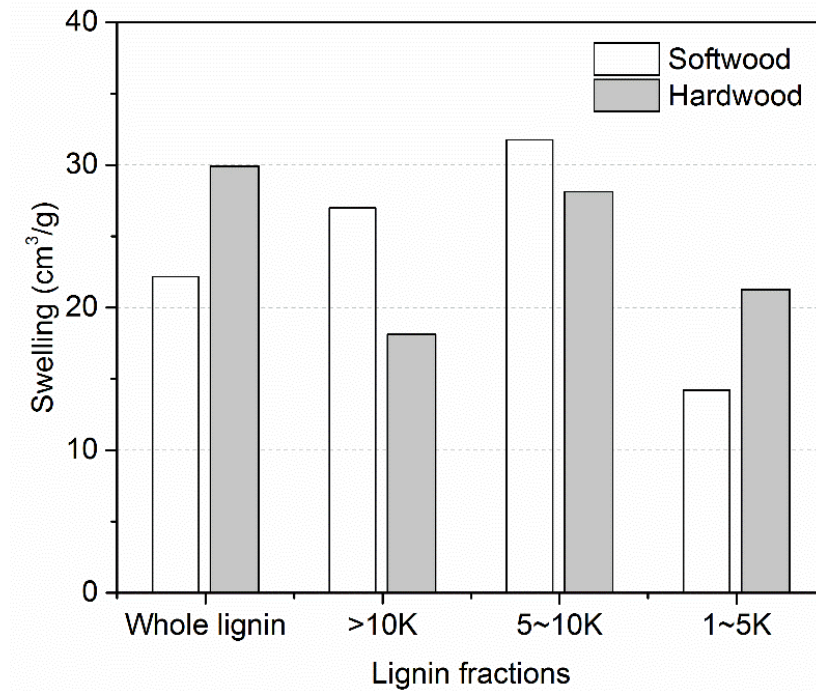


FIGURE 18 The swelling of different lignin-organic acids mixtures.

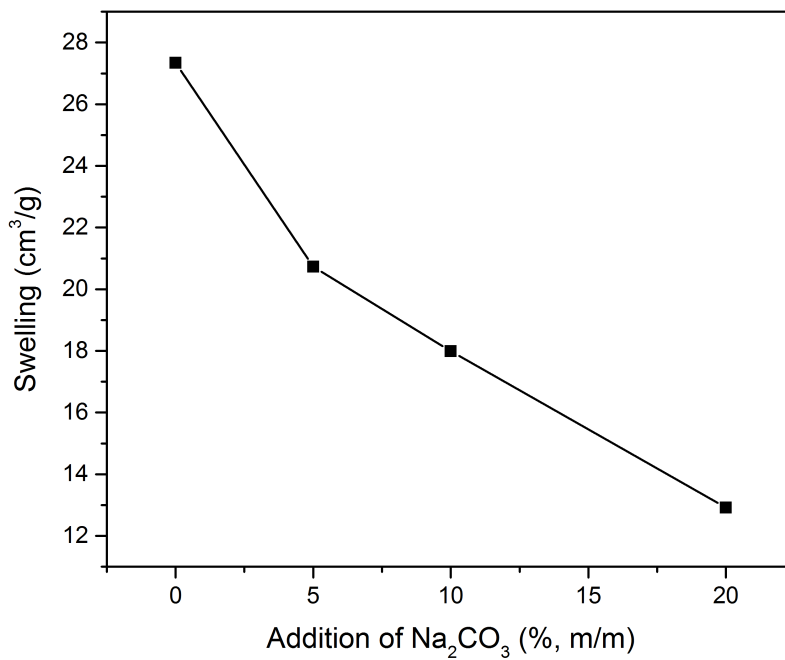


FIGURE 19 Influence of the addition of Na_2CO_3 on droplet swelling.

3.3 Combustion behavior of kraft and sulfur-free black liquors

The combustion behavior of kraft BLs has been studied extensively during the 1980s-1990s, while BLs from sulfur-free pulping are less researched. Integrating a pretreatment stage prior to pulping is thought to be a reasonable way towards pulp mill biorefining, provided that the extracted materials could be effectively converted into value-added products. The pretreatment of wood raw materials includes different chemical, chemimechanical, and biochemical approaches, among which HWP (also known as pre-hydrolysis or autohydrolysis) is considered an environmental-friendly and inexpensive method for extracting certain carbohydrate-based materials and LMM lignin from wood (Alén 2011). HWP of wood chips/sawdust has also been shown to be capable of modifying the fiber matrix of the feedstock, leading to somehow unique delignification behavior during pulping. Such an integrated pulping method has been shown to change the traditional distribution of the organic constituents dissolved in BL, which is expected to influence the combustion behavior of the resulting liquor droplets.

3.3.1 Influence of HWP on liquor composition

HWP affects the chemical composition of BL mainly through two actions: (i) removal of certain hemicelluloses, extractives, and LMM lignin from feedstocks; (ii) modifying the fiber matrix of feedstock to be more accessible to the cooking chemicals. Treating the wood chips at 150°C for 60 minutes removed 10-20% of the feedstock (10% for softwood and 17% for hardwood) (Table 1), and treating the wood sawdust at 160-170°C for 30, 40, and 60 minutes separated 20-30% of the raw materials (Table 2). It could be seen that, due to its smaller size, sawdust was more sensitive to the HWP than the wood chips having a larger size. It could also be seen from the chemical constituents of wood chips and sawdust that a considerable amount of hemicelluloses and a minor amount of lignin were extracted after the HWP (Papers IV and V). Most of the extractives were removed during the HWP; the hydrolysates contain mainly carbohydrates, acetic acids, and LMM lignin (Tunc and van Heiningen 2011, Lehto 2014).

Kraft pulping and sulfur-free soda and O₂-NaOH pulping of the softwood and hardwood chips and sawdust with and without the HWP produced a series of BLs that could be used to generalize how the main organic composition varied after the HWP and among different pulping methods and species. Partial removal of acetyl groups from the feedstock hemicelluloses during the HWP resulted in a considerably lower amount of acetic acid in all the BLs; thus, less alkali was consumed for neutralizing the acetic acid, and more alkali was present for delignification during the subsequent pulping process. As a result, higher concentration of dissolved lignin was found in almost all the BLs, except that for the kraft and soda-AQ BLs from sawdust was not affected much. Undesirably, higher alkalinity facilitated the degradation of polysaccharides, leading to higher concentration of hydroxy acids in all BLs after the HWP (Figs. 22-24).

The content of different organic fractions in BLs revealed the delignification behavior of different pulping processes. Apparently, the content of dis-

solved lignin for all BLs increased appreciably after the HWP. On the contrary, the content of total organic acids reduced after the HWP because of the much lower content of volatile acids (even though that for the hydroxy acids increased). Therefore, the ratio of lignin-to-total organic acids gained an increment for almost all BLs (Figs. 22-24). It was interesting that this ratio was much lower for the O₂-NaOH BLs than for the other BLs (Figs. 23 and 24).

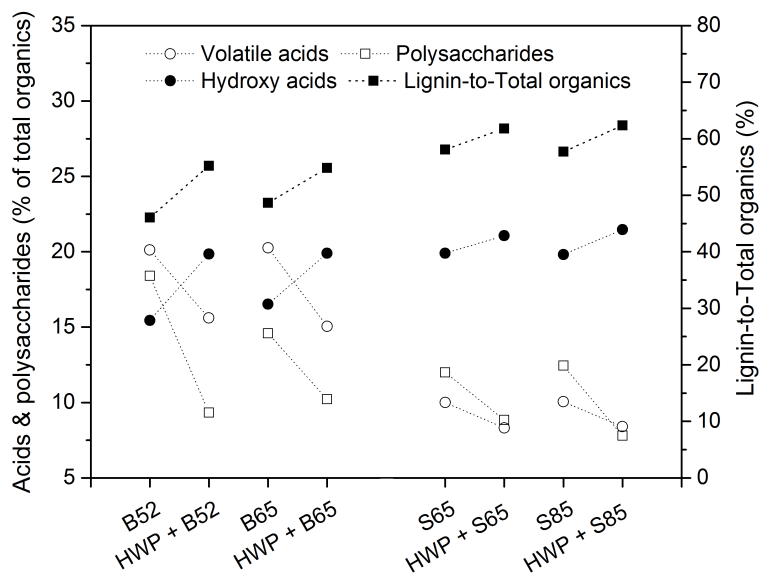


FIGURE 20 Main organic composition in BLs from chips.

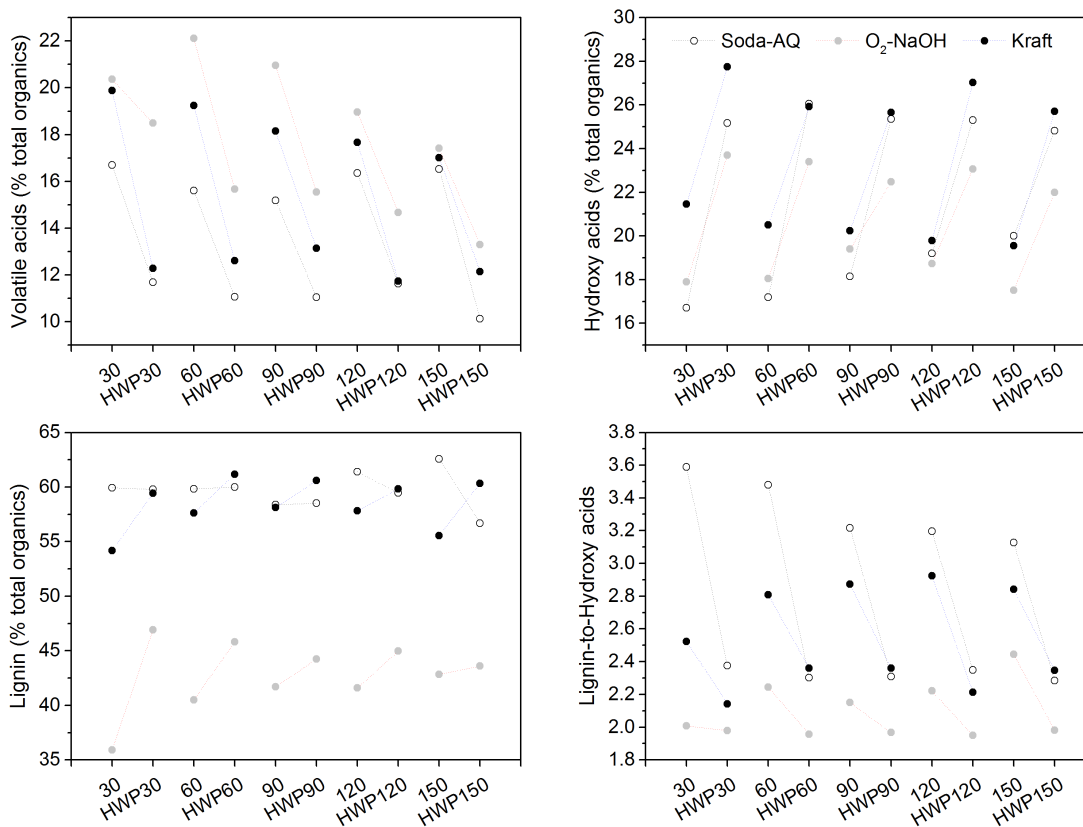


FIGURE 21 Chemical composition of birch BLs from sawdust.

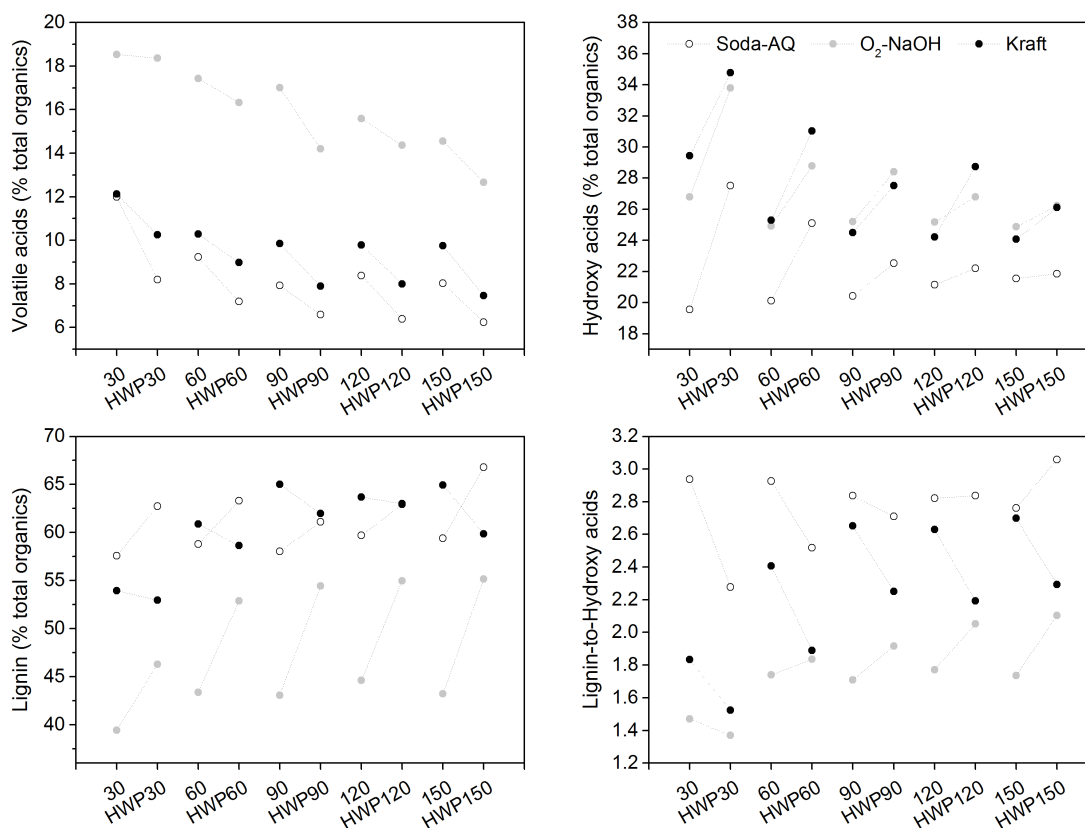


FIGURE 22 Chemical composition of spruce BLs from sawdust.

3.3.2 Combustion behavior of black liquor droplet

The combustion times and droplet swelling are important droplet behavior relevant to the RB process (see 1.2.2 Combustion behavior of black liquor droplet). In general, the hardwood (birch) BLs swelled more than the softwood (spruce) BLs based on similar cooking conditions, and the kraft BLs swelled more (25-45%) than the sulfur-free BLs: kraft BLs > soda-AQ BLs > O₂-NaOH BLs (Figs. 25-27). The HWP of wood chips resulted in higher swelling for the kraft BLs (Fig. 26), which was considered to be associated with the increased ratio of lignin-to-organic acids because lignin plays an important role in determining the degree of swelling and the organic acids are necessary for the creation of a plastic state essential for swelling (Paper I). However, in the case of the BLs from sawdust, most of them swelled less after the HWP (except for the birch O₂-NaOH BLs that swelled more) (Figs. 26 and 27), opposite to the trend for the wood chip BLs. It was unknown why higher lignin-to-organic acids ratio led to lower swelling for most of the sawdust BLs.

In general, the sulfur-free BLs burned longer than the kraft BLs (Figs. 25-27). The HWP of birch chips reduced the combustion times for the corresponding BLs ("B52 vs. HWP + B52" and "B65 vs. HWP + B65"), while it seemed not to greatly affect those for the spruce BLs ("S65 vs. HWP + S65" and "S85 vs. HWP + S85") (Fig. 25). The birch sawdust O₂-NaOH BLs had the longest pyrolysis time, while the corresponding kraft BLs had the shortest pyrolysis time (Fig. 26). The pyrolysis time for the spruce sawdust BLs increased after the HWP,

and particularly the char burning time for the soda-AQ BLs was longer (33-41%) than that for the other BLs (Fig. 27). The combustion times for the birch sawdust BLs from the same cooking conditions were not clearly affected by the HWP (Fig. 26), and the spruce sawdust BLs had a slight increase in pyrolysis time after the HWP (Fig. 27).

It appeared that higher swelling was often accompanied by shorter pyrolysis time in the cases of the hardwood BLs (Figs. 25 and 26), and consequently the char burning time also shortened, probably due to the larger specific surface area leading to faster mass transfer during the char burning stage. The influence of liquor composition on the combustion times of droplet was not clear. In addition, it was still not possible to quantitatively predict the degree of swelling or the combustion times based on the available data obtained.

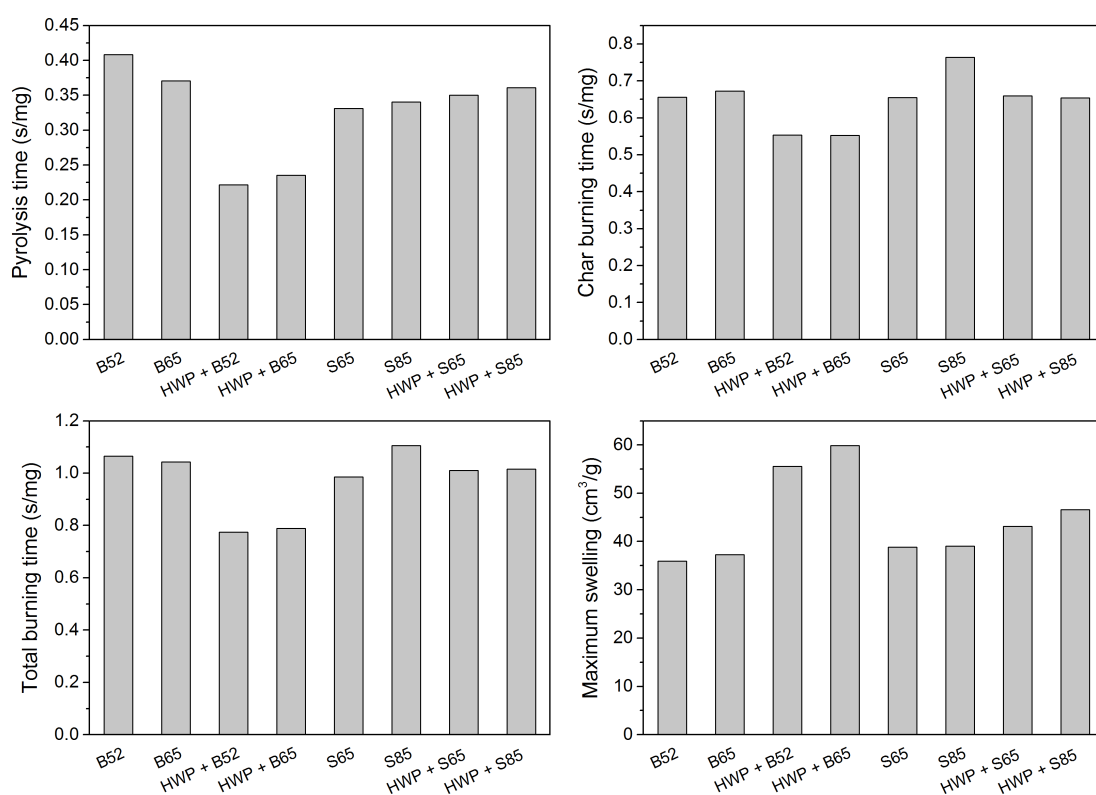


FIGURE 23 Combustion behavior of kraft BLs (wood chips). HWP refers to hot-water pretreatment.

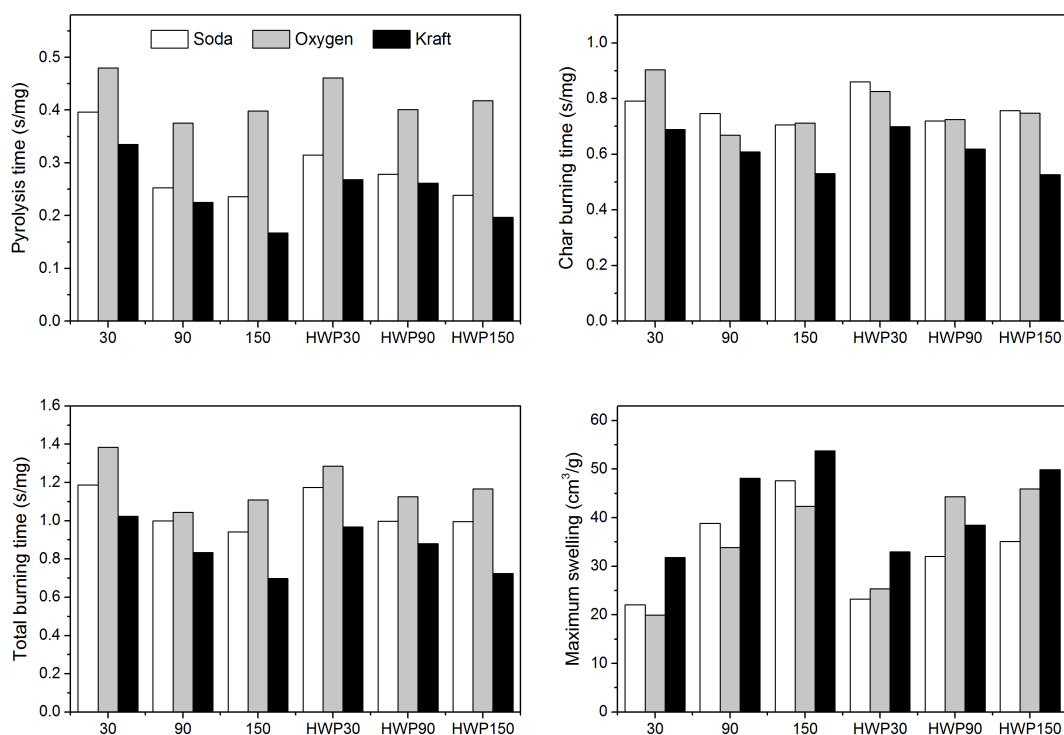


FIGURE 24 Combustion properties of birch BLs (sawdust). HWP refers to hot-water pretreatment. Cooking times: 30, 90, and 150 min.

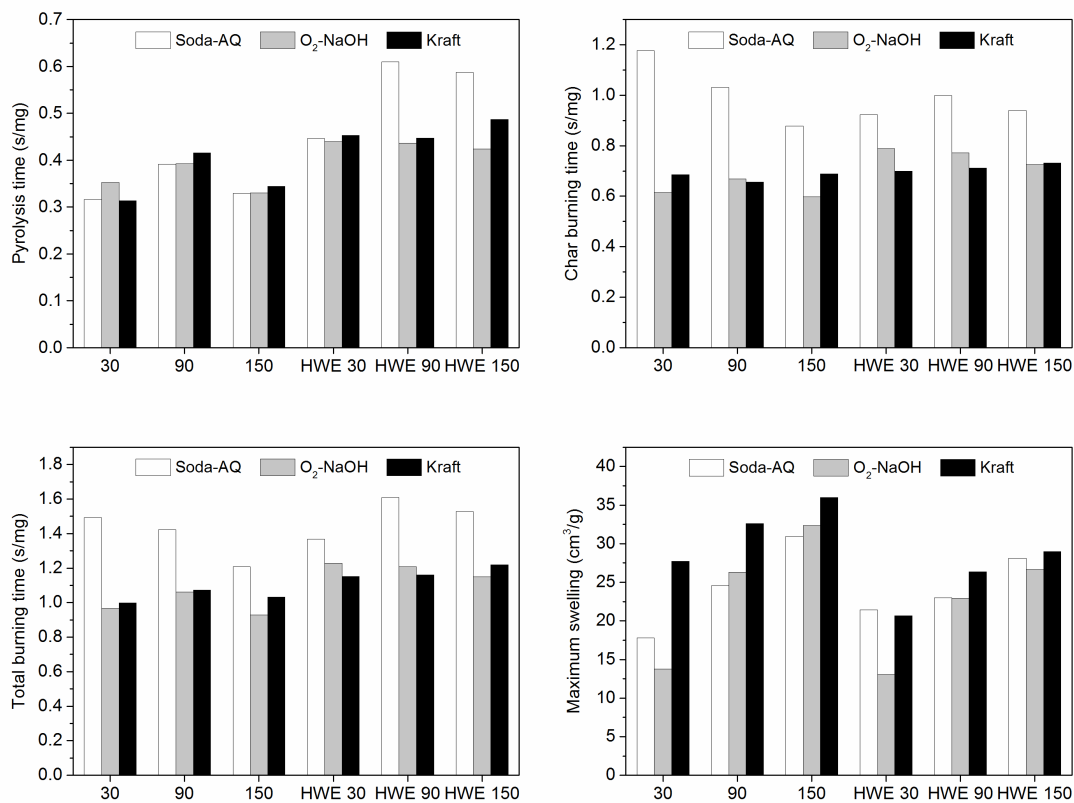


FIGURE 25 Combustion properties of spruce BLs (sawdust). HWP refers to hot-water pretreatment. 30, 90, and 150 are cooking times (min).

4 CONCLUDING REMARKS

The melting of aliphatic carboxylates and NaOH was found to be critical for the formation of a plastic state essential for the swelling of BL droplets. The swelling of BL droplets was shown to involve three basic phenomena: (i) the creation of a plastic state through the successive and continuous melting of an array of sodium aliphatic carboxylates and NaOH over 230–500°C; (ii) the production of large amount of volatiles by the decomposition of lignin and other organics for expanding the droplet at a plastic state; and (iii) the progressive formation of a rigid char surface with the carbon materials mainly derived from lignin. This gives an insight for the development of CFD models for recovery boiler designs and operations. With the new findings of BL droplet swelling process, it is possible to derivate a function with more detailed thermal degradation characteristics of lignin, aliphatic carboxylic acids, and other minor components, which is a step forward to the numerical prediction of BL swelling.

When looking into the different molar mass fractions of BL lignins, HMM lignin had higher carbohydrate content. MMM lignin of 5-10 kDa seemed to swell more than other lignin fractions (i.e., LMM lignin of 1-5 kDa and HMM lignin of 5-10 kDa). Increased amount of sodium carbonate in the BL reduced the swelling of droplets. Biorefining subprocess using carbonation to partially separate lignin from the BL during the evaporation process led to lower maximum swelling for the resulting BL droplets, which were found to result mainly from reduced lignin content and new introduction of Na₂CO₃. Lower lignin content in the BL means lower gross heat input to the recovery boiler, which will directly affect the heat and mass balance of the boiler operation. To maintain a stable level of energy production, higher amount of lignin-lean BL should be fed into the recovery boiler, which challenges the char bed and spraying operations. The flight path of BL droplets will change due to their varied swelling behavior. Lower swelling lignin-lean BL droplets tend to be less entrained. It would need to adjust the liquor spraying to avoid BLs reaching the char bed too early. Relatively higher inorganic matters (less lignin, more Na₂CO₃) in the BL would also affect the char bed reduction process and efficiency.

The HWP of feedstock prior to cooking led to increased dissolution of lignin and the formation of hydroxy acids in the BLs but a reduced amount of vol-

atile acids after pulping. The mass ratio of lignin-to-organic acids for all the BLs increased after HWP. HWP had a significant influence on the swelling behavior of BL droplets, which also varied with wood morphologies (chips and sawdust) and species (hardwood and softwood). The lignin-to-organic acids ratio seemed to be a useful indicator for predicting the trend of swelling for the BL droplets. All of the BLs (chips) swelled more and burned faster, while most of the BLs (sawdust) swelled less but the combustion times remained unaffected after HWP; only the pyrolysis time for the spruce BLs (sawdust) increased. The kraft BLs tended to swell more and burn faster than the sulfur-free BLs. Among all BLs, the birch O₂-NaOH BLs had longer pyrolysis time, and the spruce soda-AQ BLs had longer char burning time. These changes to the combustion behavior of BLs from the integrated forest biorefineries would directly influence the performance of existing recovery boilers. It is important to study how they behave differently from the traditional BLs during combustion using existing CFD models, which will be valuable information for the design and operation of recovery boilers for handling such BLs.

REFERENCES

- Adams, T.N. (Ed.) 1997. Kraft Recovery Boilers, TAPPI Press Atlanta, GA, USA.
- Adler, E. 1977. Lignin chemistry - past, present and future, *J. Wood Sci. Technol.*, 11(3): 169-218.
- Agbor, V.B., Cicek, N., Sparling, R., Berlin, A. and Levin, D.B. 2011. Biomass pre-treatment: Fundamentals toward application, *Biotechnol. Adv.*, 29(6): 675-685.
- Alén, R. 1994. Swelling behaviour of kraft black liquor and its organic constituents, *Bioresour. Technol.*, 49(2): 99-103.
- Alén, R. 2000. Basic chemistry of wood delignification. In: Stenius, P. (Ed.), *Forest Products Chemistry, Papermaking Science and Technology*. Vol. 3. Fapet Oy, Helsinki, Finland, pp. 58-104.
- Alén, R. 2011. Principles of biorefining. In: Alén, R. (Ed.), *Biorefining of Forest Resources*. Paper Engineers' Association/Paperi ja Puu Oy, Helsinki, Finland, pp. 55-114.
- Alén, R. and Hartus, T. 1988. UV spectrophotometric determination of lignin from alkaline pulping liquors, *Cellul. Chem. Technol.*, 22(6): 613-618.
- Alén, R., Jännäri, P. and Sjöström, E. 1985. Gas-liquid chromatographic determination of volatile fatty acids C₁-C₆, and lactic acid as their benzyl esters on a fused-silica capillary column, *Finn. Chem. Lett.*, 12(5): 190-192.
- Alén, R., Niemelä, K. and Sjöström, E. 1984. Gas-liquid chromatographic separation of hydroxy monocarboxylic acids and dicarboxylic acids on a fused-silica capillary column, *J. Chromatogr. A*, 301(1): 273-276.
- Alén, R., Patja, P. and Sjöström, E. 1979. Carbon dioxide precipitation of lignin from pine kraft black liquor, *Tappi*, 62(11): 108-110.
- Alén, R., Rytönen, S. and McKeough, P. 1995. Thermogravimetric behavior of black liquors and their organic constituents, *J. Anal. Appl. Pyrolysis*, 31(94): 1-13.
- Baklien, A. 1960. The effects of extraction on black liquor from eucalyptus pulping. *Appita*, 14: 5-15.
- Carlsson, P., Wiinikka, H., Marklund, M., Grönberg, C., Pettersson, E., Lidman, M. and Gebart, R. 2010. Experimental investigation of an industrial scale black liquor gasifier. 1. The effect of reactor operation parameters on product gas composition, *Fuel*, 89(12): 4025-4034.
- de Wild, P., van der Laan, R., Kloekhorst, A. and Heeres, E. 2009. Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation, *Environ. Prog. Sustain. Energy*, 28(3): 461-469.
- Demirbaş, A. 2002. Pyrolysis and steam gasification processes of black liquor, *Energy Convers. Manag.*, 43(7): 877-884.

- Frederick, W. and Hupa, M. 1994. The effects of temperature and gas composition on swelling of black liquor droplets during devolatilization, *J. Pulp Pap. Sci.*, 20(10): 274-280.
- Frederick W. and Hupa M. 1997. Black liquor droplet burning processes. In: Adams, T.N. (Ed.), *Kraft Recovery Boilers*, Atlanta: TAPPI Press; pp. 131-158.
- Frederick, W., Noopila, T. and Hupa, M. 1991. Swelling of spent pulping liquor droplets during combustion, *J. Pulp Pap. Sci.*, 17(5): 164-170.
- Huldén, B. 1968. Combustion of spent liquor droplets, *Proc. of Symp. on Recov. of Pulping Chemicals*, Helsinki, Finland, pp. 368-375.
- Hupa, M. 2014. Recovery boiler research highlights – 10 steps forward, In: Continuous development of recovery boiler technology – 50 years of cooperation in Finland, *Proc. of Intl. Recov. Boiler Conf.*, Tampere, Finland, pp. 9-10.
- Hupa, M., Solin, P. and Hyöty, P. 1987. Combustion behaviour of black liquor droplets, *J. Pulp Pap. Sci.*, 13(2): 67-72.
- Kamm, B., Gruber, P. R. and Kamm, M. 2016. Biorefineries–Industrial Processes and Products. *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co., Germany.
- Kumar, H. and Alén, R. 2016. Microwave-assisted esterification of tall oil fatty acids with methanol using lignin-based solid catalyst, *Energy Fuel*, 30(11): 9451-9455.
- Kumar, H. and Christopher, L. 2017. Recent trends and developments in dissolving pulp production and application, *Cellulose*, doi:10.1007/s10570-017-1285-y
- Lehto, J. and Alén, R. 2012. Purification of hardwood-derived autohydrolysates, *BioResources*, 7(2): 1813-1823.
- Lehto, J. and Alén, R. 2013. Alkaline pre-treatment of hardwood chips prior to delignification, *J. Wood Chem. Technol.*, 33(2): 77-91.
- Lehto, J. and Alén, R. 2015. Alkaline pre-treatment of softwood chips prior to delignification, *J. Wood Chem. Technol.*, 35(2): 146-155.
- Lehto, J. Pakkanen, H. and Alén, R. 2015. Molecular mass distribution of sulfur-free lignin from alkaline pulping preceded by hot-water-extraction, *Appita*, 68 (2): 149.
- Louhelainen J. 2003. *Changes in the Chemical Composition and Physical Properties of Wood and Nonwood Black Liquors during Heating*, Ph.D. Thesis. University of Jyväskylä, Finland.
- Maček, A. 1999. Research on combustion of black-liquor drops. *Prog. Energ. Combust. Sci.*, 25(3): 275-304.
- Milanova, E. 1988. Variables affecting the swelling of kraft black liquor solids, *J. Pulp Pap. Sci.*, 14(4): 95-102.

- Miller, P., Clay, D. and Lonsky, W.F.W. 1989. The influence of composition on the swelling of kraft black liquor during pyrolysis, *Chem. Eng. Commun.*, 75(1): 101-120.
- Monaghan, M. and Siddall, R. 1963. The Combustion of single drops of waste sulphite liquor - a preliminary investigation, *Tappi*, 46(2): 89-91.
- Naqvi, M., Yan, J. and Dahlquist, E. 2010a. Black liquor gasification integrated in pulp and paper mills: A critical review, *Bioresour. Technol.*, 101(21): 8001-8015.
- Naqvi, M., Yan, J. and Fröling, M. 2010b. Bio-refinery system of DME or CH₄ production from black liquor gasification in pulp mills. *Bioresour. Technol.*, 101(3): 937-944.
- Noopila, T., Alén, R. and Hupa, M. 1991. Combustion properties of laboratory-made black liquors, *J. Pulp Pap. Sci.*, 17(4): 105-109.
- Oye, R., Langfors, N., Phillips, F. and Higgins, H. 1977. The properties of kraft black liquors from various eucalypts and mixed tropical hardwoods, *Appita*, 31(1): 33-40.
- Pettersson, K. and Harvey, S. 2010. CO₂ emission balances for different black liquor gasification biorefinery concepts for production of electricity or second-generation liquid biofuels, *Energy*, 35(2): 1101-1106.
- Rydholm S. 1965. *Pulping Processes*, John Wiley & Sons, London, pp. 776-797.
- Sjöström, E. and Alén, R. (Eds.) 1999. *Analytical Methods in Wood Chemistry, Pulping and Papermaking*. Springer, Heidelberg, Germany.
- Sjöström, E. 1993. *Wood Chemistry: Fundamentals and Applications*. (2nd edn) Academic Press, San Diego, CA, USA.
- Stewart, D. 2008. Lignin as a base material for materials applications: Chemistry, application and economics, *Ind. Crop. Prod.*, 27(2): 202-207.
- Tran, H. and Vakkilainen, E. 2007. Advances in the Kraft chemical recovery process, In: *International colloquium on Eucalyptus Pulp*, <http://www.eucalyptus.com.br/icep03/200Tran.text.pdf.pdf>
- Tran, H. and Vakkilainen, E. 2008. *The kraft chemical recovery process*. URL: <http://www.tappi.org/content/events/08kros/manuscripts/1-1.pdf>
- Tomani, P. 2010. The LignoBoost process, *Cellul. Chem. Technol.*, 44(1): 53.
- Tunc, M. and van Heiningen, A. 2008. Hemicellulose extraction of mixed southern hardwood with water at 150 °C: Effect of time, *Ind. Eng. Chem. Res.*, 47: 7031-7037.
- Tunc, M. and van Heiningen, A. 2011. Characterization and molecular weight distribution of carbohydrates isolated from the autohydrolysis extract of mixed southern hardwoods, *Carbohydr. Polym.*, 83(1): 8-13.

- Vähä-Savo, N., DeMartini, N., Ziesig, R., Tomani, P., Theliander, H., Välimäki, E. and Hupa, M. 2014. Combustion properties of reduced-lignin black liquors. *TAPPI J.*, 13(8): 81-90.
- Vakkilainen, E. 2005. *Kraft Recovery Boilers - Principles and Practice*. Suomen Soodakattilaydistys r.y., Helsinki, Finland.
- van Heiningen, A. 2006. Converting a kraft pulp mill into an integrated forest biorefinery, *Pulp Pap. Canada*, 107(6): 38-43.
- Wallmo, H. 2008. *Lignin Extraction from Black Liquor - Precipitation, Filtration and Washing*. PhD Thesis, Chalmers University of Technology, Gothenburg, Sweden.
- Whistler, R. and BeMiller, J. 1963. α -D-Isosaccharino-1,4-lactone, action of lime water on lactose, *Methods Carbohydr. Chem.*, 2: 477-479.
- Whitty, K., Backman, R., Forssén, M., Hupa, M., Rainio, J. and Sorvari, V. 1997. Liquor-to-liquor differences in combustion and gasification processes: Pyrolysis behaviour and char reactivity, *J. Pulp Pap. Sci.*, 23(3): 119-128.
- Whitty, K., Backman, R. and Hupa, M. 2008. Influence of pressure on pyrolysis of black liquor: 1. Swelling, *Bioresour. Technol.*, 99(3): 663-670.
- Wiinikka, H., Carlsson, P., Granberg, F., Löfström, J., Marklund, M., Tegman, R., Lindblom, M. and Gebart, R. 2010. Design and methodology of a high temperature gas sampling system for pressurized black liquor gasification, *Fuel*, 89(9): 2583-2591.
- Wiinikka, H., Carlsson, P., Marklund, M., Grönberg, C., Pettersson, E., Lidman, M. and Gebart, R. 2012. Experimental investigation of an industrial scale black liquor gasifier. Part 2: Influence of quench operation on product gas composition, *Fuel*, 93(1): 117-129.
- Zhao, L., Tran, H. and Maki, K. 2015. Combustion behaviors of lignin-lean black liquor and lignin, *TAPPI J.*, 14(7): 451-458.

ORIGINAL PAPERS

I

A SALT-INDUCED MECHANISM FOR THE SWELLING OF BLACK LIQUOR DROPLET DURING DEVOLATILIZATION

by

Chengcong Chen, Raimo Alén, Esa Lehtimäki & Jarmo Louhelainen
2017

Fuel, 202, 338-344

Reprinted with kind permission from Elsevier 2017.

II

ROLE OF LIGNIN AND SODIUM CARBONATE ON THE SWELLING BEHAVIOR OF BLACK LIQUOR DROPLETS DURING COMBUSTION

by

Chengcong Chen, Hannu Pakkanen & Raimo Alén
2017

Holzforschung, <https://doi.org/10.1515/hf-2017-0092>

Reprinted with kind permission from DE GRUYTER 2017.

III

COMBUSTION BEHAVIOR OF KRAFT BLACK LIQUOR DROPLETS FROM HOT WATER PRETREATED HARDWOOD AND SOFTWOOD CHIPS

by

Chengcong Chen, Raimo Alén, Joni Lehto & Hannu Pakkanen
2016

TAPPI Journal, 15(11), 685-691

Reprinted with kind permission from TAPPI Journal 2016

IV

COMBUSTION PROPERTIES OF BIRCH (*BETULA PENDULA*) BLACK LIQUORS FROM SULFUR-FREE PULPING

by

Chengcong Chen; Raimo Alén; Joni Lehto & Hannu Pakkanen
2016

Journal of Wood Chemistry and Technology, 36(6), 401-411.

Reprinted with kind permission from Taylor & Francis Online 2016

V

**COMBUSTION PROPERTIES OF SPRUCE BLACK LIQUOR
DROPLETS: SULFUR-FREE PULPING AND INFLUENCE OF
HOT-WATER PRETREATMENT**

by

Chengcong Chen, Raimo Alén, Joni, Lehto & Hannu Pakkanen
2016

Nordic Pulp and Paper Research Journal, 31(4), 532-540

Reprinted with kind permission from Nordic Pulp and Paper Research Journal
2016