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**ADVANCED BIOREFINERY CONCEPTS RELATED TO NON-WOOD
FEEDSTOCKS**

BY

SALEEM ULLAH

Academic Dissertation for the Degree of
Doctor of Philosophy

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ABSTRACT

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Agricultural residues, such as wheat straw (*Triticum aestivum*), okra stalk (*Abelmoschus esculentus*), and giant miscanthus (*Miscanthus × giganteus*, a hybrid of *M. sinensis* and *M. sacchariflorus*) were investigated to assess their possible consumption for integrated lignocellulosic biorefining. The efficient fractionation and recovery of all important chemical components (cellulose, hemicelluloses, and lignin) of such feedstocks are a prerequisite for realistic biorefinery concepts. Water is one of the most eco-friendly solvents with the highest potential for industrial use, and it is also suitable for full-scale biorefinery purposes. For example, under pressure at elevated temperatures over 100 °C, water can degrade and dissolve a significant portion of hemicelluloses from a lignocellulosic biomass.

This study included the preparation of various hydrolysates from wheat straw, okra stalk, and miscanthus stalk under different temperatures (140 °C and 150 °C) and P-factors of 50 (at 140 °C for 60 min or at 150 °C for 25 min) and 200 (at 140 °C for 240 min or at 150 °C for 100 min), referred to herein as hot-water pretreatment, preceding sulfur-free alkaline soda-anthraquinone (AQ) pulping; to prepare the chemical fiber, NaOH charges of 15%, 20%, and 15% on oven-dried feedstock for wheat straw, okra stalk, and miscanthus, respectively were used. An AQ charge of 0.05% on oven-dried feedstock was used in each experiment. In this hot-water pretreatment stage, the most substantial mass removals of 12%, 23%, and 10% of the initial wheat straw, okra stalk, and miscanthus stalk were obtained, respectively, at 150 °C, with a treatment time of 100 min. After the pre-treatment the hydrolysates obtained were characterized in relation to the amount of various carbohydrates, volatile acids (acetic and formic acids), and furans, as well as the pH.

It was noted that the hot-water-pre-treatment step also facilitated the subsequent pulping phase, i.e., pulp yields of 57% (145 °C, 15 min, and kappa number 18), 41% (165 °C, 180 min, and kappa number 32), and 62% (165 °C, 60 min, and kappa number 23) were achieved for wheat straw, okra stalk, and miscanthus stalk, respectively, pretreated at 150 °C with a P-factor of 200 or P200. Pulp, mainly containing cellulose, were separated from the cooking black liquors, which were then analyzed in detail; the primary emphasis was given to hemicellulose-derived aliphatic carboxylic acids: volatile acids and low-molar-mass non-volatile acids (hydroxy carboxylic acids). In all cases, the

contents and molar-mass distributions of dissolved lignin (4,160 - 8,730 g/mol) in black liquors were also determined. The overall amount of aliphatic carboxylic acids decreased in order: okra/150°C/P200, 39 g/L > miscanthus/150°C/P200, 31 g/L > wheat/150°C/P200, 15 g/L. In the case of the hot-water pretreated feedstocks, fewer volatile acids and more nonvolatile acids (especially monocarboxylic acids) were detected. In conclusion, the results clearly indicate that the three non-wood materials studied were all have potential for this type of biorefining approach.

Keywords: Non-wood feedstock, hot-water extraction, alkaline pulping, aliphatic carboxylic acids, lignin, biorefining

LIST OF ORIGINAL PUBLICATIONS

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

I Ullah, S., Kilpeläinen, P., Ilvesniemi, H., Pakkanen, H. & Alén, R., Chemical characterization of okra stalk (*Abelmoschus esculentus*) as potential raw material for biorefinery utilization. *Cellulose Chemistry and Technology*, 52(2018):155-162.

II Ullah, S., Pakkanen, H., Lehto, J. & Alén, R., A comparable study on the hot-water treatment of wheat straw and okra stalk prior to delignification. *Biomass Conversion and Biorefining*, 8(2018):413-421.

III Ullah, S., Pakkanen, H., Lehto, J. & Alén, R., Hot-water extraction of *Miscanthus X giganteus* prior to soda-AQ pulping: a biorefining perspective. *Biofuels*, (2018):1-7.

IV Ullah, S., Pakkanen, H., Lehto, J. & Alén, R., Organics in soda-AQ black liquors from hot-water-extracted non-wood feedstocks. *Biofuels*, (2018) (submitted).

Author's contribution

The author was mainly responsible for the experimental work and evaluation of the results in all of the papers. The publications were written together with the co-authors.

OTHER SUPPORTING PUBLICATIONS

Ullah, S., Ahmad, I., Alias, Y., Yusoff, I. & Ashraf, M.A., Characterization of tri-phenylamino based polymethine dyes. *Journal of Chemistry*, (2013):1-5.

Ashraf, A., Ullah, S., Ahmad, I., Qureshi, K., Balkhair, K.S. & Rehman, M.A., Green biocides, a promising technology: Current and future applications. *Journal of the Science of Food and Agriculture*, 94(2014):388-403.

Ghalibaf, M., Ullah, S. & Alén, R., Fast pyrolysis of hot-water-extracted and soda-AQ-delignified okra (*Abelmoschus esculentus*) and miscanthus (*miscanthus x giganteus*) stalks by Py-GC/MS. *Biomass & Bioenergy*, 118(2018):172-179.

Alén, R., Lehto, J., Kumar, H., Ullah, S., Ghalibaf, M. & Halmemies, E., The chemical aspects on integrated biorefineries in the pulp industry. Baltic Conference Series, Stockholm, Sweden, May 14-17, (2018).

Ullah, S., Pakkanen, H., Lehto, J. & Alén, R., Hot water extraction prior to soda-AQ pulping of *Miscanthus X giganteus* – Biorefining perspective, 9th Edition of International Conference on Biofuels and Bioenergy, Edinburgh, Scotland, March 29-30, (2018).

PREFACE

This study was carried out at the University of Jyväskylä, Department of Chemistry, Laboratory of Applied Chemistry during 2015-2018. I would like to express my deepest gratitude to my research supervisor Professor Raimo Alén for giving me the opportunity to work in his group and his valuable guidance, support, and encouragement during my PhD studies.

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Jyväskylä, November 2018

Saleem Ullah

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ABBREVIATIONS

4- <i>O</i> -Me- α -D-GluAp	pyranoid 4- <i>O</i> -methyl- α -D-glucuronic acid
α -L-Araf	α -L-arabinofuranose
ACN	acetonitrile
AFEX	ammonia fiber explosion/expansion
AQ	anthraquinone
ARP	ammonia recycle percolation
β -D-Xylp	β -D-xylopyranose
CEPI	Confederation of European Paper Industries
DAD	diode array detector
DM	dispersity index
EA	effective alkali
ED	electrodialysis
FID	flame-ionization detector
GC	gas chromatography
GPC	gel permeation chromatography
H	H-factor
HMF	5-(hydroxymethyl)furfural
HPAEC	high-performance anion-exchange chromatography
HPLC	high-performance liquid chromatography
HWE	hot-water extraction
IC	ion chromatography
IEA	international energy agency
IFBR	integrated forest biorefinery
LCM	lignocellulosic material
LLA	low-liquid ammonia
LMAA	low-moisture anhydrous ammonia
MF	microfiltration
MM	molar mass
MMD	molar mass distribution
MS	mass spectrometry
MWCO	membrane weight cut-off
\bar{M}_w	weight average molar mass
NF	nanofiltration
o.d.	oven dry
P	P-factor
PAD	pulse amperometric detector
RO	reverse osmosis
SAA	soaking in aqueous ammonia
SEC	size exclusion chromatography
SEM	scanning electron microscope
TAPPI	Technical Association of the Pulp and Paper Industry
TFA	trifluoroacetic acid

x

TMP

thermomechanical pulping

UF

ultrafiltration

UV/Vis

ultraviolet/visible

1 INTRODUCTION

Globally, the increase in demand for energy; necessity of non-renewable resources; increased fears about carbon dioxide emissions; and lignocellulosic biomass exploitation, such as feedstocks for the manufacturing of chemicals formerly produced from fossil fuels, have firmly attracted researchers' attention. Within the last twenty years, several biorefinery ideas have arisen, primarily due to diminishing fossil fuel resources, as well as the greater demand for energy and biodegradable materials [Dincer 2000; Alén 2011; Brosse et al. 2012]. According to the International Energy Agency (IEA) Bioenergy Task 42, a biorefinery is defined as the renewable processing of every type of biomass into a range of bio-based products (e.g., food, feed, chemicals, and materials) and bioenergy (e.g., biofuels, power, and/or heat). However, a biorefinery as such is not a new concept for pulp and paper makers, since, for example, chemical pulp mills can already be considered as typical chemical/thermochemical biorefineries because they utilize many practical advances to fractionate and transform wood and non-wood feedstocks into a wide range of byproducts derived from the main components, i.e., cellulose, lignin, and extractives [Jong et al. 2015; Pandey et al. 2015]. Furthermore, in the short-term, biomass can offer unconventional transportation fuels, like bioethanol or biodiesel.

A number of non-wood feedstocks, like annual crops, can possibly be utilized as an alternative to the increasingly declining forest wood feedstocks in many regions [Potůček & Milichovský 2011]. The plant families Gramineae, Leguminesoae, and Malvaceae contain promising non-woody species used for the production of fibers. Among them, agricultural feedstocks, such as okra stalk, wheat straw, and miscanthus, could provide great alternative sources for lignocellulosic biorefineries. This is mainly due to the fact that these kinds of feedstocks have a high polysaccharide content and a low dietetic benefit for human intake, with extensive production worldwide [Nieschlag et al. 1960; Olsson et al. 1994; FAOSTAT 2011; Jahan et al. 2013]. To fully exploit and obtain value-added chemicals from biomass, the disintegration of the biomass structure is needed in order to release the bound polysaccharides to be

hydrolyzed, for example, for fermentation. Various economical pre-treatments are needed to achieve this purpose [Kumar et al. 2009; Kumar & Sharma 2017].

In recent years, one of the most favorable developments for biorefineries; has been the introduction of the hot-water extraction step, by which lignocellulosic feedstocks can be treated and partly dissolved in different conditions (e.g., pH, temperature, and treatment time) before delignification [Gong et al. 2012; Kärcher et al. 2016]. The pre-treatment prime objective is to overcome the recalcitrance of raw material and maximize its reactivity; leading to an increase in pulping performance, the recovery of by-streams (carbohydrates, aliphatic carboxylic acids, and lignin), and the significance of the lignocellulosic biomass; it would also diminish waste production [Zhu et al. 2010; Alén 2011]. In general, during the process of non-wood pulping, some of the key difficulties include the deposition of silica and a high amount of fines. These kinds of problems can also be solved by hot-water extraction (HWE) preceding soda-anthraquinone (AQ) pulping [Jahan et al. 2012].

According to our research-based integrated biorefinery concept (HWE preceding alkaline sulfur-free pulping), a broad spectrum of products can be obtained, apart from pulp. In addition, HWE hydrolysate can provide various carbohydrates and volatile acids (acetic and formic acids). Indeed, after delignification, aliphatic hydroxy acids and sulfur-free lignin can be obtained from black liquor [Sánchez et al. 2008; Zhu et al. 2010; Lehto 2015; Lehto & Alén 2015]. Hence, applying this kind of practice to non-wood feedstocks like okra, miscanthus, and wheat straw is of prime significance.

2 AIMS OF THE STUDY

The basic idea of this research was to evaluate the effect of HWE on popular Asian and European non-woods and the behavior of the hot-water-extracted feedstocks during the subsequent soda-AQ pulping. This approach included the following phases:

- HWE experiments conducted under various conditions (pH, temperature, and time) and with different non-wood feedstocks.
- Characterization of the chemical compositions of pre-treatment hydrolysates containing carbohydrates, lignin, and their degradation products.
- Sulfur-free pulping experiments (soda-AQ pulping) conducted with hot-water-pre-treated and reference feedstock materials, accompanied by an analysis of the final black liquors.
- Determination of the overall effects of HWE on pulping performance.

The main objective of this research was to evaluate possibilities of applying HWE, a biomass hydrolysis technique, to sulfur-free pulping of certain potential Asian and European non-wood feedstocks (wheat straw, okra stalk, and miscanthus stalk). The formation, recovery, and utilization of the potential by-streams generated during the different process stages were taken into consideration. The research was performed with the “integrated forest biorefining principles” in mind, leading to a more efficient utilization of biomass resources, production of value-added chemicals, and minimization of waste.

3 STRUCTURE AND CHEMICAL COMPOSITION OF NON-WOODS

3.1 Fiber morphology

Fiber morphology is important in order to know the fiber properties essential for various end uses and the products made from the fibers, and it should be qualified based on certain parameters. The different properties are a high fiber length-to-width ratio, tenacity, flexibility or pliability, cohesiveness, and uniformity. For evaluating fiber pulp quality, fiber length and width as well as chemical composition and cellulose microfibril angle are significant [Jackman et al. 2003; Oluwafemi et al. 2007; Marques et al. 2010]. In the case of paper production, the fibers that are most suitable have a ratio of fiber length to width of about 100:1, whereas in textile fibers, the ratio is more than 1000:1. In non-woody species, fiber length and width vary according to the plant types and the plant part from which the fiber is derived [Ilvessalo-Pfäffli 1995]. The average fiber length ranges from 1 mm to 30 mm. The shortest is found in grasses, and the longest is found in cotton; for example, Pima cotton is up to 42 mm. For end use, the average ratio of fiber length to diameter is important; in non-wood species, it ranges from 50:1 to 1500:1 [Hurter 1988].

Non-wood plant fibers can be categorized into several groups, based on the position of the fibers in the plant. Four main fiber types were described in detail by Ilvessalo-Pfäffli [1995]: grass, bast, leaf, and fruit. Grass fibers are also termed *stalk* or *culm* fibers [Hurter 1988; Thakur & Thakur 2014].

3.2 Chemical composition

The chemical composition of non-woody feedstocks is crucial in order to know how suitable the plant material would be as a raw material for biorefining. The

important factor is the fibrous nature of the plant. The composition and number of fibers is reflected in the properties of the plant cell walls [McDougall et al. 1993; Saini et al. 2015; Sorieul et al. 2016]. The main chemical constituent of plant cell walls is cellulose, while the non-cellulosic components consist of hemicelluloses, lignin, pectins, and proteins, as well as certain minerals in the epidermal cells [Neill & York 2003; Alén 2011]. The proportional chemical content of non-wood feedstock differs among plant species due to different morphology, even among plant parts. This kind of chemical distribution affects the biorefining properties of the plant material. The proportional chemical content of non-woody feedstocks is shown in Table 1. While there is differentiation in the chemical content among various plant species, the composition cannot be precisely defined for a given species, as the materials are heterogeneous; thus the reported values are always averaged estimations of the feedstock content [Hunsgi 1989; McDougall et al. 1993; Pakkanen 2012].

TABLE 1. Proportional chemical content of non-woody feedstocks (% of dry matter) [Alén 2011]

Component	Content
Carbohydrates	50-80
Cellulose	30-45
Hemicelluloses	20-35
Lignin	10-25
Extractives	5-15
Proteins	5-10
Inorganics	0.5-10
SiO ₂	0.5-7

3.2.1 Cellulose

Cellulose is considered to be the most abundant polymer in nature. Just a year after the discovery of the diffraction of X-rays on crystalline materials in 1912, cellulose was the first polymer on which X-ray investigation was performed. Cellulose is a linear polymer of β -(1 \rightarrow 4)-linked glucose units, as presented in Fig. 1, which plants synthesize. The degree of polymerization is usually 10,000 to 15,000, corresponding approximately to molecular masses of 1.6 and 2.4 million Da. Cellulose is not soluble in water, dilute acidic solutions, and dilute alkaline solutions at normal temperatures. The cellulose chain is composed of repeating units of cellobiose, which are inverted 180°, forming a flat, ribbon like structure. This flat ribbon structure allows extensive hydrogen bonds to be formed between individual cellulose chains. The result is the crystallization of cellulose into microfibrils, which are insoluble, cable-like structures that essentially add to the physical properties of the cell wall. As cellulose is a major cell wall component of all higher plants, it is responsible for the strength of the plant cell [Richmond 2000; Zugenmaier 2001; Taylor 2008; Chen 2014; Lehto 2015].

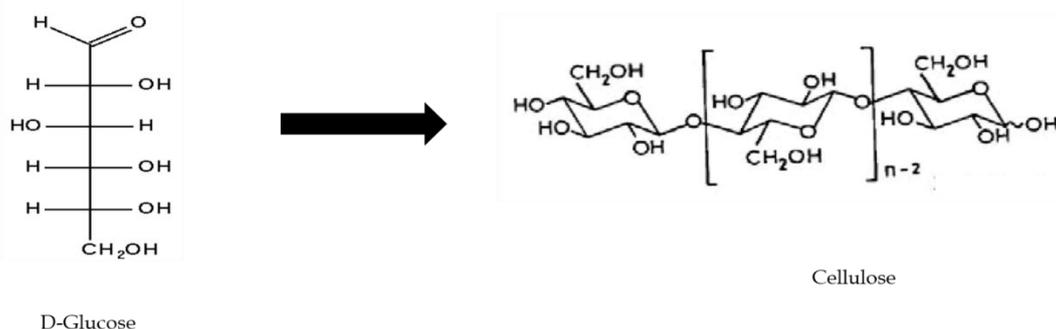


FIGURE 1. Molecular chain structure of cellulose.

3.2.2 Hemicelluloses

Hemicelluloses form another key component in plant materials. Hemicelluloses were reported in 1891 by Schulz as a semifinished product of cellulose, or the precursor molecules of cellulose, easily separated from plant tissues; thus, these polysaccharides were named *hemicelluloses* [Fengel & Wegener 1984; Sjöström 1993]. He also observed that this component can be easily hydrolyzed to monosaccharides in hot and dilute mineral acid. Unlike cellulose, hemicelluloses are copolymers made of different amounts of several saccharide molecules. The hemicelluloses of cereal straws from the Graminae family have a backbone of (1→4)-linked β -D-xylopyranosyl (β -D-Xylp) units, as presented in Fig. 2. The degree of polymerization of hemicelluloses in Gramineae is less than 100. In general, it is believed that hemicelluloses are heterogeneous polysaccharides in the matrix of the cell and are composed of the main components, like xylan, xyloglucan, glucomannan, and galactomannan [Zhang et al. 2006; Yang 2008; Pakkanen 2012; Stoklosa 2014; Chen 2014].

However, in cereal straws and grasses, hemicelluloses are among complex components in the cell wall. The hemicelluloses in non-wood materials, are made of arabinoxylan, with a branched chain of glucuronic and *O*-acetyl groups. They form various bonds with other cell wall components, like hydrogen bonds with cellulose, covalent bonds (mainly α -benzyl ether linkages) with lignin, and ester linkages with acetyl units and hydroxycinnamic acids [Ren & Sun 2010]. Acetyl groups are commonly a part of hemicelluloses [Sjöström 1993; Teleman 2009]. In plant xylans, the acetyl group content varies: for example, in bamboo, the content of acetyl groups has been found to be 6-7% of the total xylan [Matsuo & Mizuno 1974; Dea & Morrison 1975; Higuchi 1980; Alén 2011].

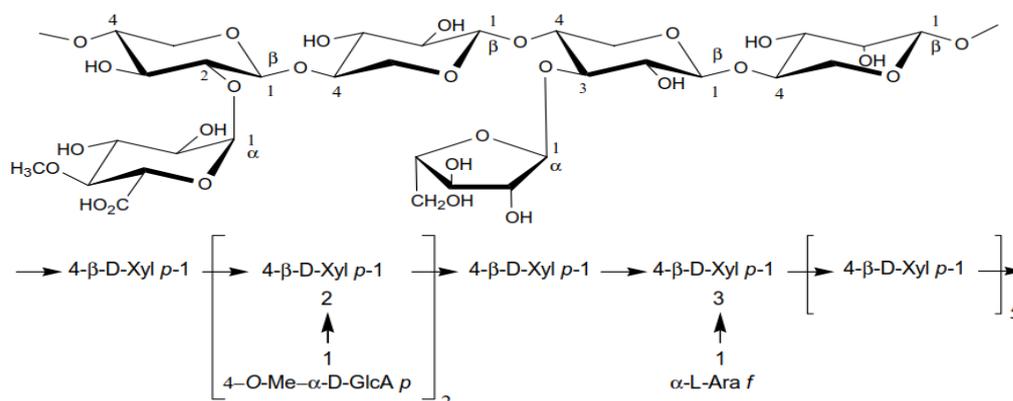


FIGURE 2. Major structure of xylan from hardwood (close to straw xylan) [Laine 2005].

3.2.3 Lignin

Lignin is the only aromatic polymer and is a complex chemical compound present in wood; it is mainly concentrated in the middle lamella. Lignin makes bonding together with cellulose and hemicelluloses and forms lignin-carbohydrate complexes [Glennie & McCarthy 1962]. It is a very complex polymer consisting of phenylpropane units (C9 units) combined in a random formation, where *p*-hydroxyphenyl alcohol (H), guaiacyl alcohol (G), and syringyl alcohol (S) are the main precursors, interconnected heterogeneously via several types of C-C and C-O linkages (Fig. 3) [Freudenberg & Nash 1968; Hatfield & Vermerris 2001; Toledano et al. 2010].

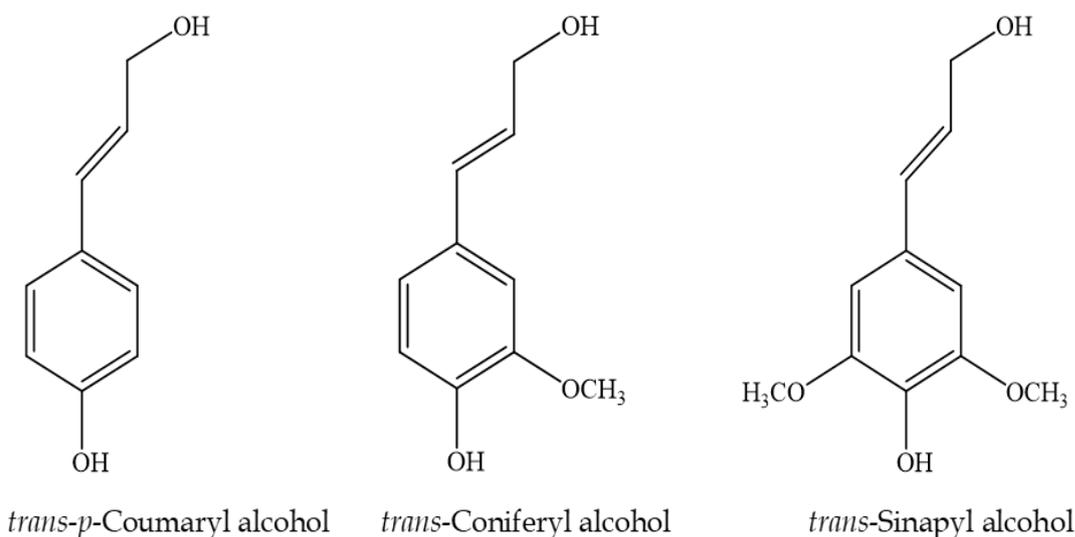


FIGURE 3. Major monolignols from which “natural” plant lignins are biosynthetically formed.

The bond types of non-wood lignins are mainly the same as those of wood lignins. Lignin structural units are principally composed of aromatic glycerol β -aryl ether bonds, roughly reaching half of the lignin in softwood and over 60%

in hardwood as shown in Table 2 [Adler 1977; Tao & Guan 2003]. In non-woods the proportion of carbon-carbon bonds, for example, β -5 and β - β bonds, is higher than in hardwoods. In grass lignins, most of the *p*-hydroxyphenylpropane units link with phenylpropane units in their ester form. For example, in straw, 60% of the *p*-hydroxyphenylpropane units of lignin are connected in the form of esters. A small amount of ferulic acid esters also make a part of grass lignin [Chen 2014].

TABLE 2. The frequency of the bonds in lignin [Adler 1977]

Linkage types	Dimer structure	Percent of total linkages	
		Softwood	Hardwood
β -O-4	Arylglycerol- β -aryl ether	50	60
α -O-4	Noncyclic benzyl aryl ether	2-8	7
β -5	Phenylcoumaran	9-12	6
5-5	Biphenyl	10-11	5
4-O-5	Diaryl ether	4	7
β -1	1,2-Diaryl propane	7	7
β - β	Pinosresinol/lignin type	2	3

3.2.4 Extractives

Extractives are a large number of low-molar-mass non-structural compounds present in plants, and they can be extracted using polar or non-polar solvents [Alén 2000; Taylor 2002]. Various compounds, like alkaloids, waxes, fats, proteins, phenolics, gums, pectins, resins, terpenes, and essential oils, are included in this group [Routa et al. 2017]. Most extractives are secondary metabolites. These are the compounds that are not directly involved in plant growth and cell development. Their main role is protection of the tree against pathogens or other biotic attacks, as well as giving color, odor, and taste to plants [Barnett & Jeronimidis 2003; Ekeberg et al. 2006].

Extractives are mostly lipophilic and can be extracted with organic solvents (i.e., diethyl ether, acetone, or hexane). Sometimes, the term *extractives* is used more broadly, also including water-soluble substances; thus, they cover essentially all wood components other than cellulose, hemicelluloses, and lignin [Holmbom 1999; Pakkanen 2012].

3.2.5 Inorganic components

Inorganics in the form of minerals are essential for plant growth. Minerals can be divided into macro- and micro-nutrients. The macro nutrients, mostly composed of calcium, potassium, magnesium, nitrogen, phosphorous, and sulfur, are essential to organics, like proteins and nucleic acids, which play a role in maintaining osmotic pressure. The concentration of these macro-nutrients in

plants varies from 0.1% to 1.5% of their dry mass [Epstein 1965; Pahkala 2001]. Micronutrients contain mainly iron, zinc, copper, molybdenum, nickel, and manganese, and they contribute to enzyme production; they are available in low concentrations in plants. Silica is also essential in some plant species. The highest silica concentration (5-10%) is usually found in grass plants growing under water, such as rice [Epstein 1965; Marchner 1995; Esch et al. 1996]. During pulping minerals in the raw materials are considered impurities and should be removed. Inorganics are present both in woody and non-woody plants, but in contrast to non-woods, the concentrations are lower in woody plants, rarely exceeding 1% of wood dry mass [Misra 1980; Hurter 1988; Sjöström & Westermarck 1999].

4 BIOMASS PRE-TREATMENTS

Pretreatment plays a significant role in modern biorefinery concepts based on lignocellulosic feedstocks biomass. The pre-treatment applied depends on the raw materials, as well as the main conversion method and the desired products. Even prior to pre-treatment, some steps are needed, such as washing or separating inorganic matter, pebbles, and size reduction by grinding, milling, or crushing [Galbe & Zacchi 2007; Lehto 2015]. In bioprocess engineering, pre-treatment is defined as a process that can convert any type of lignocellulosic feedstock from its natural form, which is reluctant to cellulase enzyme hydrolysis, into a soft form in which enzymatic hydrolysis is effective [Lynd et al. 2002].

In the near future, the expected worldwide increase in energy demands, the exhaustion of cheaper fossil fuel reserves, and global warming have created an urge to develop renewable biomass-based energy systems. Cellulosic materials are the primary attraction as residues for biofuel production due to their comparatively low cost, easy availability, and sustainability. Cellulosic biomass converted into biofuel production has become the major emphasis of rigorous research and development [O'Sullivan 1996; Lynd et al. 1999, 2002; Zhang & Lynd 2006]. Usually, pre-treatment is needed to release carbohydrates from lignocellulosics, making their structural matrix more open for further fractionation and conversion techniques, such as soda-AQ pulping (Fig. 4).

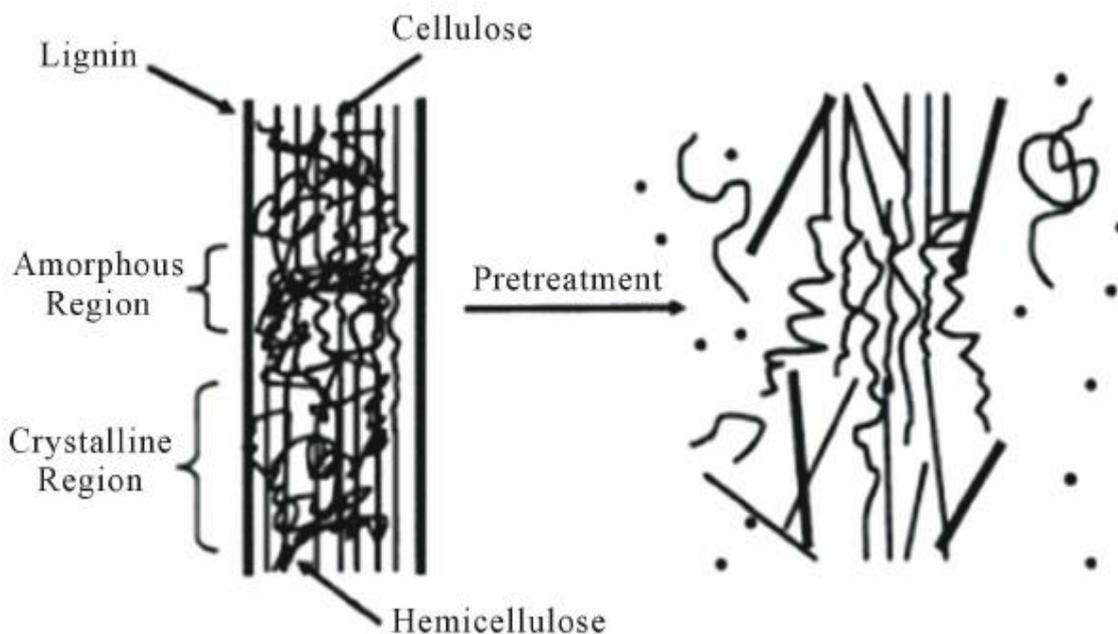


FIGURE 4. Effect of pre-treatment on lignocellulosic biomass [Harmsen et al. 2010].

The pre-treatment process must be cost-effective, efficient in lignocellulosic degradations, and able to release carbohydrates as monosaccharides, oligosaccharides, and polysaccharides. Such carbohydrate units are further converted into fermentable sugars after hydrolysis, while maintaining pulp quality. In this chapter, the following three pre-treatment processes are discussed, classified roughly according to pH:

- 1) hot-water extraction
- 2) alkaline pre-treatment
- 3) acidic pre-treatment

4.1 Hot-water extraction

HWE has been studied for several years, and HWE conditions are typically checked through the “P-factor” (pre-hydrolysis factor). This is the same as the “H-factor,” used in kraft pulping [Sixta 2006; Tunc et al. 2009]. The P-factor indicates the effect of HWE time and temperature as a single mathematical value derived by the formula presented in equation (1):

$$P = \int_{t_0}^t \exp \cdot \left(40.48 - \frac{15,106}{T} \right) \cdot dt, \quad (1)$$

where t represents time (hours), and T represents temperature (K). Making a correlation between the materials removed by HWE from lignocellulosic feedstocks and the process variables, such as temperature and time, is important in order to regulate the best process conditions for obtaining the desired lignocel-

lulosic products, which can lead to a comparison of processes performed under different conditions.

The hydrolysis of hemicelluloses is one of the main process as during HWE, and the disintegration behavior of hemicelluloses in the HWE process is generally divided into three steps [Yu et al. 2012; Zhuang et al. 2016]: the formation of primary products due to reactions on the surface of the biomass, the dissolution of these primary products into water, and the additional breakdown of the primary products. For example, the HWE process of miscanthus is shown in Fig. 5.

In the initial step of HWE, hemicelluloses are depolymerized into xylose oligomers, glucuronic acid, and acetic acid. In the second step, these primary products are converted into additional products like xylose monomer, furfural, glycolic acid, formic acid, and so on. The overall hemicellulose hydrolysis model can be written in one phase, as follows:

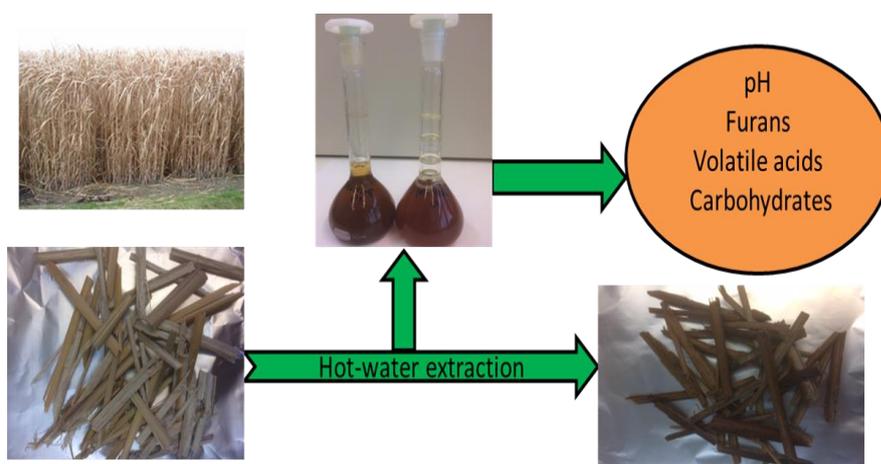
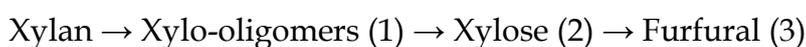


FIGURE 5. Hot-water extraction process for miscanthus.

4.2 Alkaline pre-treatment

Alkaline pre-treatment is one of the chemical pre-treatment technologies. This chemical process's main purpose is the same as that of kraft pulping, i.e., delignification, and it has arisen as the best feasible process option, primarily due to its robust pre-treatment effect and comparatively simple scheme. In these alkaline treatments, the used chemicals, such as ammonia (aqueous, liquid, and gaseous), sodium hydroxide, sodium carbonate, and calcium hydroxide (lime) are usually not considered to be polluting and corrosive. An advantage of alkaline pre-treatment is its processing under milder conditions compared to the hot-water and acidic pre-treatments, which retain the produced pulp's yield and quality with some times major sugar degradation. Alkaline reagents react with lignin; therefore, they are effective in lignin removal. A number of alkaline

pre-treatment technologies have been used so far. Some of these techniques have included, for example, ammonia recycle percolation (ARP), ammonia fiber explosion/expansion (AFEX), soaking in aqueous ammonia (SAA), low-liquid ammonia (LLA), low-moisture anhydrous ammonia (LMAA), and additional alkaline technologies using NaOH and Ca(OH)₂ [Lehto 2015; Kim et al. 2016]. Alkaline pre-treatment technologies relating to various reagents for the purpose of improving lignocellulosic biomass enzymatic digestibility have been studied. The most common ones in this group are presented in Table 3.

TABLE 3. Several alkaline pre-treatment reagents and their conditions and actions [Kim et al. 2016]

Catalysts	Conditions	Actions
Sodium hydroxide	0.5–10.0% NaOH, 60–180 °C, 5–60 min, solid charge: 10–30%	50% hemicellulose solubilization, 60–80% delignification, difficulty in recovery of NaOH
Sodium carbonate	1–30% Na ₂ CO ₃ , 60–180 °C, 5–60 min, solid charge: 10–30%	20–40% hemicellulose breakdown, 40–60% delignification, easier recovery than NaOH
Ammonium hydroxide	5–30% ammonia, 30–210 °C, high pressure (2–17 atm), 5–60 min, solid charge: 10–50%	10–50% hemicellulose dissolution, 0–80%, deep swelling delignification, lignin elimination or modification
Anhydrous gaseous ammonia	Gaseous ammonia 25–80 °C, ~72 h, solid charge: approx. 50% (moisture ~ 50%)	No washing need, little liquid feed (only ~ 50% moisture is enough), mild reaction condition
Liquid anhydrous ammonia	70–90 °C, 5 min, anhydrous ammonia, high pressure (15–20 atm), solid charge: 60–90%	No hemicellulose dissolution, no lignin removal, rapid evaporation and liquefaction of ammonia
Lime	25–130 °C, 1 h–8 weeks, Ca(OH) ₂ water/g of biomass 0.05–0.15 g, solid charge: 5–20%	20–40% hemicellulose degradation, 60–80% delignification, deacetylation, low energy requirement

4.3 Acidic pre-treatment

Acidic pre-treatment is the main conventional method used to pre-treat lignocellulosic feedstocks. In order to carry out pre-treatment with acids, and due to the harsh and toxic nature of most of the acids, an appropriate material is needed for constructing the reactor, one that can withstand the required experimental conditions and corrosive nature of acids. With this method, high amounts of inhibitory products, such as 5-(hydroxymethyl)furfural (HMF), phenolic acids, and aldehydes, are generated, which makes this avenue less attractive. Regardless, it is still industrially a very common pre-treatment method [Saha et al. 2005]. Two types of acid pre-treatments are developed by keeping in mind the type of end use: 1) high temperature (over 180 °C) for short durations (1-5 min) and 2) low temperature (<120 °C) for long durations (30-90 min). When lignocellulosics are treated in acidic media, the primary degradation reactions occur, which include the hydrolysis of glycosidic linkages in polysaccharides and the breakage of main α - and β -aryl ether bonds in lignin. Acidic pre-treatment is mostly used together with other hydrolysis techniques, like enzymatic hydrolysis. However, the enzymatic hydrolysis step can be avoided in some cases, as the acid itself hydrolyses the biomass into fermentable sugars. In this case, proper rinsing is important to remove acid prior to the fermentation of sugars [Sassner et al. 2008; Lehto 2015].

Acidic pre-treatment has been performed for the removal of constituents from lignocellulosics with different acids, such as TFA, HCl, H₂SO₄, HNO₃, and H₃PO₄. Among these acids, dilute sulfuric acid (H₂SO₄) has been used most often for commercial purposes. It has been widely used to pre-treat switch grass, corn stover, wheat straw, and rice straw. However, it definitely has some drawbacks, such as the production of inhibitory compounds and the deterioration of the reaction vessel. In order to avoid such disadvantages associated with sulfuric acid, other classes of dicarboxylic acids, like oxalic and maleic acids, have been used for pre-treatment. In comparison to sulfuric and acetic acids, oxalic acid has been shown to be less poisonous to yeasts and other microorganisms, and to be odorless. Additionally, it does not hinder hydrolysis, and it produces far fewer inhibitors [Marzioletti et al. 2008; Lee & Jeffries 2011; Kumar & Sharma 2017].

5 POTENTIAL PULPING OF NON-WOOD RAW MATERIALS

Pulping generally refers to a process during which fibers are removed from lignocellulosic feedstocks [Alén 2011]. The pulping techniques can be subdivided as chemical, semichemical, chemimechanical, and mechanical pulping. Various chemical pulping approaches that have been industrialized include the kraft, sulfite, soda, and organosolv pulping processes. Lignocellulosic chemical pulping means that lignin and part of the hemicelluloses are degraded into small water-soluble molecules, which are then removed from the cellulose fibers [Kamoga et al. 2013]. The high concentration of inorganics, especially silica, is the main obstacle in pulping non-wood. In pulp mills, when the black liquors containing silica are evaporated in recovery boilers, the concentration of SiO_2 mounts to such an extent that it may cause severe problems, like scaling, in the process. Several methods have been developed that make the removal of SiO_2 possible. It has been known that, for non-woody plants, about 40 different processes are appropriate, but only a few of them have been used commercially [Alén 2000; Pahkala 2001]. The generally used methods are described in this chapter.

5.1 Kraft pulping

Kraft, or sulfate pulping, is the most frequently used chemical process today. Worldwide, about two-thirds of the virgin pulp production and more than 90% of chemical pulp are produced by the kraft process [Alén 2011]. During this process, raw materials are treated in a pressurized vessel (digester) with a highly alkaline aqueous solution of NaOH and Na_2S . Sodium hydroxide mainly splits lignin, but it also removes part of the hemicelluloses, while sulfide is added to degrade lignin. About 50% of the initial feedstock dissolves in the cooking

liquor after pulping [McDougall et al. 1993; Alén 2000; Tran and Vakkilainen 2007]. The general kraft pulping process is shown in Fig. 6.

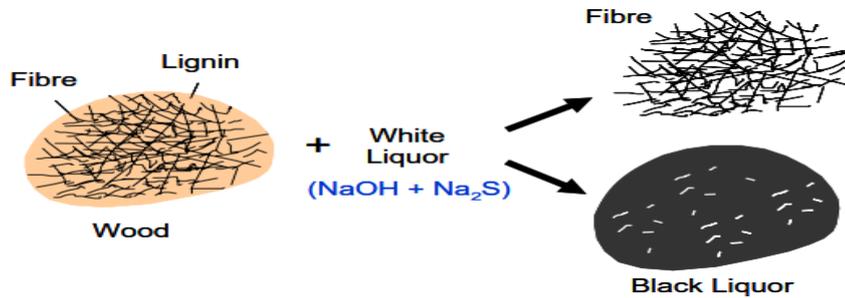
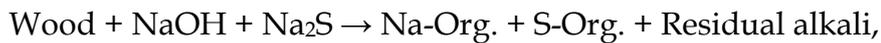


FIGURE 6. Kraft pulping process [Tran & Vakkilainen 2007].

During kraft cooking, various chemical reactions occur whose main objective is to facilitate the disintegration of wood into fibrous product. This objective is fulfilled by bonds cleavage in the lignin macromolecule. The main chemical reactions can be presented as follows:



where the word “*wood*” represents all of wood’s organic compounds. Alkali in the cooking liquor is consumed in three different reactions:

- 1) with lignin and the neutralization of products,
- 2) with carbohydrates and the neutralization of organic acids (aliphatic acids mainly formed in the degradation of hemicelluloses), and
- 3) with wood extractives and the neutralization of products.

Fig. 7 shows the basic reactions and phenomena between active alkali and the main wood constituents, resulting in the formation of various soluble fractions.

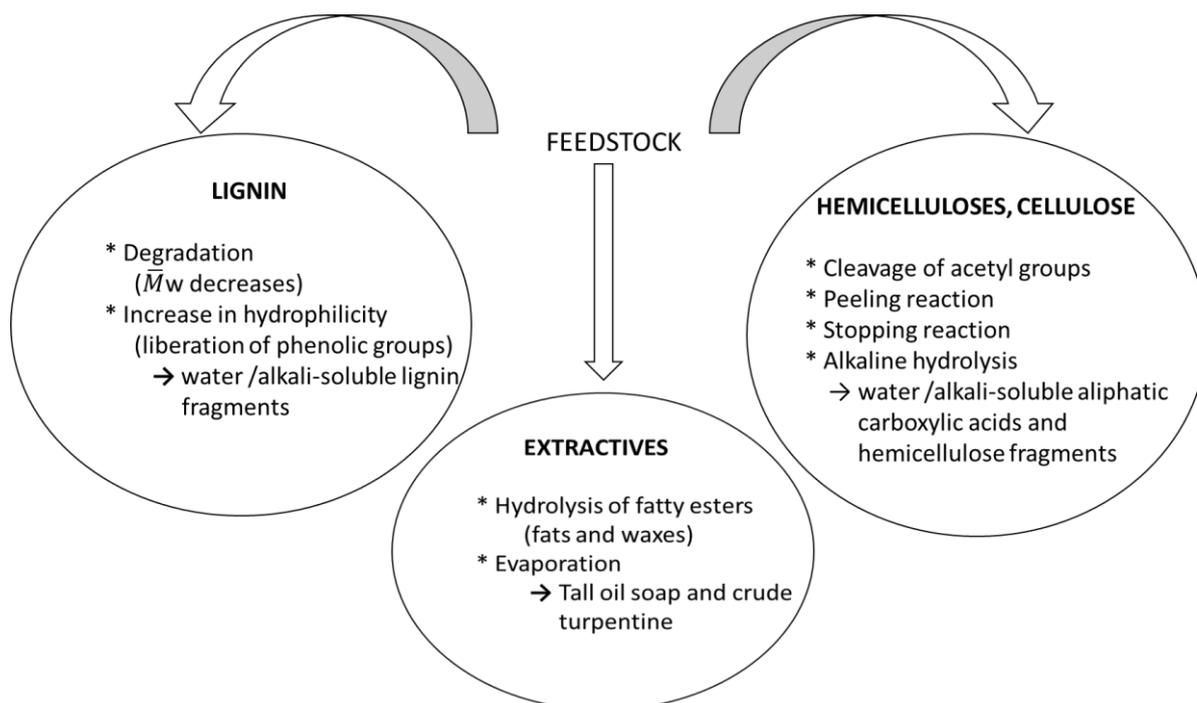


FIGURE 7. Main reactions in the feedstock constituents during kraft pulping. Modified from [Alén 2018].

5.2 Soda-AQ pulping

The soda-AQ pulping process is largely used for non-wood materials to produce non-wood or straw pulp. Due to the odor problem from sulfur in kraft pulping, soda-AQ pulping has an advantage in that it is sulfur-free, and the strength of the pulp is almost the same as that of kraft pulp. The main cooking chemical in this process is NaOH, while AQ is considered a catalytic additive. It works as a redox catalyst, shifting electrons from wood carbohydrates to intermediate structures formed from lignin decomposition, which ultimately gives rise to higher yields and a lower kappa number. Hence, AQ is useful because it reduces the damage to carbohydrates in the feedstock in the presence of high alkali, thus, accelerating the pulping process. However, due to its potential cancer-causing effects, the Confederation of European Paper Industries (CEPI) has endorsed the minimal use of AQ and its use for producing food contact materials is prohibited [EFSA 2012; Almeida & Gomide 2015; Lehto 2015; Alén 2018].

5.3 Other methods

The most traditional alkaline pulping methods are not appropriate for many non-wood feedstock materials; moreover, they cause severe ecological problems.

In order to find more environmentally friendly pulping methods worldwide, various alternative pulping processes have been introduced. Pulping non-wood feedstocks with organic solvents, known as *organosolv processes*, has captured more attention. In this process, alcohols or organic acids are used as organic solvents for non-wood pulping. The most common alcohols used are methanol and ethanol, and the organic acids are usually formic acid and acetic acid. When alcohols are used in cooking, usually high cooking temperatures and high pressures are needed, whereas, in the case of organic acids, low temperatures and normal pressures, close to atmospheric pressure are required. Apart from these solvents used for cooking, many other solvents including various phenols, amines, glycols, nitrobenzene, dioxane, dimethylsulfoxide, sulfolane, and liquid carbon dioxide, can be used [Sundquist, 2000].

Recent research related to organosolv pulping processes has improved the proficiency of many organosolv methods for producing pulp, yielding properties close to those of kraft pulp. Among the various processes that use alcohols for pulping, the most noticeable are those of Kleinert [Aziz & Sarkanen 1989], the Alcell alcohol-cellulose process [Young & Akhtar 1998], the Organocell MD process using methanol (50%)/NaOH [Mielenz et al. 2007], Organocell [Stockburger 1993], ASAM (alkaline sulfite-AQ-methanol) [Lönnerberg et al. 1987], and ASAE (alkali-sulfite-anthraquinone-ethanol) [Kirici et al. 1994]. Apart from these, some other chemical based processes are ester pulping, phenol pulping, Acetocell, Milox (peroxyformic acid pulping), and Formacell [Rousu et al. 2002; Sridach 2010]. The ultimate aim of these processes is not only the production of chemical pulp, but the exploitation of lignin and carbohydrates without significant degradation; organosolv methods may play a significant role in the future [Alén 2018].

6 VALUE-ADDED PRODUCTS FROM PULPING

Currently, to increase the value from biomass residues, for example, forest and agricultural residues are being turned into profitable bio-based products; however, special attention is required for refining biomass feedstocks. These biomass residues hold many valuable extractable compounds; their full exploitation requires an improvement in the proficient extraction, fractionation, concentration, and purification processes to recapture the good quality of natural bio-based chemicals and polymers [Lehto 2015; Almanasrah 2017]. The aim of this chapter is to 1) show the main value-added products that could be obtained during HWE (i.e., from hydrolysate) and the subsequent soda-AQ pulping (i.e., from black liquor) and 2) separate these bio-based products that could be useful on an industrial scale for the retrieval of some important value-added compounds from several types of biomass residues.

6.1 Hot-water-extracted hydrolysates

Hot-water-extracted liquor comprises a blend of various carbohydrates: in addition to oligo- and polysaccharides, some monosaccharides are present, alongside low amounts of other organics, including aliphatic carboxylic acids, furans, and heterogeneous fractions of lignin- and extractives-based materials [Alén 2018]. They all could be good sources for different green chemicals. A few inorganics are also present. Further hydrolysis, for example by enzymes, is normally needed when aiming at the production of platform products by fermentation.

Many processes have been carried out for the fractionation, purification, and production of components from HWE hydrolysates. Solvent extraction has been used for eliminating non-saccharide components from hydrolysates, giving rise to both an aqueous phase comprised of sugars and a solvent-soluble portion including phenolics and extractives-based compounds [Palmqvist & Hahn-Hägerdahl 2000a,b; Peng et al. 2012; Lehto 2015]. Solvent precipitations carried out with ethanol and acetone have been applied successfully to the frac-

tion of carbohydrate components from lignocellulosic hydrolysates [Kalapathy & Proctor 2001; Peng et al. 2009]. On a laboratory- scale for analytical purposes, various other chromatographic fractionation methods have been applied, including, high-performance anion-exchange chromatography (HPAEC) and size exclusion chromatography (SEC), for the recovery of hemicelluloses from hydrolysates with high purity. Various types of resins, like acrylic, polystyrene-based, and formaldehyde-phenol, as well as activated charcoals, have been used to recover plant extracts, such as flavonoids and hydroxycinnamates. Moreover, adsorbent resins have been used for the recovery of phenolics and ion-exchange resins and for the purification of lignocellulosic hydrolysates [Mourne et al. 2006; Jeong et al. 2014]. Processing hydrolysates with membrane assistance has attracted significant in the fractionation of hemicelluloses, especially from aqueous extracts.

In the pulp and paper industry, various filtration methods, for example, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are used, mainly for process water cleaning and reuse, spent liquor concentration, and fractionation, to remove color, and to treat bleaching effluents. For example, UF has been recommended for the separation of hemicelluloses from the thermomechanical pulp (TMP) production mills' process waters. The desired degree of purification can be achieved by designing membrane separation processes, by selecting the correct membranes with proper weight cut-offs (MWCOS), and by precisely choosing the effective conditions, such as applied pressures [Bhattacharya et al. 2005; Persson & Jönsson 2010; Almasrah 2017].

6.2 Soda-AQ black liquors

The black liquors obtained after soda-AQ pulping are the most significant by-products; they mainly consist of organic material and primarily include degraded products of lignin, and carbohydrates, and a slight portion of extractives, together with inorganic substances. This by-product is usually burned in the pulp mills' recovery boiler to get energy and cooking chemicals [Louhelainen and Alén 2009; Alén 2015]. So far, the only key marketable by-products obtained from black liquor are turpentine, tall oil, and lignin. In order to recover aliphatic acids from black liquor, there is still a deficiency in the economically viable technical separation process, potential industrial uses, and market. Apart from turpentine and tall oil, the fractional recovery of lignin and aliphatic carboxylic acids shows that commercial attractiveness will be a factor in the future [Alén & Sjöström 1980b, Alén 2015]. A number of marketable techniques have been presented for the separation and refinement of lignin from kraft black liquors, while the separation and purification of hydroxy acids and other impurities are still challenging. Several methods have been proposed in order to recover hydroxy acids after the removal of lignin and inorganics. Apart from that—an industrial process developed for the recovery of volatile acids—no

such process for the separation of other hydroxy acids exists on a mill-scale [Biggs et al. 1961; Alén & Sjöström 1980b; Niemi et al. 2011].

Membrane filtration technology has recently captivated researchers' attention due to its low energy, chemical requirements, and simple control features related to membrane pore size, process streams, and effective parameters. Moreover, no further pre-treatments are required for the process streams, so they can be directly processed. Typically, MF (0.1-10 μm), UF (1-20 nm), and NF (>2 nm) are three main membrane-based techniques instigated on an industrial level to isolate molecules on the base of different molar masses. Such membrane technology permits the separation of precise MM lignin from black liquor for the production of a number of high-value-added products [Toledano et al. 2010; Jönsson 2013; Almanasrah 2017]. Lignin can be recovered from alkaline black liquors by acidification methods using carbon dioxide or mineral acids, such as sulfuric acid [Alén et al. 1979]. Recently, electrodialysis (ED) has been proven to be one method for the recovery of organic acids, such as acetic, butyric, citric, formic, gluconic, lactic, and malic acids. This technique has been shown to be promising for recovering chemicals from acid-sulfite-spent liquors and alkaline black liquors in pulp industries, which can be reused during the pulping process. [Kumar 2016]. Ion-exclusion chromatography has also been studied recently for recapturing various aliphatic carboxylic acids, and it has been used for purification of these acids from other constituents. This technique seems promising, not only for volatile acids, but also for hydroxy acids, since they can be entirely cleaned from the inorganic fraction. However, more research is required for the improvement of this process [Alén et al. 1990; Alén 2015].

Another interesting technique used to distill volatile carboxylic acids using reduced pressure is vacuum distillation. This method can be effective for the purification of carboxylic acids present in black liquor when released from sodium salts [Pigman 1957; Alén 2015]. The esterification technique can be more effective for recovering selective carboxylic acids. In this case, when alcohol is used in the presence of a catalyst, the concentrated and acidified black liquor can be easily esterified to the corresponding esters. By further distillation, single fractions of acid esters, depending on their comparative volatilities, can be fractionated. However, attention should focus on the esterification of carboxylic acids for their complete recovery from black liquor [Kumar & Mahajani 2007; Alén 2015].

7 EXPERIMENTAL

7.1 Raw materials

For the laboratory-scale HWE experiments, two feedstocks of European origin, including wheat straw (*Triticum aestivum*) and giant miscanthus (*Miscanthus × giganteus*), from Finland and Germany, respectively, and one feedstock of Asian origin, okra stalk (*Abelmoschus esculentus*) from Pakistan, were used. All of the feedstocks were manually screened; leaves, nodes, and other visible impurities were removed from all straw samples, whereas only nodes were removed from the okra stalk samples. The air-dried feedstocks were then cut into lengths less than 5 cm [I-III]. For the laboratory-scale alkaline cooking experiments, both untreated and hot-water-extracted feedstocks were used [II-IV].

7.2 Hot-water pre-treatment

Laboratory-scale hot-water extractions were put in 1.25 liter rotating stainless steel reactors heated in a decene bath (CRS Autoclave System 420, Stenkullen, Sweden). Oven-dried feedstock of 80 g was fed in each reactor [II-IV]. HWEs were performed at the highest temperatures of 140 °C and 150 °C with P-factors of 50 and 200, respectively, as shown in Table 4. To obtain the maximum temperature, a heating time of 30 min was added to the total treatment time. In all of the experiments, the liquor-to-raw-material ratio (L/kg) was 5. After completion of each extraction, reactors were transferred directly from the oil bath to the cold water reservoir for rapid cooling. After HWE, the hydrolysates of each feedstock were then separated by filtration bags and stored in a freezer for further analysis after their pH was measured. The moisture content of the hot-water-extracted and untreated reference feedstock samples was determined. For a more detailed chemical analysis of the main components, such as the

overall content of carbohydrates, lignin, and extractives, these feedstocks were stored in a freezer.

TABLE 4. Experimental data on hot-water extractions

Sample	TM ^a (°C)	t ^b (min)	P-factor	Dry solid yield (%)	pH
OK ^c -140-P50	140	60	50	85.6	4.6
OK-140-P200	140	240	200	77.5	4.4
OK-150-P50	150	25	50	82.4	4.6
OK-150-P200	150	100	200	76.7	4.4
M ^d -140-P50	140	60	50	95.2	4.6
M-140-P200	140	240	200	93.2	4.4
M-150-P50	150	25	50	92.8	4.3
M-150-P200	150	100	200	90.0	4.2
W ^e -140-P50	140	60	50	94.2	5.6
W-140-P200	140	240	200	93.3	5.1
W-150-P50	150	25	50	91.5	5.5
W-150-P200	150	100	200	88.0	5.0

^a TM refers to maximum temperature, ^b t to time at maximum temperature, ^c OK to okra stalk, ^d M to miscanthus stalk, and ^e W to wheat straw.

7.3 Soda-AQ pulping

All of the laboratory-scale pulping experiments (soda-AQ) were conducted with the same reactors used during HWEs [II-IV]. As a reference, one untreated sample from each feedstock and two HWE samples from each, treated at 140 °C and 150 °C with a P-factor of 50 and 200, respectively, were pulped. During all of the experiments, each reactor was charged with 80 g of o.d. feedstock, and an AQ charge of 0.05% on o.d. initial material was used. An effective alkali (EA) charge was 15% on o.d. initial material for wheat straw, 20% on o.d. initial material for okra stalk, and 15% on o.d. initial material for miscanthus stalk. The liquor-to-feedstock (L/kg) ratio was 5. After the completion of each cook, reactors were directly shifted from the oil bath into a cold water reservoir for rapid cooling. The black liquor after separation from the pulp by squeezing, was kept in cold storage. The overall cooking criteria and experimental plan is shown in Table 5 and Fig. 8.

The pulp achieved was properly rinsed with water and based on o.d. initial material; the overall pulp yield was determined. Screening of all pulp samples was performed with a 0.2-mm laboratory screening device (a Somerville-type apparatus from Serlachius Oy, Finland), and the amount of “process yield” (HWE + pulping) was measured. Process yield also included the amount of ma-

terial loss in the HWE stage, as well as the amount of rejects during the pulp screening.

TABLE 5. Soda-AQ cooking parameters for the used non-wood feedstocks

Parameter	Okra stalk	Miscanthus stalk	Wheat straw
EA (% on o.d. feedstock)	20	15	15
AQ charge (% on o.d. feedstock)	0.05	0.05	0.05
Maximum cooking temperature (°C)	165	165	145
Cooking time (min)	180	60	15
H-factor	1960	355	44

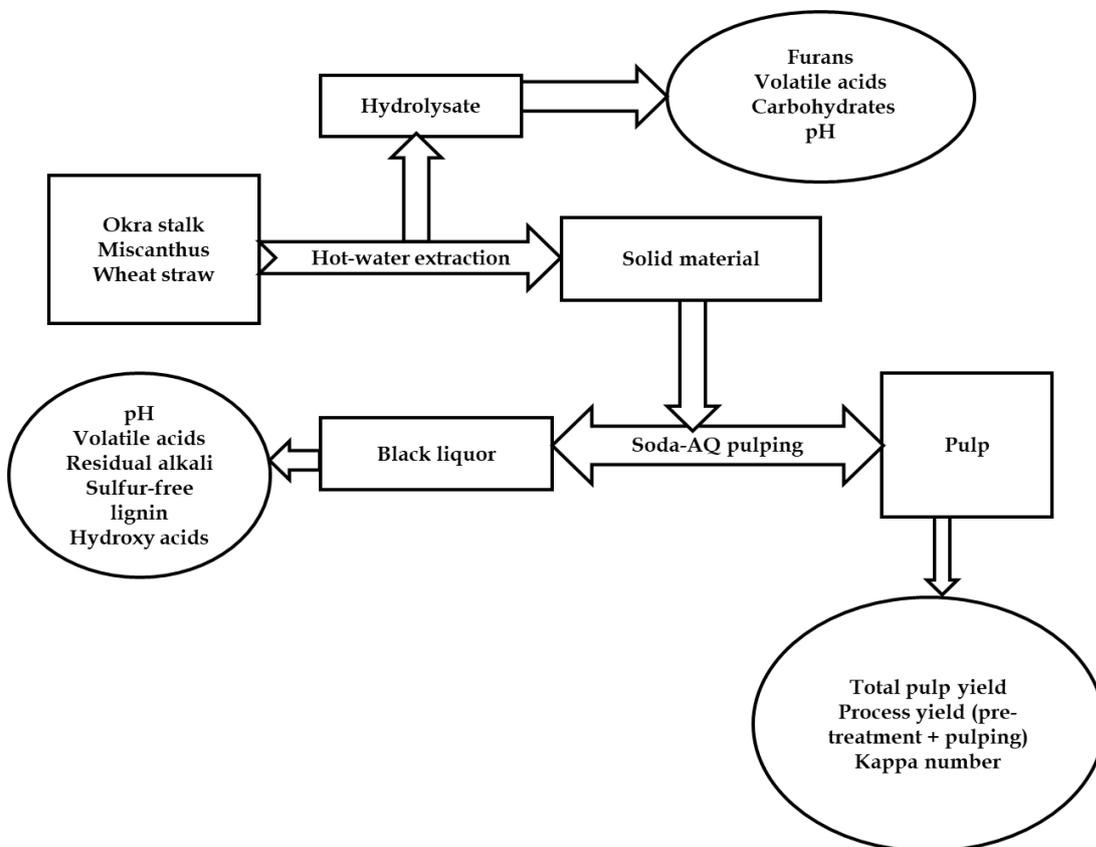


FIGURE 8. Schematic representation of experimental work.

7.4 Chemical analyses

7.4.1 Raw materials

Samples of raw materials were prepared for compositional analyses according to TAPPI (The Technical Association of Pulp and Paper) standards T257 cm-02 and T264 cm-07. The dry mass of all of the samples from feedstocks, pre-treated

raw materials, and pulps were measured by keeping a sample for twenty-four hours in an oven at 105 °C. Extractives analysis was performed by using the TAPPI standard 280 pm-99. TAPPI standard T222 om-98 was used to determine the content of lignin (acid-insoluble Klason lignin + acid-soluble lignin) gravimetrically from the extractives-free untreated and hot-water-extracted feedstocks. The measurement of acid-soluble lignin was taken by using a Beckman DU 640 UV/Vis spectrophotometer (Beckman Industries Inc., USA), as stated in the TAPPI um 250 procedure. The wavelength used was 205 nm, and the absorptivity value was 110 L/(gcm) [Swan 1965]. From klason hydrolysates, the content of various simple sugars comprised of arabinose, galactose, glucose, mannose, and xylose were analyzed with a high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) from Dionex Corp., Sunnyvale, CA, USA [Pakkanen & Alén 2013]. A flow rate of 1.0 mL/min was maintained for separation by using a Dionex CarboPac PA-1 column (250 mm x 4 mm inner diameter (i.d.)). Post-column alkali (300 mM NaOH) having a flow rate of 0.2 mL/min was added to boost the performance of PAD. In addition, for the identification of the peak and the mass-based calibrations between an internal standard (L-fucose, from Fluka Chemical Corp., Seelze, Germany) and each monosaccharide, separate runs were carried out with model monosaccharides. From acid hydrolysates, the content of the carbohydrates was determined and stated as anhydro forms of the measured monosaccharides. Furthermore, during acid hydrolysis, the decrease in the monosaccharide yield was determined separately. This yield decrease occurred due to the various side reactions, and by-products; the furan formation was also taken into account. The overall chemical contents of non-wood materials are shown in Table 6.

TABLE 6. Chemical composition of initial non-wood material (% of dry matter)

Component	Okra stalk	Miscanthus stalk	Wheat straw
Monosaccharides ^a	56.6	71.7	63.6
Arabinose	0.9	1.7	2.3
Galactose	0.8	0.4	0.8
Glucose	41.8	48.3	42.1
Xylose	12.2	21.3	18.3
Mannose	0.9	0.0	0.1
Lignin	20.5	17.8	22.2
Acid insoluble	17.3	17.7	20.1
Acid soluble	3.2	0.1	2.1
Extractives	5.0	1.5	3.2
Others ^b	17.8	9.0	11.0
Total	100.0	100.0	100.0

^aMonosaccharide moieties are presented as their anhydro forms.

^bOthers containing mainly acetyl and uronic acid groups of xylan, some pectins and other polysaccharides, and inorganics.

7.4.2 Hot-water hydrolysates

Carbohydrates

The overall content of various monosaccharides, such as arabinose, galactose, glucose, mannose, and xylose, and free monosaccharides was analyzed from the HWE hydrolysates after sulfuric acid hydrolysis, by using HPAEC-PAD from Dionex (Dionex Corp., USA), as mentioned in Chapter 7.4.1.

Volatile acids

Volatile acids from the HWE hydrolysates, such as acetic and formic acids, were measured by using a Dionex IC25 ion chromatography (IC) [Käkölä et al. 2008]. An EG40 eluent generator (KOH/ultra-high purity water) and a gradient elution maintaining a flow rate of 1.0 mL/min were used with a Dionex IonPac AS 11-HC analytical column (250 mm x 4 mm i.d.). Sodium acetate and sodium formate, both from Sigma-Aldrich, USA, were used as model substances as a basis for the identification of chromatographic peaks.

Furanoic compounds

Furanoic compounds such as furfural and HMF, formed during HWE, were determined by using a Hewlett Packard (Palo Alto, USA) 1100 series HPLC supplied with a Phenomenex Gemini C18 column [II-III]. A diode array detector (DAD) was used with a wavelength of 280 nm, and the injection volume was 25 μ L. For eluents, ultra-high quality water/acetonitrile (ACN) and pure ACN were used. A gradient program from 5% to 80% in 12 minutes, according to ACN, was used for elution and for keeping the eluent flow rate at 0.8 mL/min. Model substances, such as furfural and HMF (both from Sigma-Aldrich, USA), were used for the determination of chromatographic peaks.

7.4.3 Pulps

The pulp obtained after cooking was properly rinsed with water and, based on the o.d. initial feedstock, the total pulp yield was calculated. TAPPI standard T274 sp-04 was applied for the determination of screened pulp yields. A 0.2 mm laboratory screening device was used for screening pulp samples; the process yield (HWE yield plus pulping yield) was calculated by considering the material loss during HWE and the possible rejects volume in the process of pulp screening. The TAPPI standard 236 cm-85 was applied for the determination of the kappa number from the pulp [II-III].

7.4.4 Black liquors

A Beckman DU 640 UV/Vis spectrophotometer (280 nm in 0.1 M NaOH) using an absorptivity value of 20.9 L/(gcm) was used for the measurement of the dissolved lignin concentration according to Alén & Hartus [1988]. The mass bal-

ance of the overall pulping process also calculated the concentration of dissolved lignin in the black liquors. To measure the content of various monosaccharides, such as arabinose, galactose, glucose, mannose, and xylose, in Klason hydrolysates, a high performance anion exchange chromatograph with pulsed amperometric detection (HPAEC-PAD) from Dionex (Dionex Corp., USA) was used [Pakkanen & Alén 2013].

An anion exchange method (Dionex IC) was used for the determination of volatile acids (see above) in the black liquors [Käkölä et al. 2008]. Gas chromatography (GC) combined with a flame-ionization detector (GC/FID) was used for determining aliphatic hydroxy acids (hydroxy mono- and dicarboxylic acids) as their per(trimethylsilyl)ated derivatives. The sodium salts of hydroxy acids presenting in black liquors were first converted to ammonium salts, which were then per(trimethylsilyl)ated prior to the GC measurement [Alén et al. 1984]. The KCL procedure (number 67a:87) was applied for the determination of residual alkali in black liquors by using 1 M hydrochloric acid solution for titrating the diluted and carbonated black liquor sample to pH 11.5.

A gel permeation chromatography (GPC) system (a Waters HPLC equipped with a Superdex 75 gel column using 0.1 M aqueous NaOH as the eluent at a flowrate 0.3 mL/min) was used to measure the molar mass distribution (MMD) of dissolved lignin in black liquors. For the determination of MMs a Waters 996 photodiode array detector was used with a wavelength 280 nm [IV]. The GPC system calibration was carried out with a commercial set of protein standards (from Sigma) and a number of model compounds, similar to the monomers and oligomers in lignin [Pakkanen & Alén 2012].

7.4.5 Morphological surface analyses

A scanning electron microscope (SEM) (Zeiss Evo 50 SEM) was used to determine the morphology of the screened pulp (untreated/soda-AQ and hot-water-extracted/soda-AQ) samples. In this analysis, an adhesive carbon tape was used to hold a tiny droplet of fiber suspension, and it was dried in an oven at 80 °C for a half hour. A JEOL Fine Coat Ion Sputter JFC-1100 apparatus at lowered pressures applying a current of 5-6 mA for 4 min was used for preparing sputter-coated samples with gold.

8 RESULTS AND DISCUSSION

8.1 Removal of material during hot-water extraction

Table 3 shows the effect of HWE on the dry mass yield of initial non-wood feedstocks performed under various conditions. It can be clearly observed that with the increase in the P-factor of the pre-extraction process, an increase in the material loss occurs. This mass loss in okra stalk was from 14.4% in the mildest condition (140 °C and P-factor 50) to 23.3% in the harshest condition (150 °C and P-factor 200); for miscanthus, it ranged from 4.8% (at 140 °C and P-factor 50) to 10.0% (at 150 °C and P-factor 200), and for wheat straw, it ranged from 5.8% (at 140 °C and P-factor 50) to 12% (at 150 °C and P-factor 200). It could be observed from these results that the material loss was proportional to the increase in the P-factor, and such relation matched the results reported previously by Paredes et al. [2008]. When aiming at beneficial and qualitative pulp with good yield and minimal loss the adequate mass losses of 10-15% during the HWE phase were achieved at higher P-factors for the wheat straw and miscanthus than those for okra stalk. The higher mass loss in okra in comparison to that of wheat and miscanthus feedstocks obviously indicated that okra is more vulnerable to HWE. The porous structure of okra stalk in comparison to that of wheat straw and miscanthus could probably be the reason for this increasing extraction, since their chemical compositions were almost the same [Kleen et al. 2011].

8.2 Hot-water-extraction hydrolysates

Carbohydrates

The HWE also affected the formation of mono-, oligo-, and polymeric carbohydrates. The amount of carbohydrates increased with the severity of the HWE conditions, as presented in Appendices (I-III). The results from the hydrolysates

from the okra stalk showed that the amount of total carbohydrates were almost fourfold more than those in the equivalent hydrolysates from miscanthus and wheat straw. The reason for this rise in the carbohydrate content from okra stalk hydrolysates might be due to the fractional dissolution of “fluffy material” in the okra's stalk inner part, which seemed to be comprised mainly of carbohydrate substances. The amount of overall carbohydrates from all of the feedstock hydrolysates is shown in Fig. 9. As expected, the maximum amount of total carbohydrates derived from okra stalk, miscanthus, and wheat straw was achieved with a P-factor of 200 (at 150 °C, 100 min), which covered 20%, 6%, and 6%, respectively. Furthermore, it was noticed that the content of total carbohydrates in okra stalk hydrolysates was almost the same as that of soft wood. These cases were also reported earlier by Lehto [2015]. This can lead one to conclude that these carbohydrates in hydrolysates, i.e., after further enzymatic hydrolysis, will have a high possibility of offering a base for a broad spectrum of useful industrial chemicals (i.e., alcohols, acids, and other products) by fermentation [Alén 2011].

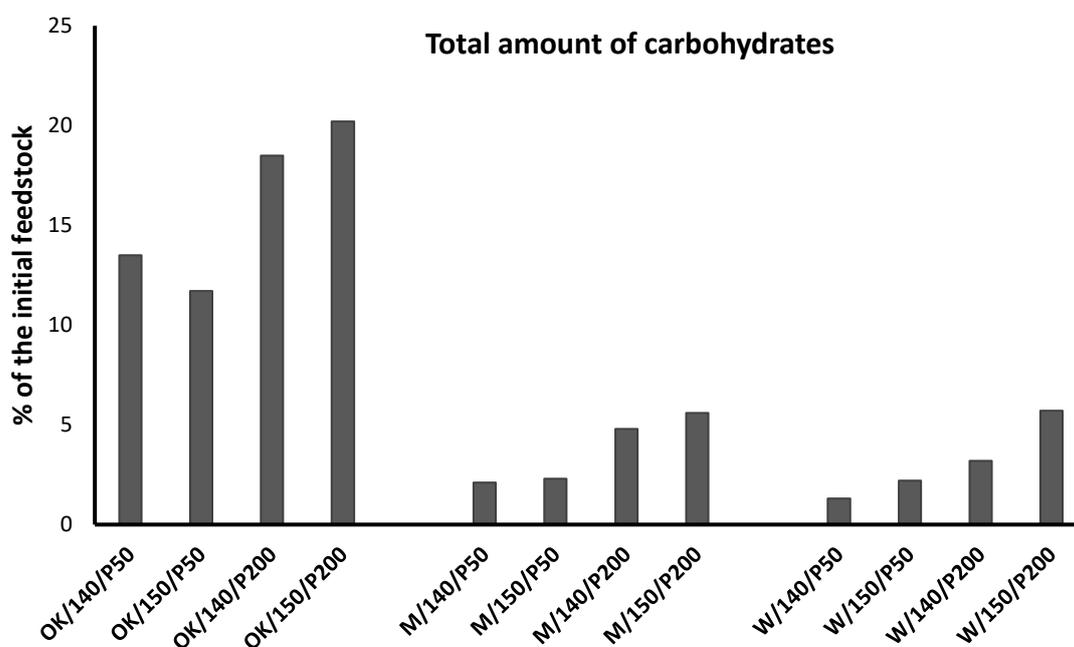


FIGURE 9. Total amount of carbohydrates in HWE hydrolysates [II-IV]. Ok for okra, M for miscanthus, and W for wheat straw.

Volatile acids and liquor pHs

Figs. 10 and 11 show the content of volatile acids in the hydrolysates. An increase in the amount of these acids occurred with an increase in temperature and P-factor; this was principally due to the deacetylation of hemicelluloses, but also partially due to additional increased degradation reactions [Zhang et al. 2011; Jönsson et al. 2013]. At higher temperatures, like in acid hydrolysis, the HWE phase led to unwanted side reactions, which generally decreased the comprehensive yield removal of hemicelluloses [Yoon et al. 2008; Tunc et al. 2010]. As a whole, a considerable quantity of acetic acid was obtained from okra,

compared to the corresponding miscanthus and wheat straw samples. These important volatile acids are chemicals that are extensively used industrially, and they can simply be obtained from hydrolysates by distillation and then utilized as popular industrial chemicals.

The pH is shown in Table 3. Based on the table, the pH of okra stalk and miscanthus hydrolysates ranged from 4.4 to 4.6 and 4.2 to 4.6, respectively, while the pH of wheat straw liquors (from 5.0 to 5.6) was comparatively high. The acetyl groups present in hemicelluloses underwent self-catalyzed acidic hydrolysis (deacetylation), which probably led to this pH drop, along with the formation of formic acid, for example, the total content of volatile acids. This kind of organic acid formation also assisted in breaking lignin-carbohydrate linkages, mostly typical for non-woods, and endorsed the further separation of hydrolysable hemicelluloses [Carvalho et al. 2008; Zhang et al. 2011].

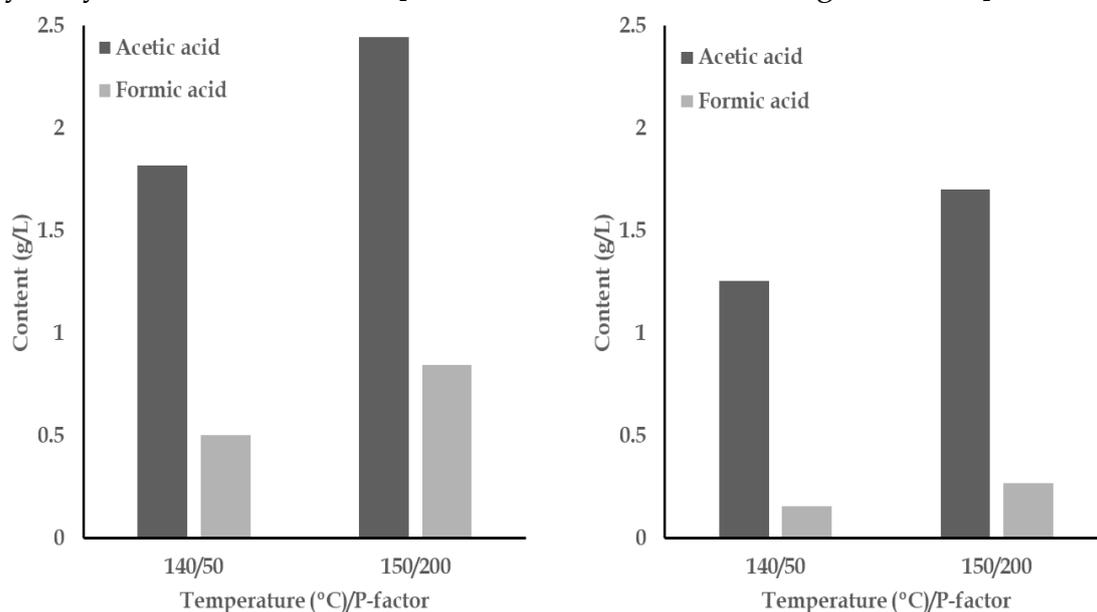


FIGURE 10. Volatile acids (acetic and formic acid) in okra stalk (left) and wheat straw (right) hydrolysates [II].

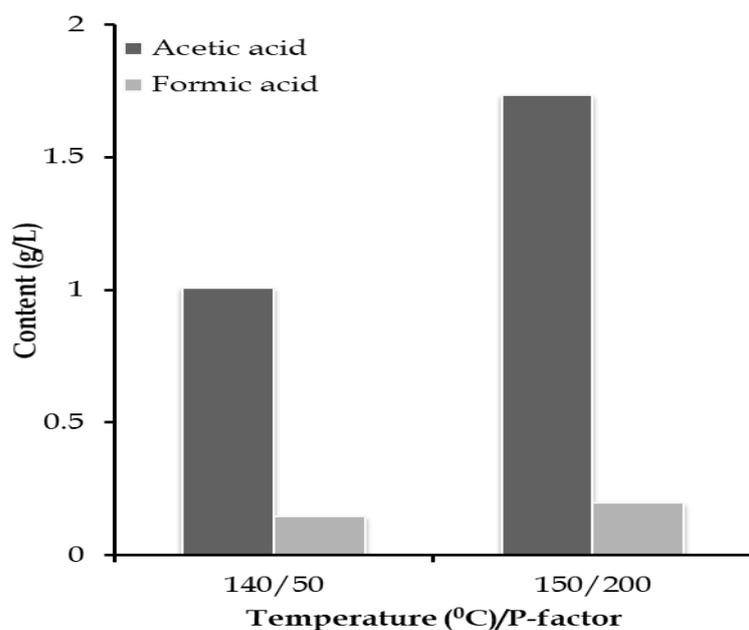


FIGURE 11. Volatile acids in miscanthus stalk hydrolysates [III].

Furans

Figs. 12 and 13 show the content of furans in the hydrolysates from okra stalk, wheat straw, and miscanthus. As can be seen, the formed volatile acids and the drop in pH facilitated the fractional breakdown and dissolution of hemicelluloses. The further hydrolysis of these hemicelluloses led to mono- and oligosaccharides [Lehto 2015]. Moreover, because of the acidic pre-treatment conditions, some monosaccharides were additionally dissolved into furans [Cardeiro et al. 2013; Jönsson et al. 2013]. The results indicate that, with the rise in the P-factor, the amount of both HMF (formed from hexosans, like glucomannan and cellulose) and furfural (formed from pentosans, like xylan and arabinan) improved. The maximum amount of furans obtained from all feedstocks was realized at a harsher pre-treatment condition; i.e., 150 °C with a P-factor of 200. It is noticeable that the amount of HMF in wheat straw and miscanthus hydrolysates was clearly lower than that of furfural while in the case of okra hydrolysates, the formation behavior of these components was the opposite (i.e., HMF was the dominant furanoic compound in the okra hydrolysates). These differences could be explained by the dissolution of different carbohydrates from each feedstock during the HWE phase. The main dissolved carbohydrates were hexoses (i.e., glucose, mannose, and galactose) in okra hydrolysates, while in the wheat straw and miscanthus hydrolysates, pentoses (i.e., xylose and arabinose) were the prime ones. Furthermore, the content of the furans in the hydrolysates from okra stalk was almost tenfold in comparison to the equivalent wheat straw and miscanthus liquors [II and III]. This higher amount of furans was justifiable since the hydrolysates from okra stalk also contain a higher amount of dissolved carbohydrates (i.e., the source for furanoic components). Furans must be

removed, as in some fermentation applications; they may act as inhibitors [Lehto 2015].

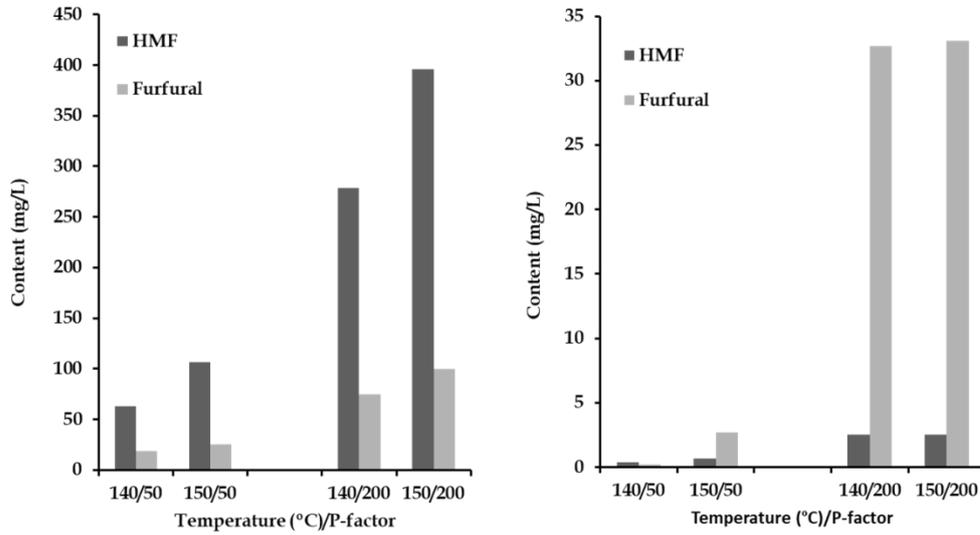


FIGURE 12. Furans in okra stalk (left) and wheat straw (right) hydrolysates [II].

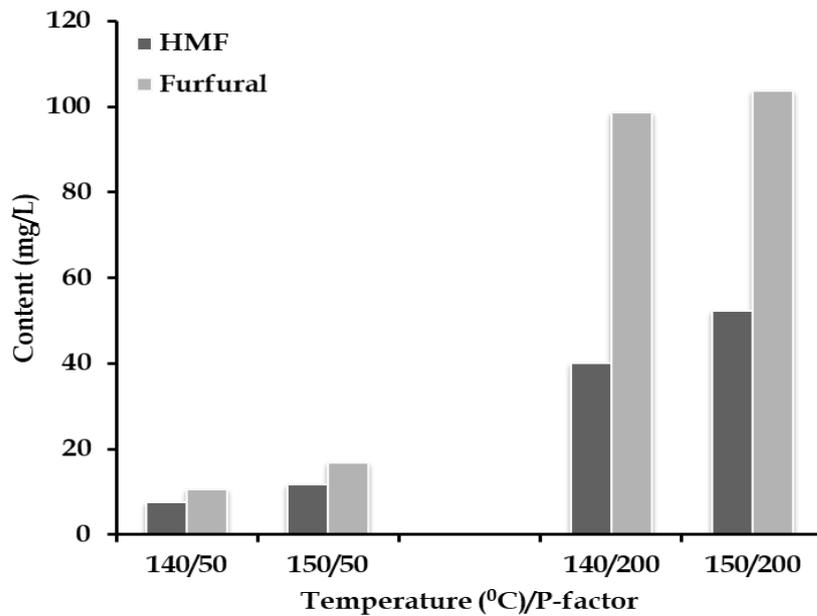


FIGURE 13. Furans in miscanthus stalk hydrolysates [III].

8.3 Soda-AQ pulping

Fig. 14 shows pulp yields. It can be seen from the soda-AQ cooking (EA 15%, 145 °C, and 15 min, see Table 4) that pre-treated and untreated wheat straw samples gave rise to comparatively reasonable pulp yields, whereas, under the same conditions, the okra stalk 1 samples were not pulped at all, as indicated by a very low screened yield. In the case of wheat straw, the total process yields (HWE + pulping) were about 50%. It is worth noting that, in the case of the HWE feedstocks, the pulp yield enhanced slightly with a rise in temperature and P-factor, but the total process yield was reduced to some extent, as the effect of HWE was also included [II and III].

With the aim of obtaining a reasonable pulp yield for okra stalk compared to that of other feedstock pulp yields, the cooking conditions for okra stalk 2 needed to be modified (i.e., EA 20%, 165 °C, and 180 min); the highest yield achieved was 39% for the untreated okra, as shown in Fig. 14. Additional material loss from the okra stalks during HWE affected the process yield of okra stalk pulp, which was lower than that of wheat straw pulp.

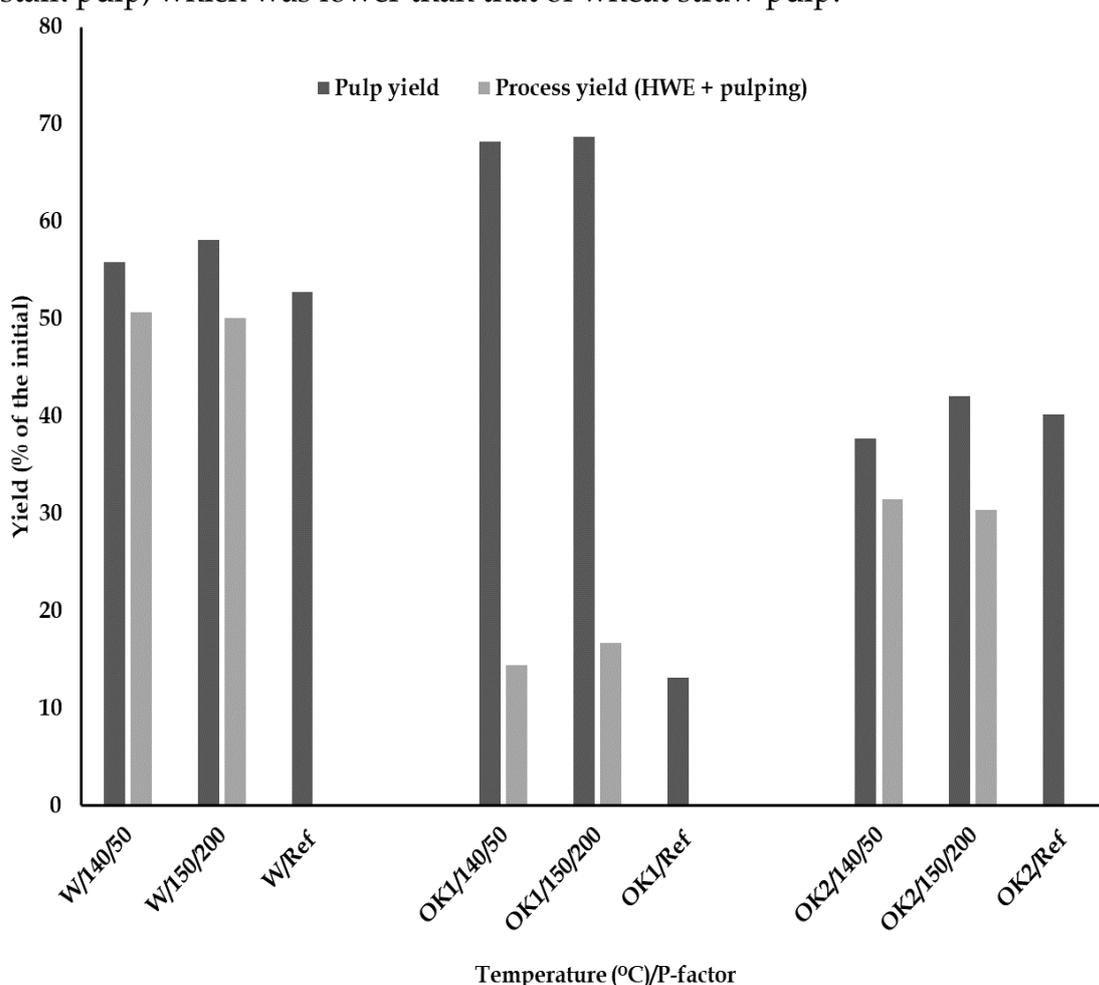


FIGURE 14. Soda-AQ pulp yields and total process yields [II]. W refers to wheat straw, OK1 to okra initial trial, and OK2 to okra secondary trial (under modified conditions).

From the difference in yields, it is clear that morphological variations exist between wheat straw and okra stalk. Fig. 15 shows the kappa numbers. In wheat straw pulps, the decreasing order $W/140/P50 > W/150/P200 > W/Untreated/Ref$ was observed, while the order of okra stalk pulps was $OK/150/P200 > OK/Untreated/Ref > OK/140/P50$. From the results, it is worth mentioning that the lowest and the highest kappa number was obtained under the same parameters ($150^{\circ}\text{C}/P200$) for the hot-water-extracted wheat and okra, respectively. The variance in kappa number might be due to differences in the structure of okra stalk and wheat straw lignin or, on the other hand, because of the partial and selective retainment of lignin on the surface of the fibers during HWE [Araya et al. 2015]. Fig. 15 also shows the residual alkali, mostly representing the total content of neutralized aliphatic carboxylic acids, such as acetic and formic acids, as well as various hydroxy acids produced during delignification [Alén 2011]. The results obtained showed that, in the case of okra straw black liquors, the concentration of residual alkali was visibly lower; this observation points out to the increased formation of organic carboxylic acids in the pulping phase when compared to the wheat straw cooks (Fig. 15).

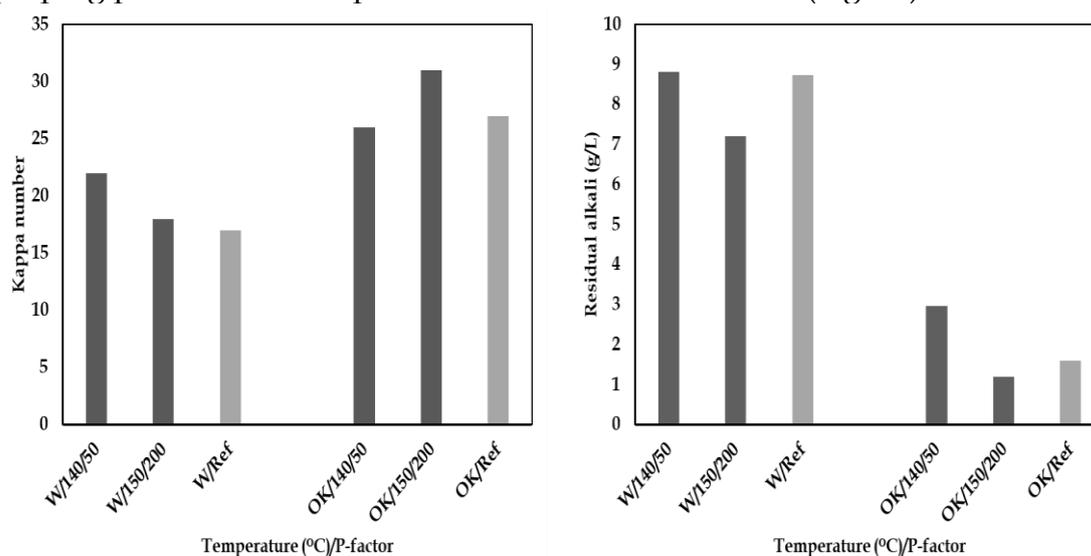


FIGURE 15. Kappa number (left) and residual alkali (right) in wheat straw and okra stalk black liquors [II].

In the case of miscanthus, the pulping behavior was somehow between that of okra stalk and wheat straw pulping. Fig. 16 indicates that the maximum process yield of 51% was achieved at 140°C and 60 min, which was probably due to the smaller loss in fines. It was observed that the harsher pulping conditions only slightly increased the total pulp yield, but no substantial difference could be detected. However, HWE showed an enhancing effect on the total pulp yield compared to the untreated miscanthus sample. In contrast, a decrease was observed in the process yield under severe conditions, i.e., at a high temperature and P-factor, which might be because of screening loss of fines and short fibers. In order to attain the desired target pulp yield with minimal loss

from miscanthus, 140 °C with a P-factor of 50 appeared to be the appropriate cooking condition.

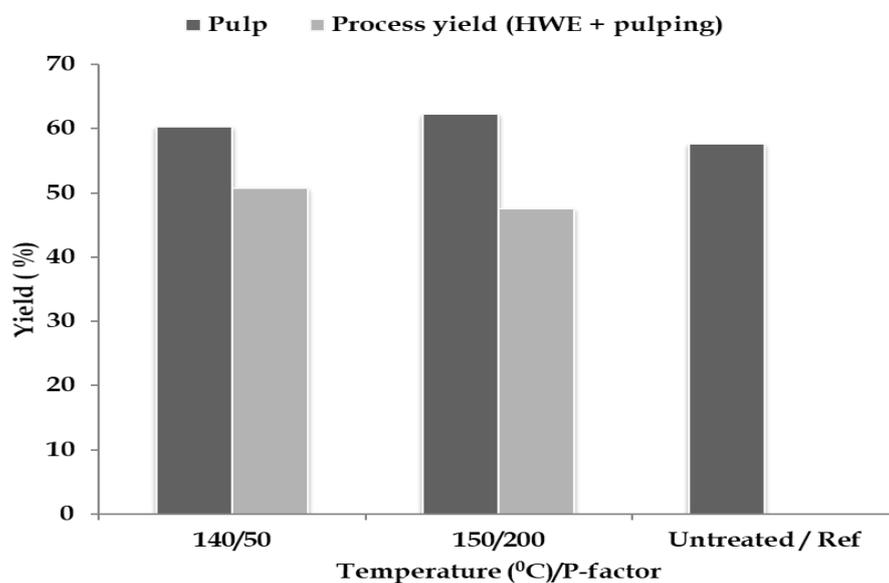


FIGURE 16. Soda-AQ pulp yields and total process yields of miscanthus [III].

8.4 Black liquors

The amount of volatile acids can be seen in Table 7, such as acetic and formic acids in black liquors from okra stalk, wheat straw, and miscanthus stalk, respectively. Pre-treatment affected the content of acetic acid in wheat straw black liquors, and an increase was observed with the rise in pre-treatment temperature, mainly indicating the enhanced removal of acetyl groups from hemicelluloses under harsher pre-treatments. Black liquors from untreated feedstocks resulted in the lowest content of formic acid formed by various degradation reactions of carbohydrates. The pre-treatment led to the enhanced formation of formic acid which could be explained by the creation of fresh reducing end groups to the carbohydrate chains; hence, large peeling reactions occurred in the subsequent pulping. In the case of okra black liquors, the content of the volatile acids was mainly the same for all feedstock materials, but it was significantly higher than that for the wheat straw feedstocks.

TABLE 7. Concentration of volatile acids in black liquors (g/L) [II-IV]

Sample^a	Acetic acid	Formic acid	Total
Wheat straw			
W/Untreated/Ref	3.4	1.3	4.7
W/140/P50	1.3	1.4	2.7
W/150/P200	2.0	2.7	4.7
Okra stalk			
OK/Untreated/Ref	11.0	4.2	15.2
OK/140/P50	11.1	5.3	16.4
OK/150/P200	13.2	6.8	20.0
Miscanthus stalk			
M/Untreated/Ref	9.5	2.0	11.5
M/140/P50	9.7	2.7	12.4
M/150/P200	9.5	4.5	14.0

^a OK refers to okra, M to miscanthus, and W to wheat.

In the case of miscanthus black liquors, the amount of acetic acid appeared to be identical at all temperatures, like okra stalk black liquor, but the amount of formic acid showed an increase along with a rise in the P-factor. The fractional recovery of these acids along with sulfur-free lignin is possible, and these acids can be utilized for several applications [Alén 2011].

Hydroxy acids

The content of individual non-volatile carboxylic acids in black liquors for untreated and pre-treated feedstocks is presented in Appendix IV. The results indicate that, in the cases of miscanthus and wheat black liquors, more hydroxy acids were formed from the pre-treated feedstocks than from the untreated feedstocks. It is known that the distribution of these acids strongly depends on the feedstock material and pulping conditions [Alén et al. 1989; Alén 2011]. Several alkali-catalyzed peeling reactions produced a wide range of hydroxy monocarboxylic acids and minor amounts of hydroxy dicarboxylic acids. In our black liquors, of the 22 acids analyzed, the main components were lactic, glucoisosaccharinic, glycolic, 2-hydroxybutanoic, xyloisosaccharinic, 2,5-dihydropentanoic, 3-deoxy-tetronic, and malic acids, with compositions similar to those of hardwood black liquors [Niemelä & Alén 1999; Alén 2011].

The overall maximum concentration of non-volatile hydroxy acids for the different feedstock-type samples was in the following order: okra black liquor (from the untreated feedstock) (28.7 g/L) > miscanthus black liquor (from the hot-water-extracted feedstock: 150°C/P200) (17.1 g/L) > wheat black liquor (from the hot-water-extracted feedstock: 150°C/P200) (11.5 g/L). The total concentrations of aliphatic monocarboxylic acids (volatile plus non-volatile acids) and non-volatile dicarboxylic acids are shown in Fig. 17. The results clearly show that, as the pre-treatment became harsher, the concentration of monocarboxylic acids increased, while that of dicarboxylic acids decreased.

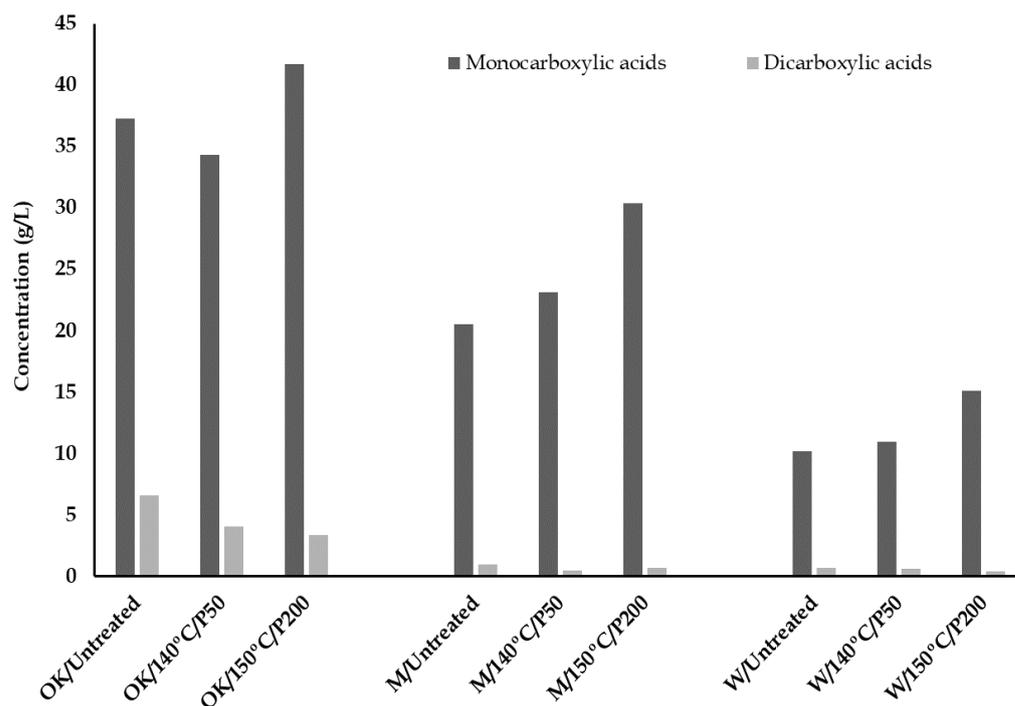


FIGURE 17. Total amount of carboxylic acids in okra (OK) stalk, miscanthus (M) stalk, and wheat (W) straw black liquors [IV].

Soda-AQ lignin

The rise in pre-treatment temperature led to an increase in the amount of lignin in black liquors, as shown in Fig. 18. As can be seen, the content of lignin in wheat straw black liquor was higher compared to that of okra stalk and miscanthus stalk. The maximum lignin amount was 45 g/L and 35 g/L at 150°C/P200 for wheat straw and miscanthus stalk, respectively, while in the case of okra stalk, it was 35 g/L at 140°C/P50. The increase in the lignin content in black liquors could be explained by the fact that, during pre-treatments the structure of feedstock materials becomes more porous, and hence, an increased dissolution of lignin was caused by the rise in pre-treatment temperatures and subsequent pulping.

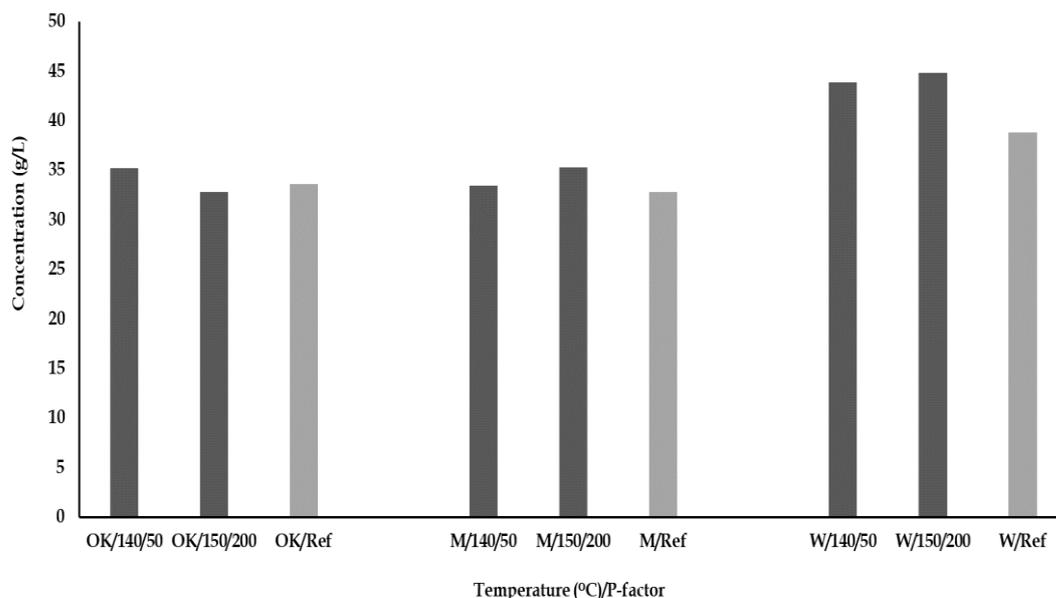


FIGURE 18. Concentration of dissolved lignin in black liquors [IV].

Molar mass distribution

Figs. 19-21 show the MMDs of the dissolved lignin in black liquors. Based on these results, pre-treatment seemed to characteristically affect the MMD. When the treatment became harsher, from P50 to P200, the relative portion of higher-molar-mass fractions ($>10,000$ g/mol) was increased with a simultaneous decrease in that of lower-molar-mass fractions ($<1,000$ g/mol). It was also noted that more lower-molar-mass fractions were found in the miscanthus black liquors than in the okra and wheat black liquors.

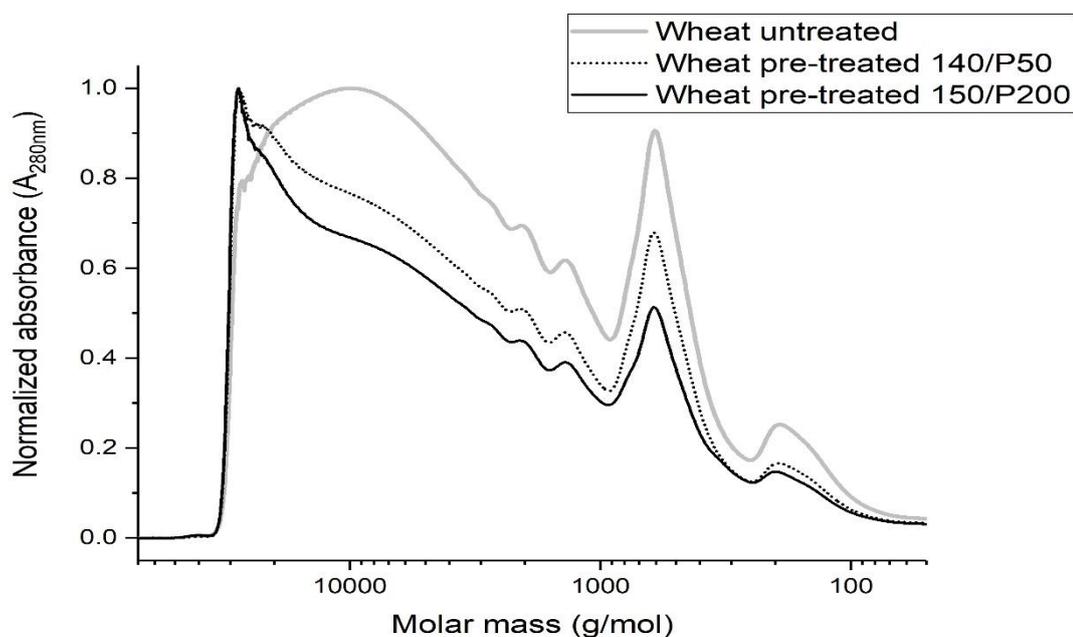


FIGURE 19. Molar mass distributions of lignin in wheat straw black liquors [IV].

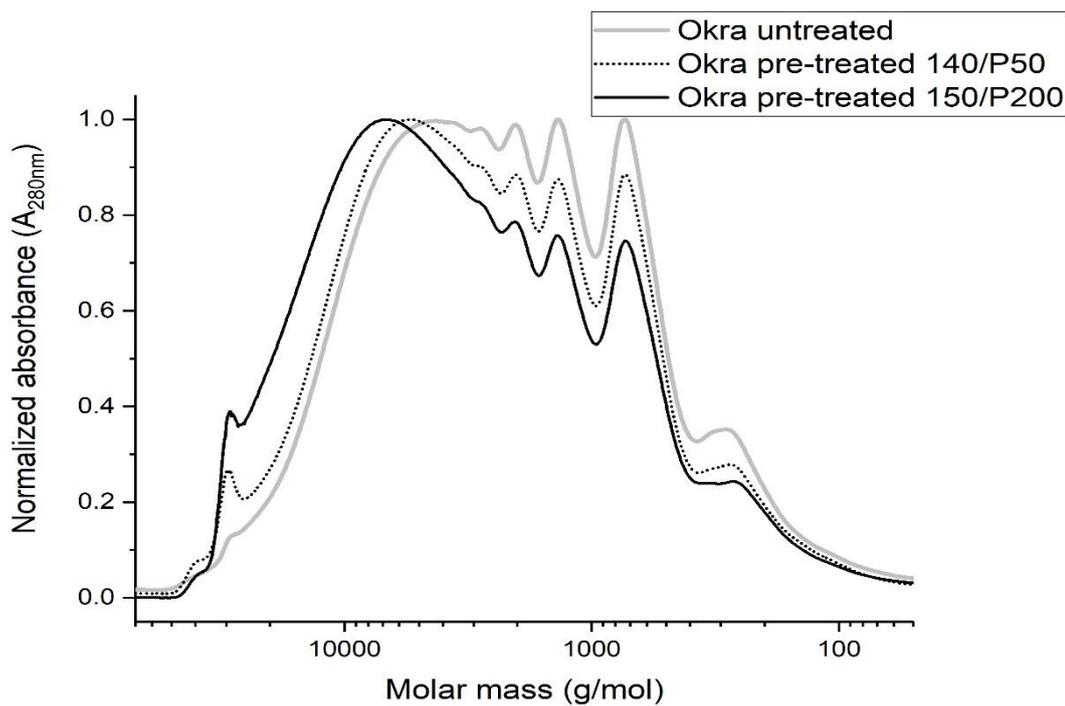


FIGURE 20. Molar mass distributions of lignin in okra stalk black liquors [IV].

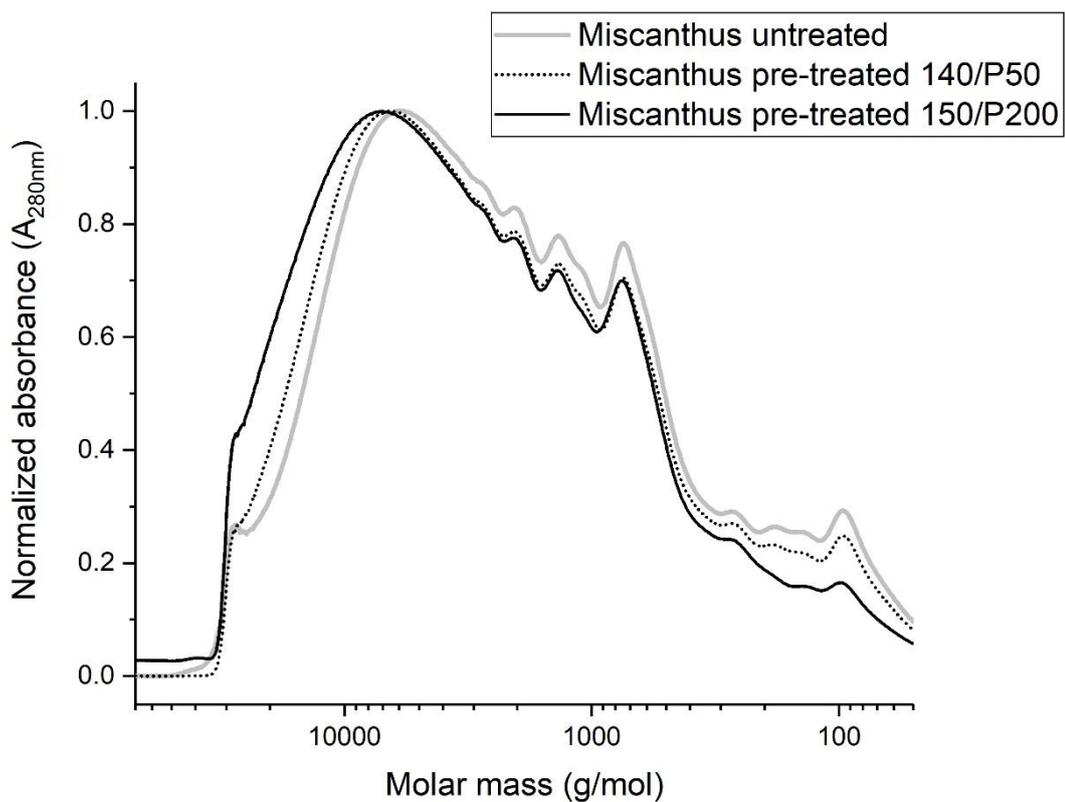


FIGURE 21. Molar mass distributions of dissolved lignin in miscanthus stalk black liquors [IV].

Table 8 shows the weight average molar mass (\bar{M}_w) values of the dissolved lignin in black liquors. When the pre-treatment conditions became harsher, the \bar{M}_w values increased; the lowest value detected was 4,160 g/mol for lignin in the okra black liquor from the untreated feedstock, and the highest value 8,730 g/mol was obtained for lignin in the wheat black liquor from pre-treated feedstock (150°C/P200). In each case, the dispersity index ($\mathcal{D}_M = \bar{M}_w/\bar{M}_n$) of the dissolved lignin is also given in this table; the lowest value 5.2 was obtained for okra/untreated, and the highest one, 8.8, was obtained for wheat/pre-treated (150°C/P200).

TABLE 8. Weight average molar mass (\bar{M}_w , g/mol) and dispersity index (\mathcal{D}_M , in parentheses) of lignin in black liquors [IV]

Sample	Untreated/Ref	140°C/P50	150°C/P200
Okra stalk	4,160 (5.2)	5,010 (5.5)	6,160 (6.1)
Miscanthus stalk	4,800 (8.8)	5,170 (8.5)	6,020 (7.7)
Wheat straw	7,160 (8.0)	8,340 (8.1)	8,730 (8.8)

Morphological surface analyses

The SEM images indicated that HWE caused partial damage to the surface structure of miscanthus stalk, as shown in Fig. 22. The main aim of these SEM images selected as an example was only to roughly detect the structural changes that occurred in the materials. Fig. 22A shows that the untreated stalk had a more compact structure than the stalks pre-treated at 140°C (P-factor 50) and 150°C (P-factor 200) (Figs. 22B and 22C, respectively; a slight degradation in the initial structure is noticeable and pointed out by the arrows. With an increase in the P-factor, the decomposition increased, giving rise to severe disintegration. These results were in agreement with the studies conducted earlier by Boakye-Boaten [2015].

On the other hand, the miscanthus stalk structure was clearly ruptured after the soda-AQ pulping (Figs. 22D, 22E, and 22F) occurred. When comparatively studied, the SEM images clearly showed that the rigidness of the matrix was softened with the pre-treatment prior to delignification. As could be expected at severe conditions, i.e., after cooking at 150°C (P-factor 200), complete disintegration of the matrix occurred, and the matrix was changed to only single fibers.

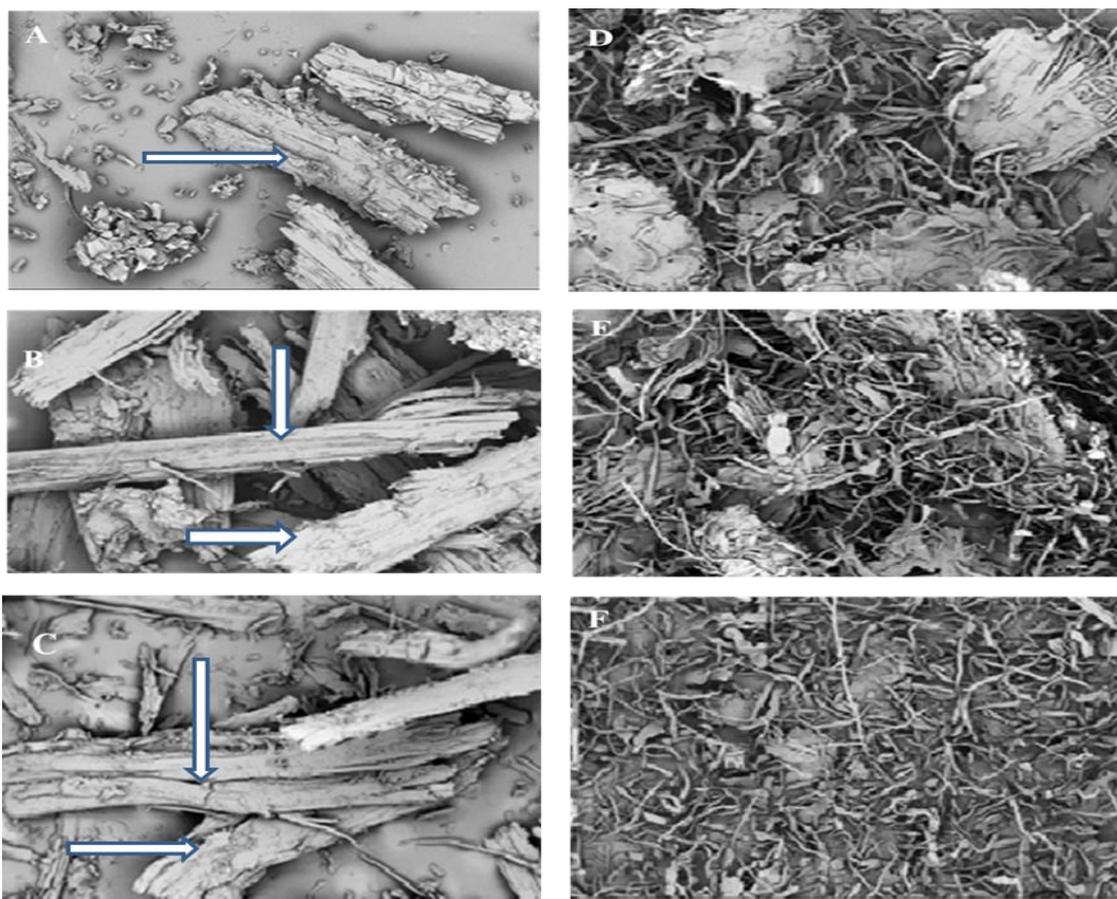


FIGURE 22. SEM images of *Miscanthus x giganteus* (magnification 100X and figure width corresponds to size 200 μm) before and after HWE [III]. Left (top to bottom); A) untreated, B) HWE 140-P50, and C) HWE 150-P200. Right (top to bottom); D) soda-AQ/untreated, E) soda-AQ/HWE 140-P50, and F) soda-AQ/HWE 150-P200.

9 CONCLUDING REMARKS

The HWE effect on the soda-AQ pulping of three different raw materials, namely, okra stalk, wheat straw, and miscanthus, was studied in detail. During the pre-treatment stage (HWE), the mass loss increased with the severity in treatment conditions, i.e., temperature and time. In addition, the fractional degradation of hemicelluloses in the forms of mono-, oligo-, and polysaccharides, as well as the production of some monomeric degradation products, volatile acids, and furans, was observed. The maximum mass loss from raw materials was 12.0%, 23.3%, and 10.0% for wheat straw, okra stalk, and miscanthus, respectively, at 150°C with a treatment time of 240 min, which also corresponded to the maximum content of dissolved carbohydrates in the hydrolysate.

In the pulping phase, the pre-treated raw materials were pulped with the soda-AQ method for achieving pulp and dissolved organic materials (sulfur-free lignin and aliphatic carboxylic acids). The maximum pulp yields obtained were 57%, 41%, and 51% for the HWE wheat straw, okra stalk, and miscanthus, respectively. In total, besides acetic and formic acids (volatile acids), 17 hydroxy monocarboxylic acids and 5 dicarboxylic acids (non-volatile acids) were detected in the corresponding black liquors. An increase in the total content of hydroxy carboxylic acids was detected for black liquors from the pre-treated materials, compared to the untreated materials. The maximum total content of aliphatic carboxylic acids (including volatile and non-volatile acids) was in the following order: okra/150°C/P200 (39 g/L) > miscanthus/150°C/P200 (31 g/L) > wheat/150°C/P200 (15 g/L). On the other hand, the total dissolved lignin was in the following order: wheat/150°C/P200 (45 g/L) > miscanthus/150°C/P200 (35 g/L) > okra/140°C/P50 (35 g/L). It could be concluded that these “opposite” results are mainly caused by morphological differences in feedstock materials.

The results showed that the pre-treatment step, prior to delignification, affected the subsequent soda-AQ pulping. The kind of biorefining approach presented in this research offers enormous possibilities for boosting the utilization of agricultural waste feedstocks, and at the same time, offers a broad spectrum of derived organic components (i.e., carbohydrates and organic acids) for pro-

ducing various value-added biomass-based industrial chemicals. Thus, for example, after utilizing carbohydrates-derived material in the pre-treatment hydrolysates, it might be possible to recover aliphatic carboxylic acids, especially from the okra black liquors, and lignin from the wheat black liquors.

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APPENDIXES

APPENDIX I: Content of carbohydrates in wheat straw hydrolysates (g/L).

APPENDIX II: Content of carbohydrates in okra stalk hydrolysates (g/L).

APPENDIX III: Content of carbohydrates in miscanthus stalk hydrolysates (g/L).

APPENDIX IV: Concentrations of hydroxy acids in okra, miscanthus, and wheat black liquors (g/L).

APPENDIX I

(1/4)

Content of carbohydrates in wheat straw hydrolysates (g/L)

	140/P50	150/P50	140/P200	150/P200
Monosaccharides	0.4	0.3	0.7	0.7
Arabinose	0.2	0.2	0.6	0.5
Galactose	-	-	-	0.1
Glucose	0.1	0.1	0.1	0.1
Mannose	0.1	<0.1	<0.1	<0.1
Xylose	<0.1	-	-	-
Oligo- and polysaccharides ^a	1.3	2.5	3.4	6.5
Arabinose	0.2	0.4	0.8	1.0
Galactose	0.4	0.5	0.7	0.7
Glucose	0.6	0.7	1.0	1.2
Mannose	0.1	0.2	0.2	0.2
Xylose	<0.1	0.7	0.7	3.4
Total carbohydrates	1.7	2.8	4.1	7.2
Arabinose	0.4	0.6	1.4	1.5
Galactose	0.4	0.5	0.7	0.8
Glucose	0.7	0.8	1.1	1.3
Mannose	0.2	0.2	0.2	0.2
Xylose	<0.1	0.7	0.7	3.4

^a Monosaccharide moieties are presented as their anhydro forms.

APPENDIX II

(2/4)

Content of carbohydrates in okra stalk hydrolysates (g/L)

	140/P50	150/P50	140/P200	150/P200
Monosaccharides	4.3	4.3	3.9	4.5
Arabinose	0.1	0.1	0.2	0.2
Galactose	0.1	0.1	0.2	0.2
Glucose	3.9	3.9	2.9	3.6
Mannose	0.2	0.2	0.4	0.4
Xylose	<0.1	<0.1	0.2	0.1
Oligo- and polysaccharides ^a	11.0	9.0	17.0	18.4
Arabinose	0.7	0.7	0.6	0.6
Galactose	1.0	0.9	1.4	1.2
Glucose	8.6	6.6	13.1	14.3
Mannose	0.4	0.5	0.4	0.4
Xylose	0.3	0.3	1.5	1.9
Total carbohydrates	15.3	13.3	20.9	22.9
Arabinose	0.8	0.8	0.8	0.8
Galactose	1.1	1.0	1.6	1.4
Glucose	12.5	10.5	16.0	17.9
Mannose	0.6	0.7	0.8	0.8
Xylose	0.3	0.3	1.7	2.0

^a Monosaccharide moieties are presented as their anhydro forms.

APPENDIX III

(3/4)

Content of carbohydrates in miscanthus stalk hydrolysates (g/L)

	140-P50	150-P50	140-P200	150-P200
Monosaccharides	1.5	1.5	2.9	4.1
Arabinose	0.4	0.5	1.1	1.5
Galactose	<0.1	<0.1	0.1	0.1
Glucose	1.0	0.8	1.0	1.5
Mannose	<0.1	<0.1	<0.1	<0.1
Xylose	0.1	0.2	0.7	1.0
Oligo- and polysaccharides ^a	1.5	1.8	4.0	3.9
Arabinose	0.2	0.3	0.5	0.1
Galactose	0.1	0.1	0.3	0.3
Glucose	0.8	0.8	0.9	0.6
Mannose	<0.1	<0.1	<0.1	<0.1
Xylose	0.4	0.6	2.3	2.9
Total carbohydrates	3.0	3.3	6.9	8.0
Arabinose	0.6	0.8	1.6	1.6
Galactose	0.2	0.2	0.4	0.4
Glucose	1.8	1.6	1.8	2.1
Mannose	0.1	0.1	0.1	0.1
Xylose	0.5	0.7	3.0	3.8

^a Monosaccharide moieties are presented as their anhydro forms.

APPENDIX IV

(4/4)

Concentrations of hydroxy acids in okra, miscanthus, and wheat black liquors (g/L)

Carboxylic acids	Okra stalk			Miscanthus stalk			Wheat straw		
	Ref ^a	140/P50	150/P200	Ref	140/P50	150/P200	Ref	140/P50	150/P200
Monocarboxylic acids	22.1	17.9	21.7	9.0	10.7	16.4	5.5	7.6	11.1
Lactic	6.5	3.4	3.6	1.7	1.7	2.1	0.8	1.0	1.4
Glycolic	3.3	2.2	2.1	1.6	1.6	1.9	0.8	1.0	1.2
2-Hydroxybutanoic	2.2	2.2	3.0	1.0	1.6	3.2	0.4	0.7	2.0
3-Hydroxypropanoic	0.1	0.1	0.1	0.1	0.2	0.5	0.1	0.2	0.4
2-Hydroxypentenoic	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
4-Hydroxybutanoic	0.2	0.2	0.1	0.1	0.1	0.2	0.1	0.2	0.2
2-C-Methylglyceric	0.3	0.2	0.2	+	+	+	+	+	+
Glyceric	0.5	0.3	0.3	0.5	0.2	0.2	0.1	0.1	0.1
Tartronic	+	+	+	+	+	+	0.1	0.1	+
3-Deoxy-tetronic	1.0	0.6	0.7	0.7	0.6	0.9	0.3	0.3	0.4
2-Deoxy-tetronic	+	+	+	+	0.1	0.1	0.1	0.1	0.1
3-Deoxy- <i>erythro</i> -pentonic	0.3	0.2	0.3	0.2	0.2	0.3	0.1	0.1	0.2
3-Deoxy- <i>threo</i> -pentonic	0.7	0.6	0.7	1.0	1.1	1.5	0.6	0.8	1.0
2,5-Dihydroxy-pentanoic	1.5	1.2	1.6	0.3	0.6	1.1	0.3	0.5	0.7
Xyloisosaccharinic	1.7	2.2	3.2	0.5	1.0	2.6	0.4	0.8	1.8
α -Glucoisosaccharinic	1.1	1.2	1.5	0.2	0.3	0.3	0.3	0.4	0.3
β -Glucoisosaccharinic	2.4	3.1	4.1	0.9	1.2	1.3	0.8	1.2	1.0
Dicarboxylic acids	6.6	4.1	3.4	1.0	0.5	0.7	0.7	0.6	0.4
Oxalic	2.2	1.5	1.4	0.2	0.2	0.2	0.3	0.3	0.2
Succinic	0.5	0.4	0.4	0.1	0.1	0.1	0.1	0.1	0.1
Malic	1.7	0.8	0.8	0.6	0.2	0.2	0.2	0.1	0.1
2-Hydroxyglutaric	1.0	0.8	0.4	0.1	+	0.1	+	0.1	+
Glucoisosaccharinaric	1.2	0.6	0.4	+	+	0.1	0.1	+	+
Total	28.7	22.0	25.1	10.0	11.2	17.1	6.2	8.2	11.5

+ indicates concentrations below 0.1 g/L.

^a indicates untreated.

ORIGINAL PAPERS

I

CHEMICAL CHARACTERIZATION OF OKRA STALK (*ABELMOSCHUS ESCULENTUS*) AS POTENTIAL RAW MATERIAL FOR BIOREFINERY UTILIZATION

by

Saleem Ullah, Petri Kilpeläinen, Hannu Ilvesniemi, Hannu Pakkanen & Raimo Alén

Journal of Cellulose Chemistry and Technology, 52(2018):155-162

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II

A COMPARABLE STUDY ON THE HOT-WATER TREATMENT OF WHEAT STRAW AND OKRA STALK PRIOR TO DELIGNIFICATION

by

Saleem Ullah, Hannu Pakkanen, Joni Lehto & Raimo Alén

Biomass Conversion and Biorefining, 8(2018):413-421

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III

HOT-WATER EXTRACTION OF *MISCANTHUS X GIGANTEUS* PRIOR TO SODA-AQ PULPING: A BIOREFINING PERSPECTIVE

by

Saleem Ullah, Hannu Pakkanen, Joni Lehto & Raimo Alén

Biofuels, (2018):1-7

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IV

**ORGANICS IN SODA-AQ BLACK LIQUORS FROM HOT-WATER-
EXTRACTED NON-WOOD FEEDSTOCKS**

by

Saleem Ullah, Hannu Pakkanen, Joni Lehto & Raimo Alén

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