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Microwave-assisted recovery of monomeric sugars from an acidic steam treated wood hydrolysate

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Abstract

Fractionation of components from bio-refinery wastes streams is complicated by the presence of both oligomer and lignin fractions. Microwave-assisted acid hydrolysis was used in this study to convert oligomer sugars in an industrial prehydrolysis liquor (PHL) to monomeric sugars. A total of 19.6 g/L monomeric sugars was obtained at a combined severity factor (CSF) of 3.2. Furthermore, it was found that xylan linked to lignin in a lignin-carbohydrate complex (LCC) could be liberated, resulting in lignin with a relatively low dispersity (3.12) and average molecular weight (1718 g/mol) that has high commercial value in the phenol−formaldehyde resin industry. This study presents for the first time a relatively inexpensive method for recovery of 100% of available sugars in the PHL without apparent loss in monomeric sugar as well as 50% removal of lignin as a valuable by-product. Application of this method can significantly improve the economic sustainability of forest-based biorefineries.

Keyword: Chemical engineering

1. Introduction

Hemicellulose is removed from wood chips in a prehydrolysis step prior to pulping and delignification in the dissolving pulp Kraft process. This is done to improve the quality of the cellulose for use in downstream applications such as the provision of viscose staple (Kumar and Christopher, 2017). Lignocellulose fractions in the prehydrolysis liquor (PHL), such as monomeric sugars, acetic acid and furfural, can be important sources of sustainable feedstock for bio-based fuels, chemicals and materials production. Oligomeric and monomeric sugars formed through the cleavage of polymeric acetyl groups during prehydrolysis can be used in the food, pharmaceutical and second-generation biofuels industries. Cleavage of acetyl groups also results in the formation of acetic acid (Hutterer et al., 2016), a known inhibitor of effective conversion of sugars to chemicals through biological pathways (Wang et al., 2014). Furfural, formed through dehydration of five−carbon sugars (Baktash et al., 2015) and a known inhibitor of sugar to ethanol fermentation, is a valuable platform chemical that is widely used in the oil refining, synthetic rubber, nylon and resin industries. Xylitol, a sugar substitute in many dietary and diabetic food products, can be produced from xylan/xylose. However, during prehydrolysis, some lignin fractions are co-extracted with hemicellulose sugars through cleavage of the aryl−ether bond (Wang et al., 2015). A high content of phenolic hydroxyl groups from lignin fractions in the PHL prohibits the formation of xylitol from xylan/xylose (Tong et al., 2017) and also causes undesirable side reactions during the production of furfural from xylan/xylose (Baktash et al., 2015).

Pure lignin is becoming more and more important in the biopolymer, materials and pharmaceutical industries as a sustainable source of phenolic hydroxyl groups. Fractionation of PHL streams to obtain relatively pure saccharides, acetic acid, lignin and furfural thus holds much promise for sustainable and environmentally responsible biorefineries, but the presence of both lignin fractions and oligomers with similar molecular cut-off sizes complicates their separation.

Several of studies have reported on strategies to recover sugars and acetic acid from prehydrolysis liquors, mostly through removal of lignin, but at the cost of a portion of the monomeric sugars. Most studies make use of multiple adsorptions steps combined with another separation technique such as ion-exchange, laccase treatment or membrane filtration to remove lignin, concentrate sugars or produce furfural.

Fatehi and co-workers (2013a) recovered oligomer sugars from an industrial PHL using precipitated calcium carbonate, but lignin and furfural had to be removed in a pretreatment step using a combination of dodecyltrimethyl ammonium chloride (DTAC) and membrane filtration to obtain substantial sugar recovery yields. Application of a combination of co-adsorbents polydiallyldimethyl ammonium chloride (PDADMAC) and cationic polyacrylamide (CPAM) (Fatehi et al., 2013b) increased

sugar yields to 530 mg/g. Separation of non-saccharide components (NSC) from a prepared poplar wood hydrolystate, studied by Wang et al. (2015) showed that ultra-filtration with a cut-off of between 1 and 50 Da were ineffective to remove lignin or recover sugars, even when polyaluminium chloride (PAC) was used as flocculant to improve filtration. Lime treatment, however, showed a selectivity of up to 90% towards NSC and macro-porous resins could remove almost all NSC, but at the cost of more than 20 wt.% loss in saccharides. Approximately 60% of lignin could be removed from an industrial PHL using laccase-induced polymerisation (Wang et al., 2014) and a further 15−20% lignin could be removed by subsequent flocculation using polymer flocculants and filtration. Baktash et al. (2015) could remove 84.7 wt.% lignin, 69.4 wt.% furfural and 66.8 wt.% acetic acid from an industrial PHL using a combination of adsorption by activated carbon, ion-exchange resins and nanofiltration. More recently, Zhuang et al. (2017) could increase the membrane flux of an industrial PHL through a cellulose membrane by 81.2% using PAC as flocculant to remove lignin and lipophilic substances prior to filtration. Some studies have reported on the nature and characteristics of lignin fraction present in the PHL (Hutterer et al., 2016; Tong et al., 2017). Fatehi et al. (2016) were the first to report on the presence of a lignin−carbohydrate complex present in industrial PHLs, and this observation was analytically confirmed by Hutterer et al. (2016). The presence of carbohydrates still attached to lignin implies the presence of additional sugars in the PHL that are lost when lignin is removed by the various recovery strategies.

From the current literature it can be concluded that separating the different fractions of valuable components from an industrial PHL is a complex task that requires multiple processing steps. Furthermore, recovery of all monomeric and oligomeric sugars and/or lignin can be accomplished only with a substantial increase in plant operating costs and additional capital investment.

The objective of this research is three-fold, i.e. 1) complete hydrolysis of all oligomeric sugars to monomeric sugars, 2) the removal of lignin from the PHL by precipitation and 3) ensuring the least possible loss of monomeric sugars to furfural and lignin to humins. Therefore, for the first time, we report in this paper on a selective microwave-assisted dilute acid hydrolysis methods for complete conversion of all oligomer sugars in an industrial PHL to monomeric sugars with high recovery of lignin. Furthermore, a severity factor for microwave pretreatment was used to determine the minimum pretreatment conditions that would result in the highest pure lignin recovery without loss of sugars to furfural formation or degradation products. This fractionation method results in high purity products and high sugar yields and can be implemented in-line on any paper mill with minimum capital investment.

2. Materials and methods

2.1. Prehydrolysis liquor

The steam treated acid hydrolysate used in this study was supplied from a pilot plant of a pulp and paper manufacturing company in South Africa (GPS coordinates: 25°34′0″ S, 30°40′60″ E).

Analytical grade sulphuric acid (98% H_2SO_4), acetic acid, xylose, mannose, arabinose, glucose, cellobiose, furfural and lignin were purchased from Sigma-Aldrich and use without further purification to construct a set of calibration curves for identification and quantification of components in the untreated and treated acid hydrolysates.

2.2. Microwave-assisted acid hydrolysis

All hydrolysis experiments were conducted in an industrial microwave system (Anton Parr Multiwave Pro). Microwave reaction vessels had a total volume of 100 mL each and 40 g of acidified PHL was used for each experiment.

Microwave-assisted acid hydrolysis was performed in power-controlled mode. During the power−controlled experiments microwave power was used as the set point and varied from 150 to 600 W. Acid concentration was varied between 0.2 and 0.8 wt.% with treatment times of 5−20 minutes. Since different biomass feedstocks have different neutralisation capacities (Mäki-Arvela et al., 2011) and pH effects hydrolysis, the pH of the PHL during different acidification dosages was recorded and is presented in Fig. 1.

No temperature ramping was conducted and thus the treatment time represents the time from first exposure of the PHL sample to microwave irradiation until cooling commenced at the end of the chosen treatment time. Cooling was achieved with air using the maximum fan level of 3 until a temperature of 55 °C was reached. The temperature of the system varied from 60 °C to 180 °C, depending on the power
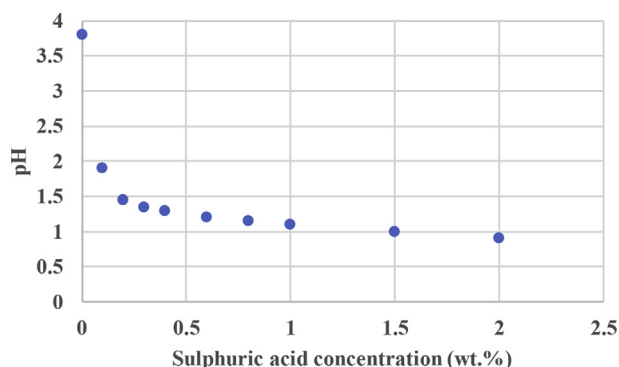

Fig. 1. Effect of acid dosage on the pH of the prehydrolysis liquor (PL) at room temperature.

setting used. Typical temperature profiles recorded at the different power settings are given in Fig. 2.

## 2.3. Quantification of oligomeric and monomeric sugars, acetic acid and furfural

High performance liquid chromatography was used to determine the concentration of monomeric sugars, acetic acid and furfural in the original PHL and treated samples.

An Agilent technology system 1200 series with an RI detector and equipped with a Biorad Aminex HPX-87P column was used with the standard method of the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008). A 5 mM sulphuric acid solution in water filtered through a 0.2 μm syringe filter was used as mobile phase at a flow rate of 0.6 mL/min and a column temperature of 55 °C. The system was calibrated for xylose, glucose, galactose, arabinose, mannose, acetic acid, formic acid, furfural, and hydroxymethylfurfural (HMF). The components were quantified using a set of standard calibration curves.

Oligomer sugars in the PHL were hydrolysed to monomeric sugars using 4% sulphuric acid at a temperature of 121 °C for 60 minutes (Fatehi et al., 2016). The treated sample was analysed for monomeric sugars using HPLC. The amount of oligomer sugars present in the PHL was determined by subtracting the initial amount of monomeric sugars from those determined in the PHL after hydrolysis.

2.4. Characterisation of lignin

Lignin was isolated from the PHL for analysis by acidification of 200 mL PHL with 180 μL of 98% sulphuric acid to a pH of 2 (Shi et al., 2011). The acidified sample was continuously stirred with a magnetic stirrer and the lignin fraction was recovered

Power setting: ●, 150 W; ●, 300 W; and ●, 450 W.
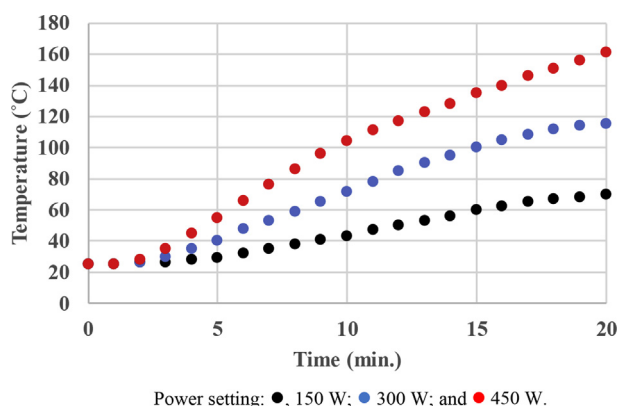
Fig. 2. Temperature profile of reaction mixture during power-controlled microwave-assisted hydrolysis in 2 wt.% sulphuric acid.

after 30 minutes using centrifugation at 6000 rpm for 5 minutes. The isolated solid lignin was collected from the bottom of the centrifuge after careful decanting of the liquid fraction and washed three times with 4% sulphuric acid solution in water to remove all unbound impurities (Sun et al., 2011). The liquid aliquot was analysed for dissolved lignin.

Fourier transform infrared spectroscopy (FTIR), ultraviolet and visible (UV-Vis) spectroscopy, and gel permeation chromatography (GPC) were used to characterise lignin−containing samples.

FTIR analysis was performed using a Shimadzu FTIR spectrophotometer (IR Affinity-1) with a wavelength range of 4000 to 400 cm^{-1}. All scans were conducted using potassium bromide (KBr) as background.

The molecular weight of lignin was determined using a Perkin Elmer Flexar System (Shelton, CT) with a refractive index (RI) detector and equipped with two Agilent PolarGel L columns (7.5 × 300 mm × 8 μm particle size). DMSO/water (9:1 v/v) containing 0.05 mol/L LiBr[20] was used as eluent. The oven temperature was 55 °C and a flow rate of 0.4 mL/min eluent was used with an injector volume of 100 μL and sample concentration of 8 mg/L. Samples were stirred for 24 h and passed through 0.45 μm syringe filters before injection. The system was calibrated with pullulan standards (Sigma Aldrich, batch BCBR0400V) with an average molecular weight distribution between 342 and 107 000 g/mol.

2.5. Quantification of acid-soluble lignin

Soluble lignin in the PHL was determine using UV spectroscopy (Shimadzu UV Mini 1240) at a wavelength of 205 nm. It has been reported that adsorption of furfural and HMF may interfere with lignin adsorption at a wavelength of 280 nm (Saeed et al., 2012). PHL samples were diluted with distilled water to achieve absorbance in the range 0.2−1. Absorbance was measured in a quartz cuvette with a path length of 1 cm. The measured absorbance was used to calculate the acid soluble lignin concentration with Eq. (1).

$$\text{Acid soluble lignin} = \frac{(\text{Absorbance})(\text{Dilution factor})}{\varepsilon\,(\text{Path length})}\ (\text{g/L}) \qquad (1)$$

where ε is the absorption coefficient with a value of 110 L/g/cm.

The amount of lignin removed during microwave pretreatment was calcualted using Eq. (2).

$$\text{Wt.\% Lignin Removed} = \frac{W_{L,Before} - W_{L,After}}{W_{L,\ Before}} * 100$$

Where $W_{L,Before}$ is the mass of lignin in the original acid hydrolysate, before treatment and $W_{L,After}$ is the mass of lignin present in the acid hydrolysate after microwave-assisted hydrolysis. The mass of lignin removed was confirmed by measuring the lignin left in the pretreated mixture as well as carefully weighing the amount of lignin (after drying) that precipitated during pretreatment.

3. Results and discussion

3.1. Compositional analysis of acidic steam treated wood hydrolysate

The compositional analysis of the PHL used in this study at a 95% confidence level is given in Table 1.

Lignin, oligosaccharides and monosaccharides constitute approximately 96.49 wt.% of the total solids in the PHL. The dilute nature of the PHL makes accurate determination of ash content difficult and therefore the ash content was determined by difference from the total solid content as 3.51 wt.%. Lignin accounted for 18.51 wt.% of the wood components in the PHL. The compositional analysis of the monosaccharides and oligomer sugars is given at a 95% confidence level in Table 2.

Table 1. Compositional analysis of PHL.

Component	Concentration (g/L)	Fraction	Concentration (g/L)
Xylose	2.16 ± 0.4	Insoluble solids	2.05 ± 0.003
Glucose	0.25 ± 0.01	Soluble solids	29.62 ± 1.05
Galactose	0.18 ± 0.03	Oligomer sugars	20.17 ± 0.64
Arabinose	0.36 ± 0.003	Monosaccharides	2.95 ± 0.1
Xylan	15.49 ± 0.49	Acetic acid	3.77 ± 011
Glucan	0.83 ± 0.005	Furfural	0.46 ± 0.05
Galactan	0.17 ± 0.06	Lignin	5.51 ± 0.26
Arabinan	0.05 ± 0.05		
Cellubiose	1.84 ± 0.12		
Citric acid	0.35 ± 0.03		
Formic acid	0.81 ± 0.12		
Acetic acid	0.35 ± 0.03		
Furfural	0.46 ± 0.05		
Glycerol	0.08 ± 0.008		
Sorbitol	0.23 ± 0.03		
Xylitol	0.07 ± 0.002		
Water	985.5 ± 14.23		

Table 2. Compositional analysis (g/L) of sugars in the PHL.

	Xylose	Glusose	Galactose	Arabinose	Acetic acid
Monosaccharides	2.16 ± 0.04	0.25 ± 0.01	0.18 ± 0.03	0.36 ± 0.03	3.77 ± 0.11
Oligomer sugars	15.49 ± 0.49	0.83 ± 0.05	0.17 ± 0.06	0.05 ± 0.05	3.62 ± 0.08
Total	17.66 ± 0.47	1.08 ± 0.04	0.35 ± 0.03	0.41 ± 0.04	7.4 ± 0.04

Oligomer sugars make up 84.56 wt.% of the total carbohydrate content of the PHL with xylan being the most abundant hemicellulose sugar present. Hardwood xylans are highly acetylated (Hutterer et al., 2016; Wang et al., 2014). The PHL contained 3.77 g/L acetic acid that was formed by cleavage of acetyl groups from the xylan chains during the prehydrolysis step. During the analysis of oligomer sugars a further 3.62 g/L acetic acid was formed through cleavage of acetyl groups that were still bound to the xylo-oligosaccharide molecules. The ratio of acetic acid released during hydrolysis of oligomer sugars to xylose was 0.58, which links the acetic acid formation during analysis to xylan hydrolysis (Li et al., 2010).

3.2. Microwave-assisted hydrolysis

Microwave power, sulphuric acid concentration and treatment time were used as variables to assess the influence of microwave-assisted hydrolysis on monomeric sugar, acetic acid, furfural and lignin concentration in an industrial PHL. Different combinations of power and time can result in the same energy input, although the manner in which the energy was applied was different. Furthermore, sulphuric acid concentration also influences the pH of the PHL and the effect of this is not readily discernible from linear data. In this study therefore, a combined severity factor (CSF) (Hsu et al., 2010; Um and Van Walsum, 2009) was used to determine the combined effect of treatment severity. The CSF used in this study is defined in Eq. (2).

$$CSF = \log\left\{ t \cdot \exp\left(\frac{T_H - T_R}{14.75} \right) \right\} - pH \qquad (2)$$

where t (minutes) is the total treatment time, T_H (°C) is the treatment temperature and T_R is a reference temperature. Although a value for T_R of 100 °C is commonly used, in this study a value 0 °C was used to ensure that all calculated CSFs had a positive value.

In an attempt to disentangle the effect of individually changed variables, treatment severity is presented as a function of each variable in the following sections. The average experimental error for this study was calculated by performing experiments in triplicate, to be 3.53% at a confidence level of 95%.
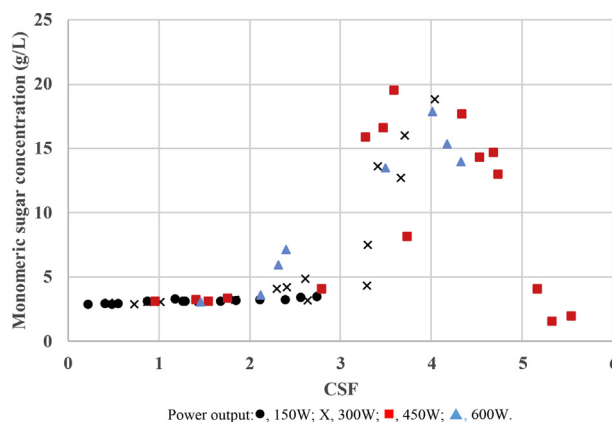
3.2.1. Effect of microwave power

During microwave irradiation, the irradiated medium is heated by means of an induced electromagnetic field (Thostenson and Chou, 1999). As the electromagnetic wave travels through the medium, energy is transferred at a molecular level through interaction with ionic groups and dipoles. The amount of energy per unit carried by the wave is proportional to the microwave power output. The effect of microwave power output in monomeric sugar concentration can be seen in Fig. 3.

No significant changes in monomeric sugar concentration were observed for a CSF lower than ∼2.8, but at higher CSF values all microwave power outputs showed a sharp increase in sugar concentration and an eventual decline with increased treatment severity (CSF > 3.5). An increase in both monomeric sugar concentration (See Fig. 3) and acetic acid concentration (see Fig. 4) is observed for CSFs between 3 and 4. Acetic acid is formed when acetyl bonds in the hemicellulose polymer is hydrolysed to yield monomeric sugars such as xylose. The simultaneous increase in both monomeric sugar and acetic acid concentration in this study therefore confirms the hydrolysis of the oligomeric sugars to monomeric sugars and acetic acid.

As microwave power output increases, more energy becomes available for the cleavage of β (1−4) glycosidic linkages in xylan and O2 and/or O3 linkages in glucan, arabinan and galactan oligomers. Acetic acid concentration steadily increased with an increase in CSF until enough energy was available to cleave the acetyl bonds in hemicellulose, resulting in the sharp increase in acetic acid concentration and monomeric sugar concentration at CSF higher than 2.8.

There are multiple depolymerisation and condensation reactions taking place simultaneously during acid hydrolysis; which bonds will be severed is dependent on the type and magnitude of available energy to supply the required activation energies (Shatalov et al., 2017). Acetic acid concentration remained approximately constant
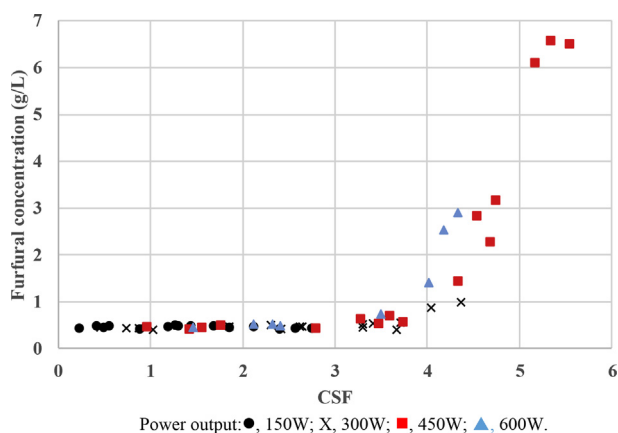

Fig. 3. Effect of combined treatment severity as a function of microwave power output on total monomeric sugar concentration.

Power output: ●, 150W; X, 300W; ■, 450W; ▲, 600W.
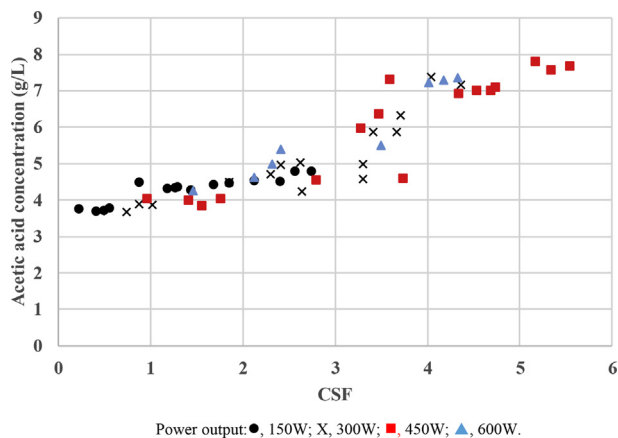
Fig. 4. Effect of treatment severity as a function of microwave power output on acetic acid concentration.

at higher CSF values where sugar concentration was seen to decline with an increase in CSF. The latter is ascribed to the formation of furfural from the dehydration of xylose as is seen in the furfural profile with increasing CSF (see Fig. 5).

Dehydration of one mole of xylose should produce one mole of furfural (Liu et al., 2015; Vallejos et al., 2015). Comparing the amount of xylose lost to furfural formed shows that much less furfural was formed than xylose lost at higher CSF. Furfural production starts only after all monomeric sugars were recovered from oligomers and lignin−carbohydrate complexes (LCCs). Therefore, from this result it can be deduced that the formation of furfural from the dehydration of xylose requires much more energy than the hydrolysis of sugars from the respective oligomer sugars. This is in agreement with reports by Yang et al. (2012) and Shatalov et al. (2017). Furthermore, a microwave power output of 450 W at a CSF of between 2.8 and 3 is sufficient to recover all sugars present in the PHL as monomeric sugars without loss to furfural formation. Also, by careful application of severity conditions, the

Power output: ●, 150W; X, 300W; ■, 450W; ▲, 600W.

Fig. 5. Effect of treatment severity as a function of microwave power output on furfural concentration.

microwave-assisted method presented here can be used either to recover all monomeric sugars, or to completely convert recovered xylose to furfural in a short treatment time.

3.2.2. Effect of sulphuric acid concentration

The effect of treatment severity as a function of sulphuric acid concentration is presented in Fig. 6.

Maximum sugar concentration was again reached at higher acid concentrations at lower CSF values. Interestingly, two maxima for monomeric sugar concentration can be observed in Fig. 6, i.e. at CSF values of between 2 and 3 and between 3 and 3.5 respectively. The same trend was observed in the acetic acid, xylose, arabinose and galactose concentration profiles but not in the glucose, furfural and lignin profiles. Hemicellulose consists of some fractions that are more easily hydrolysed than others (Esteghlalian et al., 1997; Mäki-Arvela et al., 2011). The composition of both fractions is dependent on the type and number of bonds between constituent oligomers (Ma et al., 2017). Because it is only xylose, arabinose and galactose sugars together with acetic acid in a ratio of 20:1.5:1:18 (w/w) that showed this phenomenon implies that the easily hydrolysed fractions consisted mainly of xylan bonded to arabinan and galactan by acetyl linkages. The more easily hydrolysed fraction of hemicellulose made up approximately 36 wt.% of the oligomers in the PHL. Puchart and Biely (2015), showed that acetyl groups within oligomer structures migrated during hydrolysis and that 2 O-acetyl derivatives were hydrolysed much faster that 3 O-acetyl derivatives during hydrolysis with acetylxylan esterase.

Both an increase in microwave power and sulphuric acid concentration resulted in an increase in xylose and acetic acid concentration in this study. Cleavage of acetyl groups in hemicellulose fractions should result in a mole ratio of formed xylose to

Sulphuric acid concentration: ●, 0.2 wt.%; X, 0.4 wt.%; ■, 0.6 wt.%; ▲, 0.8 wt.%.
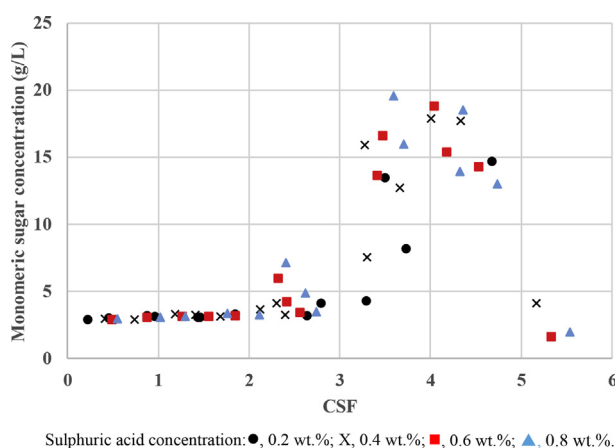
Fig. 6. Effect of treatment severity as a function of sulphuric acid concentration on monomeric sugar concentration.

acetic acid of 0.5 (Li et al., 2010; Pawar et al., 2013) and the higher ratio of 1:0.9 found in this study means that acetic acid was not only produced from cleavage of hemicellulose acetyl linkages. Takeuchi et al. (2008) and Liu et al. (2013) proposed that additional acetic acid can be produced from degradation of hexose and pentose sugars. Fig. 6 shows that sugars released from cleavage of easily hydrolysed acetyl groups were consumed at higher CSF values, while acetic acid still increased, which supports the observations of Takeuchi et al. (2008), yet the final maximum sugar concentration obtained was equal to the theoretical maximum sugar concentration predicted from the sum of initial monomeric sugars and hydrolysis of oligomer sugars present in the PHL. It has been observed that lignins in hardwoods are highly γ-acetylated (Del Río et al., 2007) with more than 45% of alkyl−aryl ether linkages in lignin acetylated. Zhao et al. (2018) showed the acetylated linkages to be highly acetylated xylans and demonstrated that LCCs can be present as either xylan-rich or lignin-rich complexes. The latter contain lignin that is less branched (mainly syringyl units). Only a portion of xylan in these type of LCCs are hydrolysed to xylose during the standard methods of determining oligomer content of the PHL (Sun et al., 2011). Therefore, the estimated potential monomeric sugar content of the PHL was underestimated. We propose that microwave irradiation together with the addition of sulphuric acid resulted in liberation of all xylan sugars in LCCs to xylose and thus the loss in sugars to acetic acid due to degradation under the less severe treatment conditions (low CSF) were not observed under more severe treatment conditions (high CSF) because it was partially obscured by the additional xylose liberated from the LCCs. The additional xylose liberated from LCCs was, however, enough to make up for monomeric sugar losses to acetic acid so that the final observed sugar concentrations were still equal to the theoretical maximum sugar yield.
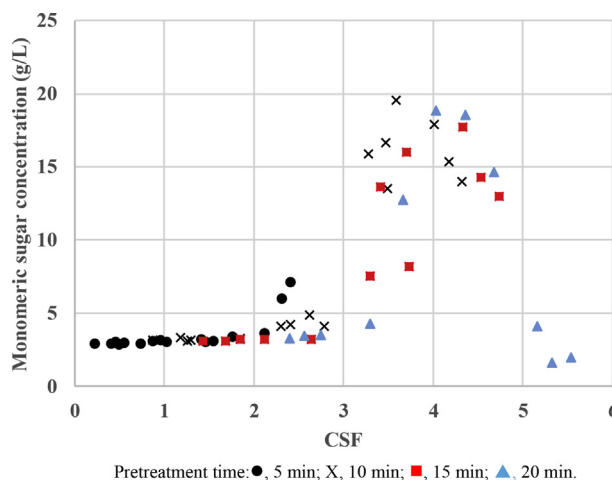
3.2.3. Effect of treatment time

The effect of treatment severity as a function of treatment time on monomeric sugar concentration is presented in Fig. 7.

Maximum sugar concentrations decreased with an increase in treatment time and treatment severity. This is in agreement with the results of Yang et al. (2012). A treatment time of 10 minutes at a CSF of approximately 3.5 resulted in complete recovery of oligomer sugars without an apparent loss in monomeric sugars.

3.2.4. The fate of lignin

The effect of treatment severity on lignin concentration as a function of microwave power output is given in Fig. 8.

Interestingly, lignin concentrations did not decrease significantly for CSF values lower than 2.8. Lignin removal only became prominent at the same CSF at which
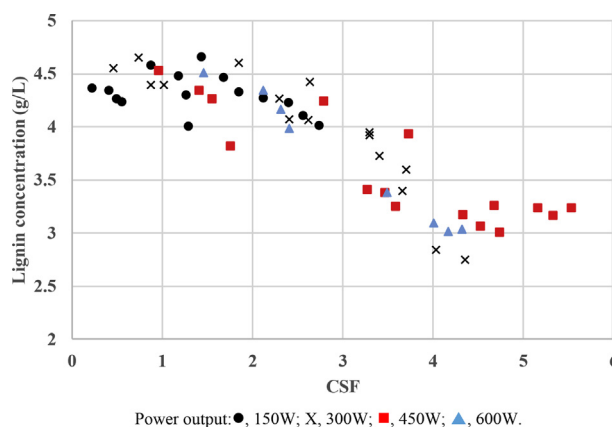
Fig. 7. Effect of treatment severity as a function of pretreatment time on monomeric sugar concentration.

increased sugar and acetic acid concentration was observed, confirming the presence of LCCs in the PHL as also observed by other researchers (Fatehi et al., 2016). Costa et al. (2017) estimated that LCCs contain as much as 40% (w/w) carbohydrate groups and Hutterer et al. (2016) showed that the carbohydrates in the LCC are primarily xylan fractions. The LCC in the PHL used in this study contained approximately 36% (w/w) carbohydrates that consisted mainly of xylan, arabinan and galactan linked by acetyl bonds.

FTIR spectra on lignin recovered through acidification of the PHL as well as lignin recovered after microwave treatment is given in Fig. 9. Assignment of most prominent peaks in the spectra is given in Table 3.

FTIR analyses on lignin recovered from the treated PHL showed a significant decrease in hydroxyl groups at adsorption band $3321 cm^{-1}$, but little change in syringyl (1328 and 1155 cm^{-1}) and guaiacyl (1260, 1220, 1121 cm^{-1}) bands. The

Fig. 8. Effect of treatment severity as a function of microwave power output on lignin concentration.
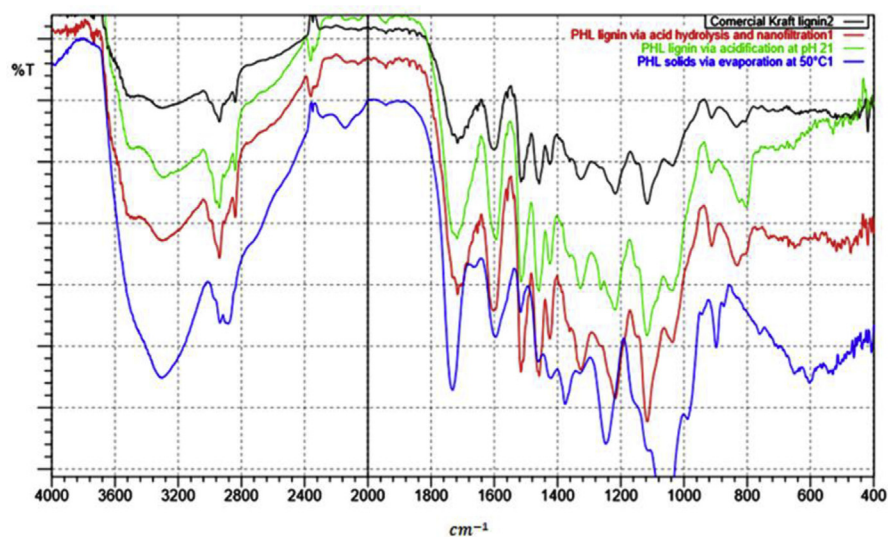
●, Kraft lignin; ●, PHL lignin recovered by microwave pre-treatment and nanofiltration;
●, PHL lignin precipitated by acidification at pH 2; ●, Dissolved solids of the PHL.

Fig. 9. Comparison of FTIR spectra of different lignin samples.

Table 3. Assignment of adsorption bands.

cm^{-1}	Assignments
3312	OH groups
2938	CH stretching of methyl and methylene or methane groups
1725	C=O stretching of unconjugated ketone and carboxyl groups
1658	C=O stretch in conjugated ketones
1600	Aromatic skeletal vibrations
1515	Aromatic skeletal vibrations
1457	Aromatic methoxyl group vibration
1425	Aromatic skeletal vibrations
1372	Aliphatic CH stretch in CH$_3$
1328	Syringyl ring breathing with CO stretching
1263	Guaiacyl ring breathing with CO stretching
1242	C-O bonds of acetyl ester units in hemicellulose
1220	Guaiacyl ring breathing with CO stretching
1155	Aromatic CH in-plane deformation of syringyl units
1121	Aromatic CH in-plane deformation of guaiacyl units
1042	C-O, C-C stretching and the glycosidic linkage contributions
989−600	Condensed lignin and hemicellulose structures, and silicate contributions
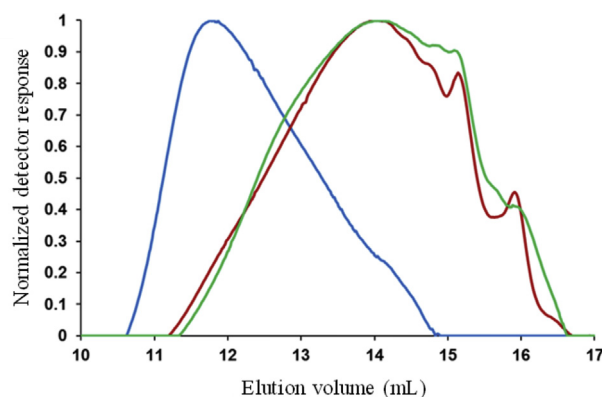
Fig. 10. GPC chromatographs of a commercial Kraft lignin −, PHL lignin isolated by acidification −, and PHL lignin recovered after acid hydrolysis −.

Table 4. Weight average molecular mass (M_w) and number average molecular mass (M_n) and dispersity index (Đ) of lignin fractions.

	Kraft lignin	Lignin recovered by acidification from untreated PHL	Lignin recovered from treated PHL
M_w	9623	1930	1718
M_n	1635	576	551
Đ	5.89	3.35	3.12

latter confirms that a loss in hydroxyl groups from the lignin is due to liberation of sugars from the attached carbohydrate groups (see Fig. 10; Table 4).

Weight average molecular mass (M_w) and number average molecular mass (M_n) of lignin fractions recovered from the treated PHL was determined by GPC analysis (see Fig. 8 and Table 3) and compared to that of synthesis grade Kraft lignin (Sigma Aldrich) and lignin isolated from the original PHL through acidification (Shi et al., 2011).

The GPC analysis showed that the lignin fractions in both the untreated and treated PHL samples had a much lower molecular mass than pure Kraft lignin and also a much narrower dispersity, making it more uniform than Kraft lignin. After pretreatment, the number of lignin fractions in the PHL with the same weight average molecular mass was slightly lower but more uniform than the untreated PHL. This is in agreement with the FTIR analysis, which showed that sugars from the LCC complexes were recovered without damage to the structure of the lignin fractions.

4. Conclusions

A one-step microwave-assisted dilute acid hydrolysis method has been achieved for the treatment of an industrial waste stream. It was shown that all sugars present in

an industrial PHL could be converted to monomeric sugars without loss of initial sugar content. Furthermore, the treatment resulted in the recovery of pentose sugars from xylan–lignin complexes (LCCs), which produced pure lignin fractions with a narrow average molecular weight distribution. Comparatively inexpensive recovery of significant amounts of monomeric sugars and relatively pure usable lignin from a waste stream can greatly improve the economic sustainability of a forest-based biorefinery.

Declarations

Author contribution statement

Sanette Marx: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Lehlohonono J Radebe: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Funding statement

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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