Optimisation of Acetic Acid Lignofibre Organosolv Process

Heli Kangas,* Terhi K. Hakala, Tarja Tamminen, Marjo Määttänen, Stella Rovio, Tiina Liitiä, and Kristiina Poppius-Levlin

Birch wood chips were cooked in acetic acid in the presence of phosphinic acid according to the Lignofibre (LGF) organosolv process. The cooking trials were performed according to an experimental design with process time, temperature, and the presence (or absence) of alkaline pre-extraction as the factors. Delignification was enhanced by increased temperature and alkaline pre-extraction. Alkaline extraction also limited xylose hydrolysis, as well as the further degradation of xylose into furfural. Degradation and condensation reactions began to take place between dissolved carbohydrates and lignin at higher temperatures and longer cooking times. Formation of pseudolignin, most likely because of reactions between lignin and furfural, was also observed under the harshest cooking conditions. To avoid these unwanted side-reactions, minimise viscosity losses, and preserve the yield, the LGF process time should be limited to 3 to 4 h at 150 °C.

Keywords: Acetic acid; Alkaline extraction; Furfural; Lignofibre; Organosolv process; Phosphinic acid; Pseudolignin; Xylose

*Contact information: VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Espoo, Finland; *Corresponding author: heli.kangas@vtt.fi*

INTRODUCTION

Global concerns regarding the depletion of traditional material and energy sources, and environmental issues have sparked interest in the use of renewable raw materials. Forest-based biomass has great potential in sustainable energy and chemical production, potentially replacing fossil fuels and oil-based chemicals in many applications. Biorefinery processes aim to recover and use all fractions of biomass and will play a key role in the future use of forest-based biomass.

Organosolv pulping is a method to fractionate the components of fiber for further processing (Hergert 1998; Aziz and Sarkanen 1989; Muurinen 2000). In organosolv pulping, wood or non-wood raw materials are treated with an organic solvent such as alcohol or organic acid to initiate delignification without sulphur. The benefits of the organosolv processes include the selectivity to separate lignocellulosic biomass components into high-value components, the suitability of acidic organosolv processes for non-wood species with high silicate contents, the absence of sulphur, and simpler chemical recovery than in the kraft process. In the past, organosolv processes were studied as alternative methods to kraft pulping to produce papermaking pulps, which led to the development of several methods of producing pulp with properties similar to those of kraft pulp. Of these, Organocell (Baumeister and Edel 1982), methanol-based ASAM (Patt *et al.* 1998), acetic acid-based Acetosolv (Nimz and Casten 1986), and Milox (based on peroxyformic and peroxyacetic acid) (Sundquist and Poppius-Levlin 1998) processes have been tested at either the pilot or full scale (Muurinen 2000), but none has been permanently applied at the industrial scale because of fibre quality issues, poor commercialisation of by-products, process cost-inefficiency, and the corrosive nature and complicated recovery of chemicals.

Because of the demand for efficient processes for biomass treatment, there has been a renewed interest in organosolv processes, leading to recent development of processes at the pilot and full scales. Examples include the CIMV process (Delmas 2008), Lignol Biorefinery Technology derived from the Alcell process (Arato *et al.* 2005), and the Formico Process (Anttila *et al.* 2009).

The Lignofibre (LGF) organosolv process was developed at VTT (Mikkonen *et al.* 2009a) and carried out in an organic solvent such as ethanol or acetic acid. The special feature of the process is the use of phosphinic acid (H_3PO_2), a strong reducing agent (Mehrotra 2013). With the LGF process, fractionation of lignocellulosics into cellulose fibers, lignin, and hemicelluloses is possible. Previous studies have shown that the process is suitable for different raw materials including softwoods, hardwoods, and annual plants, including various grasses (Mikkonen *et al*. 2008; 2009b; Liitiä *et al*. 2013). The choice of solvent is known to affect the yield and recovery of the biomass components. It has been shown that during the LGF cooking of birch with acetic acid, xylan-poor pulp was produced and only lignin and cellulose fibers were recovered (Hakala *et al.* 2010). However, the recovery of polymeric hemicelluloses can be achieved *via* alkaline extraction of the chips prior to the LGF cooking process (Kangas *et al.* 2012). It was found previously that acetic acid LGF cooking in the presence of phosphinic acid results in improved delignification as compared to other acetic acid processes in which mineral acids serve as catalysts (Kangas *et al.* 2013). According to recent results, the phosphinic acid in the acetic acid LGF process catalyses delignification by acidolysis *via* phosphinic acid esterification (Kangas *et al.* 2014). In addition, phosphinic acid can potentially protect lignin against the typical condensation reactions taking place under acidic conditions.

In the early LGF cooking experiments, low temperatures and long cooking times were used. The main reason for the moderate process temperatures was the low boiling point of phosphinic acid (130 °C) and its probable disproportionation when cooks exceeded this temperature (Shechkov *et al.* 2003). To shorten the cooking time to an industrially feasible level, the possibility of increasing the cooking temperature beyond 130 °C must be explored.

During the pulping of lignocellulosics under acidic conditions, hemicelluloses are hydrolysed, and the dissolved hemicelluloses can be degraded further. Furfural is formed from pentose sugars (mainly xylose) *via* cyclodehydration, while hexose sugars such as glucose degrade to form 5-hydroxymethylfurfural (Zeitsch 2000; Qian *et al.* 2005). Xylose degradation and furfural formation are accelerated with increased temperature, time, and acid concentration. Xylose can also be degraded into products other than furfural such as aldehydes, ketones, and carboxylic, pyruvic, formic, glycolic, lactic, and acetic acids (Oefner *et al.* 1992). In addition to furfural formation, so-called furfural loss reactions can take place, in which furfural either reacts with itself (furfural resinification) or with an intermediate of the pentose-to-furfural conversion reaction (furfural condensation). In furfural condensation, furfural can react with the first intermediate of the conversion reaction, yielding furfural pentose, or two furfural molecules react with an intermediate, yielding difurfural pentose. Furfural loss *via* condensation is many times greater than *via* resinification, and both loss reactions are suppressed with increased temperature because of the entropy effect: higher temperatures favor degradation of molecules rather than the build-up of larger ones. The extent of the loss reactions is dependent on the time for which furfural is present in the liquid phase. No loss reactions take place in the vapor phase (Zeitsch 2000).

It has been postulated that during the autohydrolysis of wood, reactive hemicellulose degradation products such as furfural and its precursors can react with lignin (Klemola and Nyman 1966; Chua and Wayman 1979). In addition, phenols, potentially those that are lignin-related, can react with furfural, yielding phenol furfurylol (Zeitsch 2000), and the dissolved lignin present in pre-hydrolysis liquor is involved in side reactions with furfural and sugars (Liu *et al.* 2013). In acidic LGF organosolv cooking, reactions between furfural and the lignin dissolved in the cooking liquor would be expected.

Pseudolignin is an aromatic material that can be detected as lignin during pulp analysis but is not itself derived from lignin. Formation of pseudolignin has been observed during steam explosion (Jakobsons *et al*. 1995; Negro *et al*. 2003) and dilute acid hydrolysis treatments (Sievers *et al*. 2009; Sannigrahi *et al.* 2011), but is also likely to take place during other processes conducted at low pH. The degree of pseudolignin formation increases with the severity of the process (greater temperature, time, and acid strength). It has been confirmed that pseudolignin is the product of the repolymerisation of polysaccharide decomposition products (Jakobsons *et al*. 1992; Sannigrahi *et al*. 2011). Pseudolignin consists of aliphatic and aromatic carbons and includes methoxyl, carboxyl, and carbonyl functional groups (Sannigrahi *et al*. 2011; Hu *et al.* 2012; Kumar *et al*. 2013).

The aim of this work was to optimise the LGF organosolv process by systematically studying the effects of cooking temperature, time, and the use of alkaline pre-extraction on the yield and properties of the cellulose fiber fraction obtained. In addition, the effects of cooking conditions on the function of phosphinic acid and the extent of side reactions involving dissolved components were monitored.

EXPERIMENTAL

Materials

Wood chips

The birch (*Betula pendula* and *pubescens*) chips used in this study were of industrial grade and contained some aspen impurities. They originated from Southern Sweden and were obtained from a Swedish pulp mill. The chips were kept frozen prior to use.

Chemicals

The organic solvent needed for the cooking experiments, glacial acetic acid, was obtained from Algol Chemicals (Espoo, Finland). Phosphinic acid (50%) was purchased from Sigma-Aldrich (Helsinki, Finland).

Standards were used for the identification and quantification of furfural, 5-(hydroxymethyl)furfural (5-HMF), and phosphorous oxo-anions in the model compound experiments and from the spent cooking liquors. Trizma base, sodium dodecyl sulphate (SDS), furfural, glacial acetic acid, and hexamethonium hydroxide were purchased from Sigma-Aldrich (St. Louis, MO, USA). 2,3-Pyrazinedicarboxylic acid (2,3-PyDC) and phosphoric acid (85%) were obtained from Fluka (Buchs, Switzerland) and sodium hypophosphite acid was obtained from Aldrich (Milwaukee, WI, USA). 5-(hydroxymethyl)furfural (5-HMF) was purchased from SAFC Global (USA). Hydrochloric acid, NaOH (Titrisol), and $Na_2HPO_3 \cdot 2H_2O$ were obtained from Merck

(Darmstadt, Germany). Ethanol (99 wt.%) was purchased from Altia (Rajamäki, Finland). All chemicals were of analytical grade and were used as received. Water was obtained from an ion exchange water purification system. Stock solutions of 10,000 mg/L were prepared for each analyte. Working standard solutions with concentrations in the range of 1 to 300 mg/L and 2 to 200 mg/L for furfural and 5-HMF and phosphorous oxo-anions, respectively, were made using appropriate dilution of the stock solutions with ion-exchanged water. The stock solutions were stored in a refrigerator (4 °C).

Methods

Thermal stability of phosphinic acid

The possible thermal disproportionation of phosphinic acid was studied by heating a solution of phosphinic acid (8.8 g/L) in water. The trials were performed in an air-bath digester (built in-house) fitted with six autoclaves (1-L volume) at 110, 130, and 150 °C for 0 to 24 h. The solutions were cooled immediately after heating and kept frozen until analysed.

Alkaline pre-extraction

Alkaline extractions prior to the cooking trials were performed by treating 1 kg of birch chips in a batch digester with 2.5 M NaOH at a liquid-to-wood ratio of 5:1 and 95 °C for 1 h. The hydrolysates were removed from the chips by filtration through a 200-mesh sieve. Further removal of the hydrolysate was done by pressing the extracted chips in a FREX press with a pressure of 150 bar for 5 min. The chips were then washed twice with water (5% for 1 and 2 h) and pressed to a solids content of approximately 52% with the FREX press at a pressure of 100 bar for 10 min.

LGF cooking trials

MODDE 9.0/10.0 software (Umetrics, Sweden) was used for the experimental design of the cooking trials. The factors selected for testing were temperature (110 to 150 °C), time (4 to 16 h), and alkaline extraction (on/off). The experimental design for the cooking trials consisted of 20 trial points as listed in Table 1 (LGF1-14, LGF18-20, LGF22-24). Four additional cooking trials were also performed to experiment with shorter cooking times than were originally planned (LGF15-17, LGF22). The model objective was optimisation (RSM) and the design used was a D-optimal, quadratic model. The model for each response was fitted with MLR.

The cooking trials were performed with screened, unextracted or alkaline-extracted birch chips in an air-bath digester fitted with six autoclaves (1-L volume). The chip batch size in the autoclaves was 100 g, and the liquor-to-wood ratio was 5:1. Acetic acid (100%) was used as the solvent, and 3.5% phosphinic acid on wood was added. As wet chips were used, the actual charge of acetic acid was around 80%.

After cooking, liquor was separated from the pulps, and the pulps were washed by three iterations of dilution washing with 70% acetic acid (1 L) and twice more with water (1 L). The pulps were then left in water overnight before being filtered and screened. The screened yield, total yield, and shives content were determined.

Table 1. LGF Cooking Trial Points Based on Experimental Design by MODDE 9.0 Software

Trial point	Temperature (°C)	Time (h)	Alkaline extraction	Trial point	Temperature (°C)	Time (h)	Alkaline extraction
LGF1	110	4	On	LGF13	135	4	Off
LGF2	110	12	On	LGF14	135	16	On
LGF3	110	16	On	LGF15	150	1	On
LGF4	110	4	Off	LGF16	150	2	On
LGF5	110	8	Off	LGF17	150	3	On
LGF6	110	16	Off	LGF18	150	4	On
LGF7	125	4	On	LGF19	150	8	On
LGF8	125	16	Off	LGF20	150	16	On
LGF9	130	10	Off	LGF21	150	2	Off
LGF10	130	10	Off	LGF22	150	4	Off
LGF11	130	10	Off	LGF23	150	12	Off
LGF12	130	10	Off	LGF24	150	16	Off

Pulp analyses

The Kappa numbers of the pulps were determined according to ISO standard 302 (2004), and their intrinsic viscosities were determined according to ISO standard 5351 (2010). To determine the chemical compositions of the pulps, the samples were air-dried and ground using a Fritch Pulverizette 14 mill. The extractives content was determined gravimetrically after Soxhlet extraction with heptane. The ground pulp samples were hydrolysed with sulphuric acid (4% w/v) in an autoclave at 120 °C for 50 min, and the resulting monosaccharide content was determined by high-performance anion exchange chromatography (HPAEC) with a Dionex ICS 3000 (Sunnyvale, USA) apparatus equipped with a CarboPac PA1 column with pulse amperometric detection (PAD) (Hausalo 1995; Willför *et al*. 2009). The polysaccharide content in the samples was calculated from the corresponding monosaccharides using an anhydro correction of 0.88 for pentoses and 0.9 for hexoses. The Klason lignin content (*i.e.*, the insoluble residue from hydrolysis) was determined gravimetrically from the same hydrolysate according to NREL methods (Sluiter *et al*. 2008). Acid-soluble lignin in the hydrolysate was detected at 215 and 280 nm against sulphuric acid (4 w/v %) blank using Eq. 1 to calculate the soluble lignin concentration, c_L (g/L) (Goldsmid 1971),

$$c_L = \frac{4.53 * a_{215} - a_{280}}{300} \tag{1}$$

where a_{215} and a_{280} are the ultraviolet absorbance values of the filtrate.

The pulp molar mass distributions were determined by size exclusion chromatography (SEC). The pulp samples were dissolved in DMAc/8% LiCl according to the solvent exchange method involving ethylisocyanate derivatisation (Berthold *et al.* 2001). The SEC measurements were performed using 2× PL gel MiniMixed A columns with a precolumn with DMAc/0.8% LiCl eluent (0.36 mL/min, 80 °C) and a refractive index (RI) detector. The average molar mass values (M_n, M_w) and the molar mass distributions were calculated according to pullulan standards using Waters Empower 2 software.

Cooking liquor analyses

The gravimetric lignin content in the cooking liquor was analysed *via* precipitation with H_2SO_4 (4% w/v) in an autoclave at 120 °C for 50 min. The precipitate was filtered and the acid soluble lignin was detected within the clear filtrate at 215 and 280 nm, and calculated according to the equation presented by Goldschmid (1971), as described above.

The furfural, 5-HMF, and phosphorous oxo-anion ($H_2PO_2^-$, HPO_3^{2-}, and PO_4^{3-}) contents were analysed with a P/ACE MDQ capillary electrophoresis instrument equipped with a photodiode array UV/Vis detector (PDA) (Beckman-Coulter Inc., Fullerton, USA). For their detection and quantification, standards were prepared as described and analysed prior to analyses of the actual samples. An optimised electrolyte solution for the furfural and 5-HMF analyses consisted of 50-mM Trizma base, 100-mM sodium dodecyl sulphate (SDS), and 5% (v/v) ethanol. The pH was adjusted to 8.3 with 1 M HCl prior to the addition of alcohol. An electrolyte solution prepared for the analysis of phosphorous anions consisted of 5 mM 2,3-PyDC, 0.5 mM hexamethonium hydroxide, and 1% (v/v) acetic acid (Stover 1999). The pH of this electrolyte solution was 2.3. The instrument conditions used for the analyses of these standards and the LGF cooking liquors are listed in Table 2. The capillary (Composite Metal Services, The Chase, Hallow, Worcester, UK) was conditioned by sequentially purging with 0.1 M NaOH (20 min), Milli-Q water (20 min), and buffer solution (20 min). In the furfural analyses, the capillary was dipped in ion exchange water between rinses with buffer solution and sample injection to prevent contamination of the sample with SDS. The LGF cooking liquor samples were diluted to 1:5 (v/v) with 5% ethanol in H_2O (furfural analysis) or with ion-exchanged water (phosphorous oxo-anion analysis), vortexed, and centrifuged at 14,000 rpm for 5 min. A supernatant was further diluted with ion-exchanged water prior to CE analyses. All standards and samples were analysed in duplicate.

Table 2. Instrument Parameters for Furfural, 5-HMF, and Phosphorous Anion Analyses

Variable	Furfural and 5-HMF analysis	Phosphorous oxo-anions analysis
UV Wavelength	283 nm	200 nm
Detection mode	Direct	Indirect
Capillary (length to detection point =L_{det}; total length=L_{tot})	L_{det} 20 cm, L_{tot} 30 cm, internal diameter 50 µm, outer diameter 375 µm	L_{det} 50 cm, L_{tot} 60 cm, internal diameter 50 µm, outer diameter 375 µm
Temperature	20 °C	15 °C
Voltage	+15 kV	-20 kV
Injection pressure and time	0.5 psi (3.447 kPa) for 5 s	0.5 psi for 8 s

RESULTS AND DISCUSSION

The thermal disproportionation of phosphinic acid to phosphonic acid (H_3PO_3) and phosphine (PH_3) at high temperatures (above 110 °C) has been reported previously (Shechkov *et al.* 2003). Disproportionation occurs most readily at 130 to 160 °C and is complete at 190 °C. To determine if disproportionation occurred to a significant extent during the LGF organosolv process, experiments were conducted in which phosphinic acid (H_3PO_2) was heated at different temperatures for various times and the content of phosphorous oxo-anions, hypophosphite ($H_2PO_2^-$, P(I)), phosphite (HPO_3^{2-}, P(III)), and phosphate (PO_4^{3-}, P(V)) were determined, as shown in Fig. 1. Most of the anions were in the form of hypophosphite (*i.e.*, in an unreacted state), but some phosphite ions were also observed following the experiments performed at 150 °C, as shown in Fig. 2. No significant formation of phosphate was observed. The overall mass balance on phosphorous indicated losses during the LGF process well within the experimental error, indicating that no toxic phosphine gas was formed. It was concluded that no significant thermal disproportionation occurred during the experiments and that cooking temperatures of up to 150 °C could be used for the LGF process.

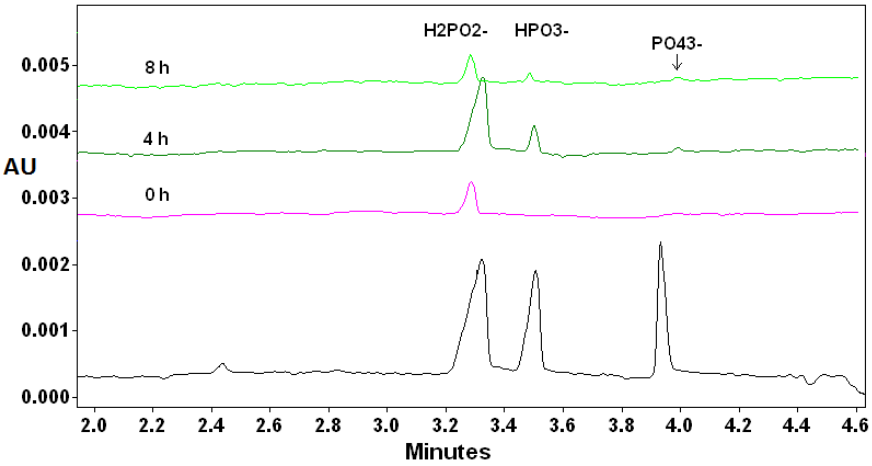


Fig. 1. Compiled electropherograms of P-anions and their changes during an 8-h time period at 150 °C. Concentrations of the standards, $H_2PO_2^{2-}$, HPO_3^{2-}, and PO_4^{3-} were 75, 40, and 25 mg/L, respectively. The electrolyte solution consisted of 5 mM 2,3-pyrazinedicarboxylic acid, 0.5 mM hexamethonium hydroxide, and 1% (v/v) acetic acid.

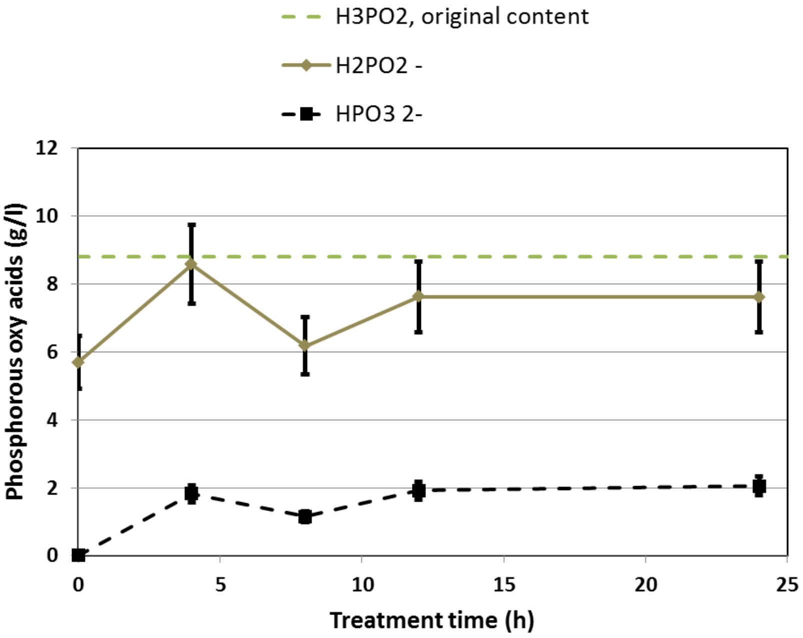


Fig. 2. The content of phosphorous oxo-anions as a function of treatment time at 150 °C

The results of the cooking trials are presented in Table 3, and the response surface plots for Kappa, viscosity, and total screened yield are shown in Figs. 3, 4, and 5, respectively. For alkali-extracted chips, the Kappa number generally decreased with increased temperature and cooking time (Fig. 3a), but in the case of unextracted chips, an increase in Kappa was observed at higher temperatures and cooking times (Fig. 3b). A temperature of 110 °C was clearly too low for efficient delignification as the Kappa number reached during the cooking series remained high. The Kappa numbers of pulps cooked at 125, 130, and 135 °C were significantly lower than those of the pulps cooked at 110 °C. Delignification at 150 °C for the alkali-extracted chips was rapid between the first and fourth hours but levelled off after that, indicating that there was no benefit in prolonging the cook beyond 4 h. For cooks performed at 110 and at 150 °C, the Kappa number was significantly lower in alkali-extracted chips than in un-extracted chips, suggesting that alkaline extraction functioned as a wood matrix-opening process, enhancing impregnation of the cooking liquor into the chips. A similar effect on impregnation was been observed with regard to the kraft cooking process (Al-Dajani and Tschirner 2008). When using alkali-impregnation in kraft cooking, the subsequent cooking stage can be performed with lower alkali charge and for a shorter cooking time. Accordingly, the LGF process could be potentially conducted with lesser severity, at lower temperature, time, or acidity, if preceded by alkali extraction.

When cooking the un-extracted chips at 150 °C, the Kappa number increased with prolonged cooking times (12 to 16 h), indicating that lignin condensation and precipitation reactions were taking place, which is another reason to limit the cooking time. However, similar phenomena were not observed in cooks performed with extracted wood chips, but according to response surface plot, such effects could become significant at temperatures above 150 °C (Fig. 3a). One possible reason is that the alkali remaining in the chips after the pre-extraction stage increased the pH during cooking, thus lowering the acidity and decreasing the severity of the process. Another reason could be the higher extractives content in the un-extracted chips (Table 4), which could potentially influence the lignin condensation and precipitation reactions.

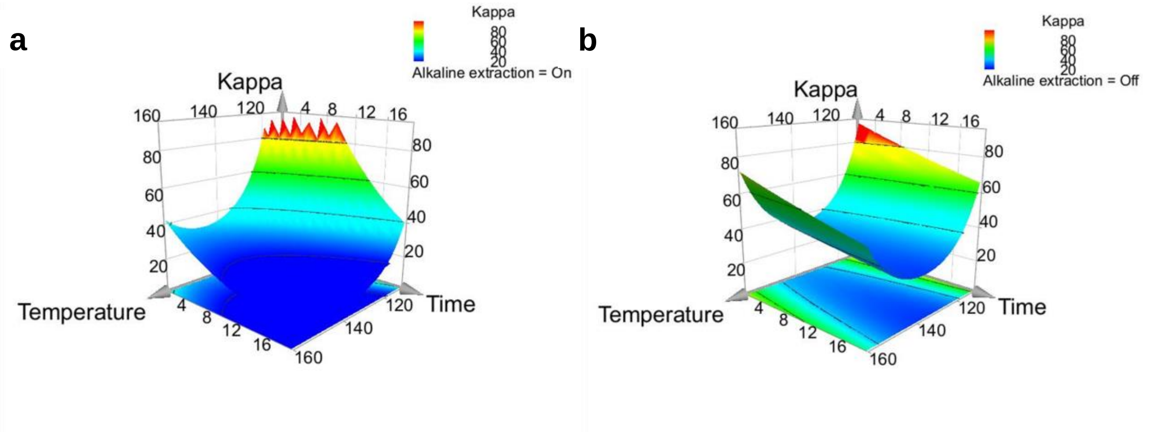


Fig. 3. Response surface plots for Kappa obtained by MODDE 10.0 software for (a) cooking trials with alkaline extracted chips and (b) cooking trials with unextracted chips. Model fit: $Q^2 = 0.57$, regression equation: y = x–6.38e-007, $R^2 = 0.80$.

Table 3. Results of LGF Organosolv Cooking Trials Performed with Cooking Temperature, Cooking Time, and Alkali Extraction as the Variables

Pulp code	Cooking conditions (T (°C), t (h), alkali extraction: AE)	Kappa number	Viscosity (mL/g)	Screened total yield (%)	Screened cooking yield (%)	Shives (%)
LGF1	110, 4, AE	88.8	NA*	61.5	82.0	1.8
LGF2	110, 12, AE	71.7	870	52.8	70.4	5.7
LGF3	110, 16, AE	66.5	830	53.3	68.5	3.9
LGF4	110, 4	94.5	NA*	79.9	79.9	3.1
LGF5	110, 8	92	NA*	71.4	71.4	2.3
LGF6	110, 16	76.7	1140	63.2	63.2	0.4
LGF7	125, 4, AE	70.8	780	56.4	72.5	1.5
LGF8	125, 16	20.4	1200	49.3	49.3	0.3
LGF9	130, 10	32.8	1140	51.0	51.0	0.2
LGF10	130, 10	26.8	1170	51.0	51.0	0.1
LGF11	130, 10	27	1120	48.8	48.8	0.5
LGF12	130, 10	28.4	1110	49.6	49.6	0.3
LGF13	135, 4	57.1	1210	54.4	54.4	1.4
LGF14	135, 16, AE	10.6	730	46.2	59.4	0.2
LGF15	150,1,AE	58.2	760	54.2	69.7	0.4
LGF16	150,2,AE	39.7	720	51.1	65.7	0.3
LGF17	150,3,AE	28.8	730	48.9	62.8	1.0
LGF18	150, 4, AE	17.1	690	47.9	61.6	0.1
LGF19	150, 8, AE	13.5	670	43.9	58.5	0.1
LGF20	150, 16, AE	9.2	570	43.3	55.7	0
LGF21	150,2	38.4	1090	50.8	50.8	0.1
LGF22	150, 4	31.4	990	47.9	47.9	0.1
LGF23	150, 12	35,9	810	44.7	44.7	0
LGF24	150, 16	56	730	47.7	47.7	0

*NA: could not be analysed due to high Kappa number. In screened total yield, the yield loss during alkali extraction was taken into account, while cooking yield is the yield of the actual cooking process.

Viscosity decreased with increasing temperature and time (Table 3, Fig. 4), and the viscosity was lower in the pulps cooked from extracted chips than in those from un-extracted chips (Fig. 4), which is likely because of the higher alkalinity in the cooks in which extracted chips were used. As the viscosity decreased with increased cooking time, preservation of viscosity is yet another reason to limit cooking to 4 h. In addition, shorter cooking times minimised overall yield losses, as yield decreased with increasing cooking temperature and time (Fig. 5). There was a slight increase in the yield at higher temperatures and longer cooking times, possibly because of reprecipitation of dissolved components onto fibers.

By cooking at 150 °C for 3 h for alkali-extracted chips and 4 h for un-extracted chips, the desired Kappa number of around 30 was reached. At this Kappa number, the total screened yield of the process was around 48%.

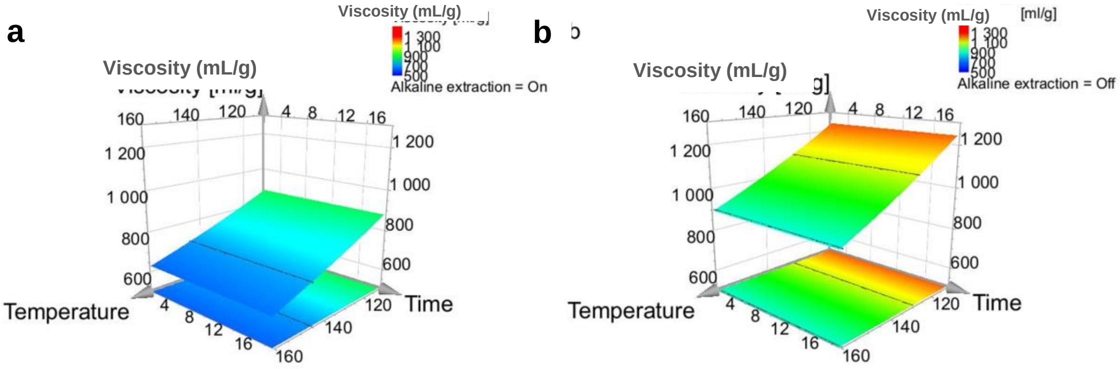


Fig. 4. Response surface plots for viscosity obtained by MODDE 10.0 software for (a) cooking trials with alkaline extracted chips and (b) cooking trials with unextracted chips. Model fit: Q^2 = 0.73, regression equation: y=x+0.0001029, R^2 = 0.80. The model for viscosity may suffer from missing values from three trial points.

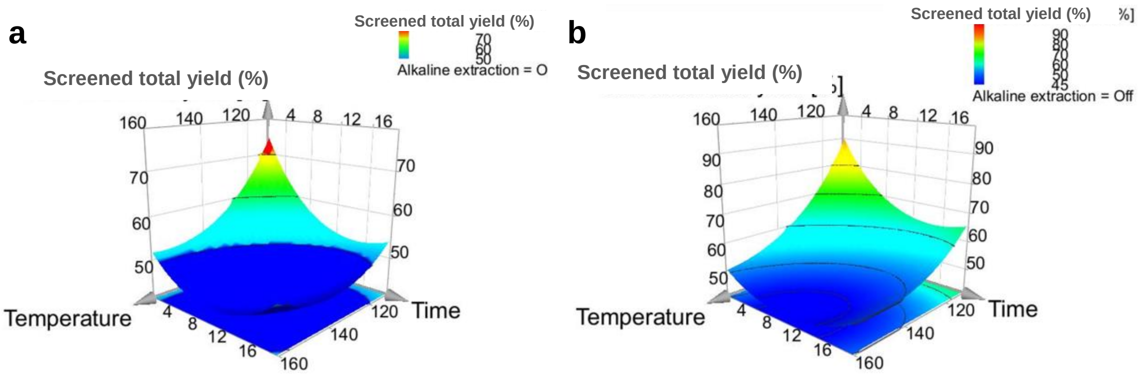


Fig. 5. Response surface plots for screened total yield obtained by MODDE 10.0 software for (a) cooking trials with alkaline extracted chips and (b) cooking trials with unextracted chips. Model fit: Q^2 = 0.89, regression equation: y=x-2.895e-006, R^2 = 0.96.

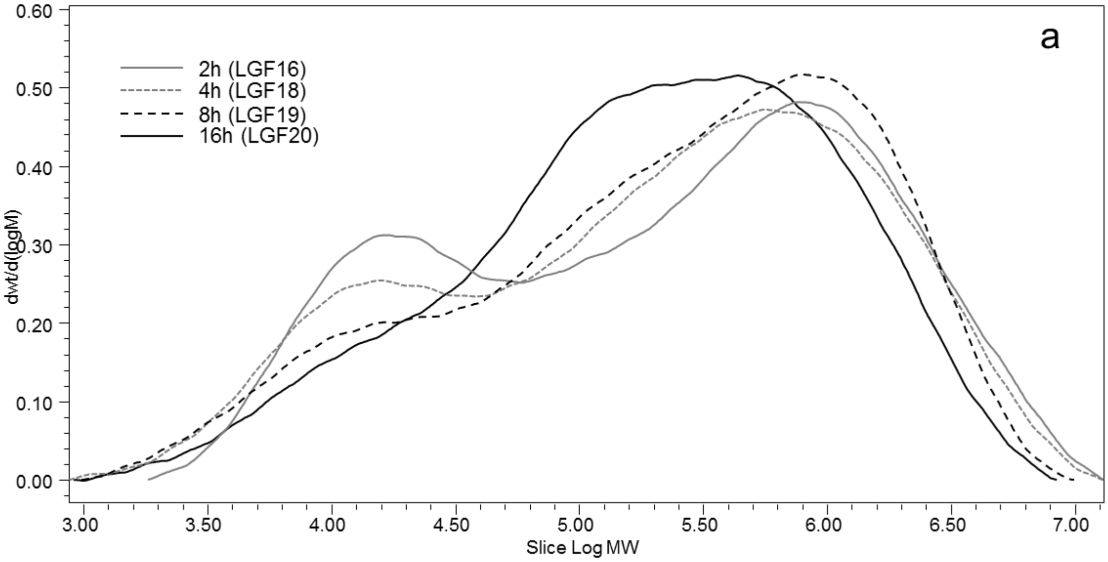
The chemical compositions of the LGF pulps cooked for 3 and 4 h are shown in Table 4 with the composition of the screened birch chips and the alkali-extracted birch chips. Contrary to what was expected, the pulp cooked from un-extracted chips (LGF22) contained less xylan than the pulp cooked from alkali-extracted chips (LGF18), suggesting that the xylan remaining in the chips after alkaline extraction was more resistant to acid-induced hydrolysis in the LGF organosolv cooking stage. The higher alkalinity of cooks performed with alkali-extracted chips could also explain the differences in xylan dissolution. The lignin dissolution, however, was more extensive from the alkali extracted chips than from the un-extracted chips, as shown by their lower Kappa number.

Overall, the acetic acid LGF pulps had high cellulose contents and low lignin contents. Compared to birch kraft pulps with xylan contents of 29% (Laine *et al*. 1996), their hemicellulose content was also low.

Table 4. Chemical Compositions of Screened Birch Chips, Alkali Extracted Birch Chips, and Selected LGF Organosolv Pulps

	Cooking conditions (T (°C), t (h), AE)	Heptane extract (%)	Klason lignin (%)	Acid-soluble lignin (%)	Cellulose (%)	Xylan (%)	Other carbohydrates (%)
Screened birch chips	-	0.9	22.2	3.0	46.4	20.9	6.6
Alkali extracted birch chips	-	0.1	24.1	2.6	54.2	15.4	3.6
LGF17	150,3,AE	0	5.1	0.4	78.8	15.2	0.5
LGF18	150, 4, AE	0	3.5	0.3	82.4	13.3	0.5
LGF22	150, 4	0	5.5	0.2	86.2	7.0	1.1

The molar mass distributions of LGF organosolv pulps cooked at 150 °C for various cooking times are shown in Fig. 6, and the average molecular weights are shown in Table 5. The pulps cooked from alkali-extracted chips (Fig. 6a) contain a typical low molecular mass fraction, suggesting the presence of hemicelluloses in the pulp. The peak corresponding to the low molar mass fraction became smaller with increased cooking time, likely because of the presence of hemicellulose rather than the degradation of cellulose. This result was also supported by the chemical compositions of the pulps as shown in Table 4, in which the xylan contents of the pulps cooked from alkali-extracted chips were surprisingly high. The peak corresponding to the low molecular mass fraction was smaller in the molar mass distribution of pulps cooked from un-extracted chips (Fig. 6b), which also had a lower xylan content. In both cases, degradation of cellulose took place with prolonged cooking times.



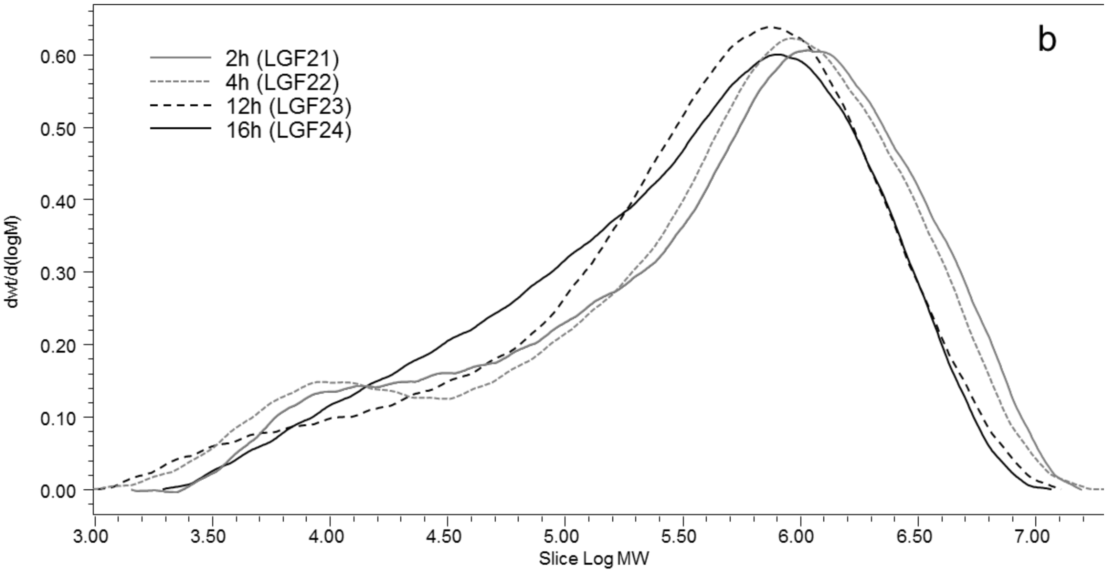


Fig. 6. Molar mass distributions of LGF organosolv pulps (a) cooked from alkali extracted chips and (b) cooked from un-extracted chips for 1 to 16 h

Table 5. Average Molecular Weights and Polydispersities (PD) of LGF Pulps Cooked at 150 °C

	Cooking conditions (T (°C), t (h), AE)	M_n	M_w	PD
LGF15	150,1,AE	38 100	854 700	22.4
LGF16	150,2,AE	37 600	804 700	21.4
LGF17	150,3,AE	32 200	790 000	24.6
LGF18	150, 4, AE	31 500	739 900	23.4
LGF19	150, 8, AE	35 900	742 800	20.7
LGF20	150, 16, AE	42 100	577 200	13.7
LGF21	150,2	66 700	1 351 500	20.3
LGF22	150, 4	46 800	1 220 600	26.1
LGF23	150, 12	49 700	940 500	18.9
LGF24	150, 16	67 500	868 700	12.9

The compositions of the spent LGF organosolv liquors are shown in Table 6. Generally, the gravimetric lignin content in the liquor increased with increased cooking time for both alkali-extracted and un-extracted chips (Fig. 7), while the content of acid soluble lignin remained relatively constant regardless of the process temperature or time used. Overall, the optimal cooking time of 3 to 4 h at 150 °C resulted in dissolution of 84 to 96% of the total lignin in the wood chips.

However, when cooking at 150 °C, a significant reduction of the lignin content in the cooking liquor was observed at long cooking times. This occurred for alkali-extracted chips between 8 and 16 h (LGF19 and LGF20, respectively) and for un-extracted chips between 12 and 16 h (LGF23 and LGF24), suggesting that further lignin condensation, repolymerisation, and degradation reactions took place during prolonged cooks at high temperatures. Similar phenomena were observed during the autohydrolysis of wood and are suggested to be due to the reaction of lignin with hemicellulose degradation products, including furfural and its precursors (Chua and Wayman 1979). Reprecipitation of lignin or coprecipitation of lignin and hemicellulose degradation products to the fibers may also have taken place as suggested by the clear increase in the Kappa number of pulps as the cooking continued at 150 °C with un-extracted chips from 12 to 16 h (Table 3, pulps LGF23 and LGF24).

At two trial points, LGF19 and LGF23, the dissolved lignin content exceeded the lignin content originally present in the chips, indicating that part of the material analysed as lignin did not actually originate from lignin. Instead, it was so-called pseudolignin, an aromatic material that is detected as Klason lignin value but is not derived from native lignin. Pseudolignin is known to form from carbohydrates under acidic conditions (Jakobsons *et al*. 1992; Sannigrahi *et al*. 2011).

Table 6. Composition of the Spent Liquors of LGF Organosolv Cooking Process

Liquor code	Cooking conditions (*T* (C°), *t* (h), alkali extraction: AE)	Gravimetric lignin (g/L)	Acid-soluble lignin (g/L)	Total dissolved lignin (% of wood lignin)	Furfural (g/L)	5-HMF (g/L)
LGF1	110, 4, AE	21.5	0.5	41.1	0.1	0
LGF2	110, 12, AE	24.6	0.4	47.0	0.3	0
LGF3	110, 16, AE	34.4	0.5	65.3	0.4	0
LGF4	110, 4	8.0	0.3	16.5	0.1	0
LGF5	110, 8	17.0	0.4	34.6	0.4	0
LGF6	110, 16	30.2	0.5	60.9	1.1	0
LGF7	125, 4, AE	36.4	0.5	69.2	0.3	0.1
LGF8	125, 16	44.5	0.5	89.2	3.7	0.1
LGF9	130, 10	42.7	0.5	85.7	3.9	0.1
LGF10	130, 10	41.9	0.5	84.1	3.6	0
LGF11	130, 10	40.7	0.4	81.6	3.7	0.1
LGF12	130, 10	43.6	0.4	87.2	3.7	0.1
LGF13	135, 4	23.9	0.4	48.2	2.1	0
LGF14	135, 16, AE	47.4	0.5	89.7	5.9	0.2
LGF15	150,1,AE	34.3	0.6	65.4	1.1	0
LGF16	150,2,AE	40.9	0.5	77.4	2.3	0.1
LGF17	150,3,AE	44.4	0.6	84.2	3.3	0.1
LGF18	150, 4, AE	44.6	0.6	84.5	4.3	0.1
LGF19	150, 8, AE	57.1	0.6	108.0	5.8	0.3
LGF20	150, 16, AE	51.3	0.5	96.9	6.3	0.4
LGF21	150,2	39.1	0.5	78.6	5.9	0
LGF22	150, 4	48.0	0.5	96.3	8.1	0.2
LGF23	150, 12	62.4	0.5	124.9	9.1	0.4
LGF24	150, 16	48.8	0.5	97.6	7.7	0.4

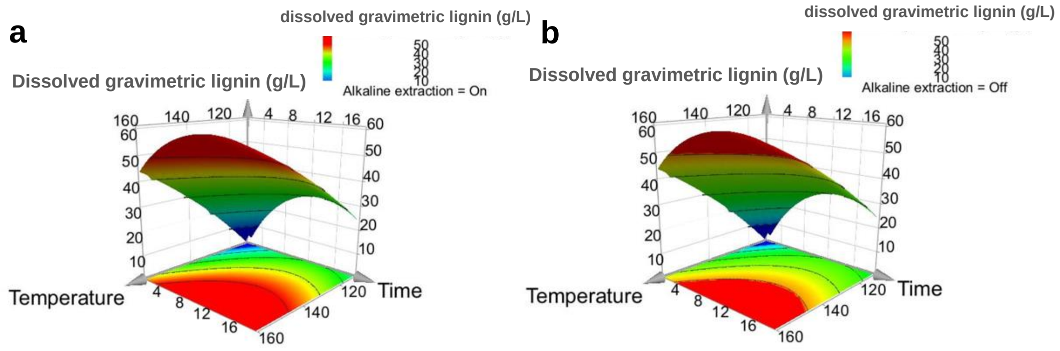


Fig. 7. Response surface plot for dissolved gravimetric lignin obtained by MODDE 10.0 software for (a) cooking trials with alkaline extracted chips and (b) cooking trials with unextracted chips. Model fit: $Q^2 = 0.77$, regression equation: y=x+1.771e-006, $R^2 = 0.84$.

Furfural is formed under the acidic conditions of LGF organosolv cooking as a degradation product of pentose sugars (mainly xylose). Similarly, 5-HMF is the primary degradation product of hexose sugars (mainly glucose). Formation of furfural was observed at every temperature, at increased levels at higher temperatures, while the formation of 5-HMF was observed under high temperatures and long cooking times (Table 6). Generally, the furfural content increased with increased cooking time at every temperature (Fig. 8). However, at 150 °C, there was only a slight change in the furfural content with alkali extracted chips between 8 and 16 h (LGF19 and LGF20, respectively) and a decrease with un-extracted chips between 12 and 16 h (LGF23 and LGF24, respectively), indicating either that the furfural loss reactions were significant or that reactions between lignin and furfural or its degradation products took place. The latter is supported by the fact that, at the trial points in which furfural loss was observed, there was also a reduction in the lignin content.

The loss of lignin and furfural from the spent cooking liquor, observed under the harshest cooking conditions, was most likely because of reactions between the two. The observed pseudolignin could have been formed by the co-precipitation of lignin and furfural.

Furfural formation was reduced when alkali-extracted chips were cooked. This is supported by findings regarding the steam treatment of wood in which the pre-impregnation of the chips with alkali resulted in cleaner depolymerisation of polysaccharides without any further acid-catalysed degradation (Li *et al*. 2005). Thus, alkali pre-treatment could be used to prevent the degradation of xylose into furfural during LGF cooking.

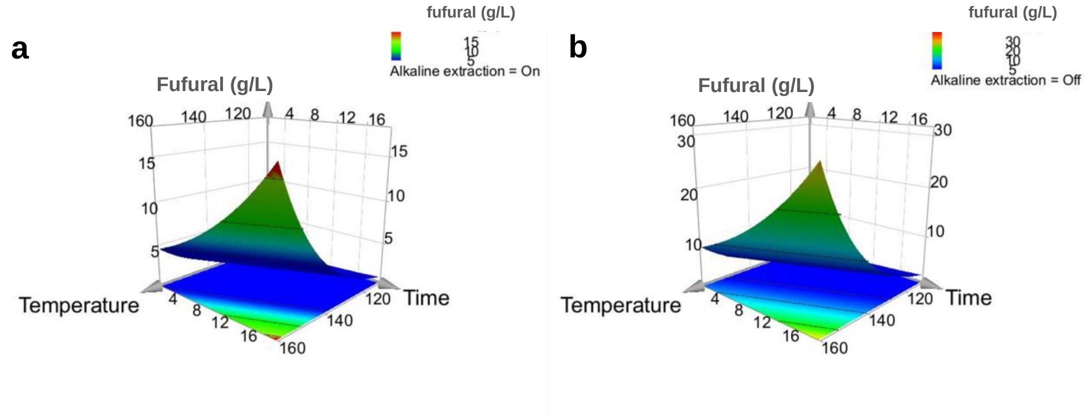


Fig. 8. Response surface plots for furfural formation obtained by MODDE 10.0 software for (a) cooking trials with alkaline extracted chips and (b) cooking trials with unextracted chips. Model fit: $Q^2 = 0.86$, regression equation: y=x+2.284e-007, $R^2 = 0.91$.

The reactions of phosphinic acid during LGF organosolv pulping were evaluated by measuring the content of different phosphorous oxy-anions in the spent cooking liquors (Table 7). As phosphinic (hypophosphoric) acid is a reducing agent, the oxidation state of phosphorous was expected to increase from +I in hypophosphite into +III in phosphite, and further into +V in phosphate during oxidation-reduction reactions (Mehrotra 2013). The original phosphinic acid charge in the cooking liquor was 7 g/L, corresponding to 1.6 g/L phosphorous. Depending on the process conditions, 24 to 62% of the added phosphorous was found as phosphorous oxo-anions in the spent cooking liquor, with the recovery generally decreasing with increasing temperature and cooking time. Some phosphorous was found attached to LGF cellulose (Kangas *et al.* 2013) and lignin (Kangas *et al*. 2014). The total phosphorous content in the spent liquor determined in earlier studies was 1.5 g/L, indicating that most of the phosphorous added to the process was found in the spent cooking liquor, but it was only partially detectable as phosphorous oxo-anions. The phosphorous remaining unaccounted for in the CE analyses could be present as esters in lignin (Kangas *et al.* 2014) and sugars.

The content of hypophosphite anion steadily decreased as a function of time when cooking at 110 °C. This was accompanied by an increase in the phosphite content, indicating that hypophosphite is involved in the oxidation-reduction reactions taking place during the LGF organosolv process. Phosphinic acid is proposed to enhance the delignification, cleaving β-aryl ether bonds in lignin *via* the formation of phosphinic acid ester derivatives, also preventing further condensation reactions. The structural characteristics of LGF lignin indicate that reduction of lignin took place (Kangas *et al*. 2014). In the cooking liquors of cooks performed at 125, 130, 135, and 150 °C, very little or no hypophosphite remained in the spent cooking liquors. For the cooks performed with un-extracted chips, the formation of phosphate ions was more significant than in those with alkali-extracted chips. At 150 °C, the formation of phosphate coincided with the increase in the Kappa number of the pulps and the decrease in the lignin and furfural contents in the spent cooking liquors, indicating that the phenomena were all related. However, it is currently unclear whether the condensation and precipitation of lignin and degradation, condensation, or polymerisation of furfural were a result of increases in the phosphate content or *vice versa*.

Table 7. Content of Phosphorous Oxo Anions in the Spent Cooking Liquors of LGF Organosolv Process

Trial point	Cooking conditions (*T* (°C), *t* (h), alkali extraction: AE)	Hypophosphite ($H_2PO_2^-$) (g/L)	Phosphite (HPO_3^{2-}) (g/L)	Phosphate (PO_4^{3-}) (g/L)	Recovery of anions as P (%)
LGF1	110, 4, AE	3.2	1.2	0	61.3
LGF2	110, 12, AE	2.5	2.3	0	62.1
LGF3	110, 16, AE	1.7	2.5	0	53.0
LGF4	110, 4	2.3	1.1	0	46.7
LGF5	110, 8	1.6	1.8	0	44.5
LGF6	110, 16	1.7	2.5	0	40.9
LGF7	125, 4, AE	2.3	2.5	0	61.6
LGF8	125, 16	0	3.2	0.2	40.3
LGF9	130, 10	0	2.9	0.2	36.0
LGF10	130, 10	0	3.1	0.3	39.7
LGL11	130, 10	0	3.0	0.3	37.6
LGF12	130, 10	0	3.0	0.2	36.8
LGF13	135, 4	0	2.0	0	23.6
LGF14	135, 16, AE	0	3.1	0	37.0
LGF15	150,1, AE	1.3	2.7	0	49.8
LGF16	150,2, AE	0.4	3.6	0	47.8
LGF17	150, 3, AE	0	3.7	0	43.2
LGF18	150, 4, AE	0	3.5	0	41.5
LGF19	150, 8, AE	0	3.9	0.4	49.5
LGF20	150, 16, AE	0	3.4	0.5	41.6
LGF21	150,2	0	3.4	0	40.0
LGF22	150, 4	0	3.1	0.6	42.0
LGF23	150, 12	0	2.4	1.3	41.2
LGF24	150, 16	0	2.0	1.4	37.4

CONCLUSIONS

1. Delignification *via* LGF organosolv cooking was accelerated at increased temperatures, thus enabling shorter cooking times. Further improvement to the degree of delignification was achieved by the alkaline pre-extraction of chips, suggesting that the extraction process functions as a wood matrix-opening process, enhancing impregnation of cooking liquor into the chips.
2. At high temperatures, cooking is best limited to Kappa numbers between 20 and 30 to avoid excessive losses in viscosity, yield loss, and unwanted side reactions of the components present in the spent cooking liquor (such as lignin, xylose, and furfural).
3. A significant reduction of the amount of furfural formed from xylose could be achieved by the alkaline pre-extraction of chips.
4. Oxidation of the cooking reagent, hypophosphite, into phosphite and phosphate, was observed using CE analysis. The reactions accelerated at increased cooking temperatures and times.

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