

## Extraction of Wheat Straw with Aqueous Tetra-*n*-Butylphosphonium Hydroxide

Uula Hyväkkö, Alistair W. T. King,\* and Ilkka Kilpeläinen\*

The stability of tetra-*n*-butylphosphonium hydroxide ( $[P_{4444}][OH]_{(aq)}$ ) solutions and their potential for wheat straw extraction are investigated. Under certain concentration ranges, aqueous  $[P_{4444}][OH]_{(aq)}$  is known to rapidly dissolve up to 20 wt% of cellulose at 25 °C. However, at elevated temperatures and at the high concentration ranges required for cellulose dissolution,  $[P_{4444}][OH]_{(aq)}$  irreversibly decomposes. This was determined by following the kinetics of decomposition at different temperatures and concentrations, using  $^{31}P$  NMR analysis of the solutions. A lower concentration range of 40 wt%  $[P_{4444}][OH]_{(aq)}$  was observed for fractionation of wheat straw, avoiding significant decomposition of the expensive phosphonium component. Herein, the possibilities for producing cellulose-rich fractions with reduced lignin contents and hemicellulose-rich extracts are discussed. A proposal is given for a full process cycle using  $[P_{4444}][OH]_{(aq)}$ , where the phosphonium salt is used in fractionation and recovered by anion metathesis as a chloride salt. Although not demonstrated in this article, the chloride salt may be converted back to the hydroxide by means of, e.g., ion exchange.

*Keywords:* Ionic liquid; Electrolyte; Biomass; Wheat straw; Fractionation; Cellulose; Phosphonium; Hydroxide; Lignin; Hemicellulose

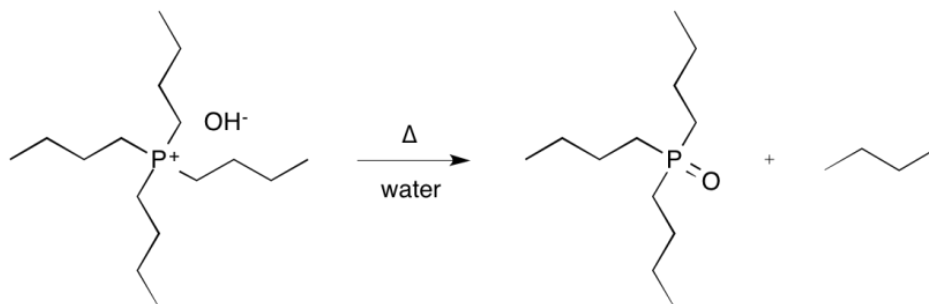
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### INTRODUCTION

Wheat straw (WS) is an agricultural side product from wheat harvesting. It is a globally accessible feedstock and it is an abundant material for new biorefinery applications. Because it has a high polysaccharide content (35 to 45% cellulose, 20 to 30% hemicellulose) and relatively low lignin content (15 to 25%), there is potential for valorisation through production of new polymeric materials or chemicals. As it is an herbaceous biomass, it also contains significant amounts of extractives (2 to 5%), starch (2 to 3%), and minerals (e.g., silicates, 5 to 10%), which can be problematic in the valorisation of all fractions.

WS may be used as a raw material for the pulp and paper industry. However, the application is limited to low-quality paper production, as the fibre properties are quite poor. WS contains a high amount of non-fibrous cells, which leads to problems in processing the pulp (Pan and Sano 2005). In a biorefinery concept, paper-related products are not the sole area of interest. Lower quality fibres can be used for various applications in which fibre properties may not be essential, e.g., enzymatic hydrolysis en route to biofuels (Brown and Brown 2013; Qureshi *et al.* 2013), cellulose derivatisation (Sirviö *et al.* 2011; Fox *et al.* 2011; Cunha and Gandini 2010), or to other value-added products.



**Fig. 1.** Decomposition of [P<sub>4444</sub>][OH] in aqueous solution

Ionic liquids (ILs) are typically described as organic salts with melting points below the arbitrary temperature of 100 °C. ILs have peculiar properties, such as negligible vapour pressures, non-flammability (below their decomposition temperatures), and the potential to dissolve biopolymers (Swatloski *et al.* 2002). These properties may offer the potential for homogenous bioprocessing of materials that are insoluble in most common solvents.

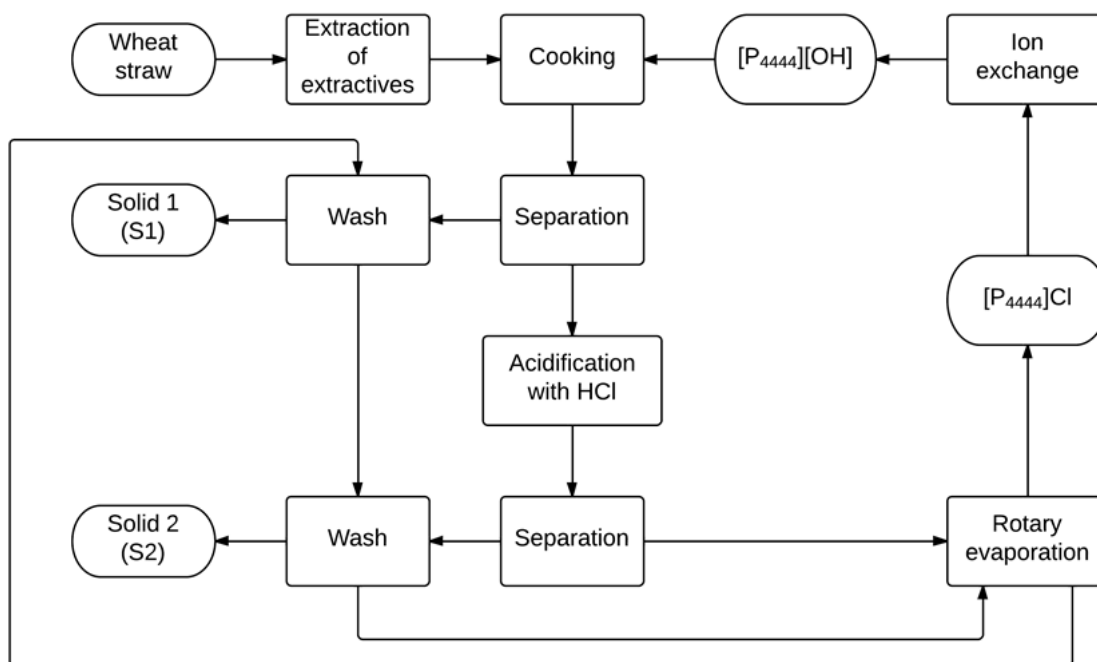
The properties of the ILs can be tuned by careful selection of anion and cation. The properties that can be affected are *e.g.*, ‘hydrophobicity’, as well as charged and polar interactions (Huddleston *et al.* 2001). These properties can also translate into efficient biopolymer dissolution (da Costa Lopes *et al.* 2013a). By noting the acidity of the cation, the cellulose dissolution capabilities of acid-base conjugate ILs can be predicted. It was found that there is an acidity threshold that needs to be avoided for cellulose to dissolve in these types of ILs, with acetate or propionate anions (Parviainen *et al.* 2013). Kyllönen *et al.* (2013) studied the effect of milling on the solubility of wood in non-derivatising ionic liquids. They found that milling drastically increases the available OH-groups and accelerates dissolution in ILs. A comprehensive review of the dissolution of polysaccharides in ILs was published by Zakrzewska *et al.* (2010).

Fu *et al.* (2010) extracted lignin from wheat straw with [emim][OAc]. They were able to lower the lignin content of WS from 15.0% to 8.2% and improve enzymatic digestibility up to 97.6%. Recently, da Costa Lopes *et al.* (2013b) developed methods to treat wheat straw with [emim][OAc], to produce solids that are highly digestible with enzymes. They also studied the recyclability of [emim][OAc] in this system.

ILs are usually relatively viscous, which can be problematic for mass transfer in biopolymer processing. However, there are means to advantageously reduce viscosity, for instance, with co-solvents, such as ionic liquid electrolytes (Iguchi *et al.* 2013). There are a number of different strategies to valorise biomass utilising electrolyte solutions. Rinaldi (2011) showed that cellulose can be dissolved rapidly in organic electrolyte solutions containing a small molar fraction of IL in polar aprotic solvents. He described the ‘instantaneous’ dissolution of 10 wt% of Avicel in 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) / 1,3-dimethyl-2-imidazolidinone (DMI) electrolytes.

Zhong *et al.* (2013) reported that cellulose can be extracted from wheat straw using tetra-*n*-butylammonium hydroxide ([N<sub>4444</sub>][OH]) solutions containing 45 to 50% water. Li *et al.* (2013) extracted cellulose in high purity from *Zoysia japonica* with 1-allyl-3-methylimidazolium acetate ([amim]Cl) / dimethyl sulfoxide (DMSO) mixtures. They obtained two thirds of the cellulose content with 99.57% purity without dissolving any hemicellulose or lignin. In a recent publication, lignin was extracted from eucalyptus with a mixture of 1-butyl-3-methylimidazolium acesulfamate ([bmim][Ace]) and organic

solvents. In the same paper, an in depth analysis was performed to determine which type of lignin was extracted in comparison to 70% ethanol containing 1 M NaOH. However, there were some indications that the acesulfamate anion may have reacted with the lignin (Sun *et al.* 2013). A procedure was found for an efficient separation of hemicellulose and cellulose from birch kraft pulp with mixtures of [emim][OAc] and water (Froschauer *et al.* 2013). Abe *et al.* (2012) showed that tetra-*n*-butylphosphonium hydroxide ([P<sub>4444</sub>][OH]) solution, containing 40 wt% water, is able to rapidly dissolve large amounts of cellulose (up to 20 wt% in five minutes) at room temperature. They also discussed the stability of aqueous [P<sub>4444</sub>][OH] solutions based on their <sup>1</sup>H NMR results. Products in the decomposition of phosphonium hydroxides are phosphine oxides and hydrocarbons. Decomposition of aqueous [P<sub>4444</sub>][OH] to corresponding tri-*n*-butylphosphine oxide and butane is illustrated in Fig. 1. The decomposition mechanisms of phosphonium hydroxides were discussed by McEwen *et al.* (1965) already in the 1960's.



**Fig. 2.** Proposed process scheme for treating wheat straw with [P<sub>4444</sub>][OH]<sub>(aq)</sub>

There is a growing interest in the use of ILs other than the imidazolium-based systems, due to the reactivity of the imidazolium cation (Ebner *et al.* 2008; King *et al.* 2012). One of the promising cation types are the phosphonium series, due to their increased stability over other series. Aqueous [P<sub>4444</sub>][OH] electrolyte solutions are particularly interesting, as the sensitivity to water should be much lower than for the pure ILs. These are also one of the few aqueous-based non-derivatising systems for cellulose dissolution (Abe *et al.* 2012). Aqueous solutions also contain smaller amounts of the expensive cation component and the concentration of water is relatively easy to control. In this paper, we discuss the potential of [P<sub>4444</sub>][OH]<sub>(aq)</sub> for the processing of biomass. A potential recyclable fractionation scheme is proposed (Fig. 2), although not completely demonstrated. However, the process technoeconomics are not expected to be exceptionally good at this point, and we disclose some limitations in using these solutions with respect to decomposition of the expensive cationic component.

## EXPERIMENTAL

### Materials and Methods

Forty percent w/w  $[P_{4444}][OH]_{(aq)}$  was purchased from ABCR and was used without further purification. The concentration of the hydroxide was confirmed by standard pH titration. The halide content was determined by the supplier to be 1.55% w/w. Acetyl bromide (99%), glacial acetic acid, xylan from oat spelts (Lot #: 096K1783), and all other reagents and solvents were purchased from Sigma-Aldrich.

UV absorptions for acetyl bromide lignin analysis were acquired using a Varian Cary 50 Conc UV-VIS spectrometer. For ash content analysis, the TGA vessels were weighed with a Mettler Toledo TGA/SDTA851<sup>e</sup> TGA apparatus.

Wheat straw (WS) and a wheat straw:bran mixture (WSN) were obtained from project partners at the Université de Toulouse, France.

### Stability of $[P_{4444}][OH]_{(aq)}$ Solutions

Fifty to sixty percent  $[P_{4444}][OH]_{(aq)}$  was produced by concentration of the commercial 40%  $[P_{4444}][OH]_{(aq)}$  solution using rotary evaporation at 15 to 25 mbar under 25 °C. If the concentration was performed at higher temperatures, a measurable amount of decomposition product was detected using <sup>31</sup>P NMR spectroscopy.

A general procedure for  $[P_{4444}][OH]_{(aq)}$  decomposition experiments was as follows: A 1.5-mL glass vial was filled with  $[P_{4444}][OH]_{(aq)}$  solution. The vial was chosen to give minimum head-space, as this introduces error into the experiment due to the concentration changes during refluxing. The vial was capped with a plastic cap with an airtight liner. The sample was placed in a regulated oven at the desired temperature. After 2, 4, 8, or 24 h, an NMR sample was prepared by taking 50 µL from the vial. Seven hundred microlitres of D<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> (aq.) solution were added as an internal standard. The solution was carefully mixed and transferred into a 5-mm NMR tube. A <sup>31</sup>P NMR spectra was recorded with [H<sub>3</sub>PO<sub>4</sub>] found at 0 ppm, tetra-*n*-butylphosphonium cation ( $[P_{4444}^+]$ ) found at 33 ppm, and the decomposition product tri-*n*-butylphosphine oxide found at 61 ppm. Integrating the  $[P_{4444}^+]$  peak against the internal standard gives a rough correlation of the decomposition. Note that integrating against the decomposition peak is ill-advised since the phosphine oxide is only slightly soluble in water. <sup>31</sup>P NMR spectra were acquired with a Varian Innova 600 MHz spectrometer at 27 °C (128 transients, D<sub>2</sub>O), with inverse-gated decoupling on the proton channel. The <sup>31</sup>P sweep width was 40,000 Hz, the transmitter offset was centred on 50 ppm, the pre-relaxation delay was 2 s, the acquisition time was 1.6 s, and the pulse-width was approximately 75 °. The collected data was processed with MestReNova v.8.1.4-12489.

The other challenge is to remove volatile butane after heating from the small liquid volume to obtain reliable results.

### Biomass Treatment

Prior to treatment, the biomass was cut to fine particles using scissors and pulverised using a ball-mill, to pass through a 45-mesh sieve. After milling, extractives were removed by washing the milled straw twice with 70% (v/v) ethanol and once with 1:1 (v/v) chloroform:methanol solution. The straw was then dried in a fan oven over several days at 60 °C.

The biomass ‘cooking’ was conducted by weighing 5 w/w% of milled and extracted wheat straw (typically 0.20 g) to a glass vial followed by weighing 95 w/w %

of  $[P_{4444}][OH]_{(aq)}$  solution (typically 3.80 g). A magnetic stirring bar was placed into the vial, and the vial was capped with an airtight plastic cap. The vial was placed into an oil bath at the desired temperature and was left to stir for various lengths of time. After the cooking, the contents of the vial, minus the stirring bar, were transferred into a 15-mL plastic centrifuge tube with excess ethanol (typically 8 mL). The mixture was briefly vortexed to homogenise the solution and then centrifuged (5 min, 3000 rpm). To remove the residual electrolyte solution, the pellet (S1) was washed four times with ethanol by vortexing for 1 min and centrifuging (5 min, 3000 rpm). In addition, the solid was washed twice in boiling water for 3 h. After centrifugation, the solid was transferred to an 8-mL vial and dried in a fan oven at 60 °C. All washing liquids were combined with the remaining electrolyte solution. This was acidified with HCl. Acidification yielded a small amount of carbohydrate-rich solid, which was separated by centrifugation, washed twice in boiling water, and dried in fan oven at 60 °C to give second fraction (S2). After acidification, the liquid was evaporated to dryness to yield  $[P_{4444}][Cl]$ . In general, the proposed process scheme in Fig. 2 was followed, except that fresh solvents were used in the washing steps to allow for reliable analysis of fractions.

### Lignin Content Determination

AcBr analysis was performed by first preparing 25% (w/w) AcBr in AcOH solution, by adding 5 mL of 99% AcBr to 23.8 mL of glacial acetic acid. Then, 4 to 6 mg of each sample was accurately weighed into glass culture tubes using an analytical balance ( $\pm 0.1$  mg). Next, 5 mL of 25% (w/w) AcBr in AcOH was added to the tubes, and the tubes were capped with plastic caps equipped with a Teflon liner. Tubes were then placed into a 50 °C water bath for 2 h to digest, while gently mixing the tubes every 15 min. The solutions were then washed into 100-mL volumetric flasks, which contained 10 mL of 2 M NaOH and 25 mL of glacial AcOH. The volumetric flasks were rinsed with further glacial AcOH to a total volume of 100 mL in the volumetric flasks. The absorbance of the diluted digestion solutions was measured with a UV-spectrometer at 280 nm. The absorption of a blank sample was used as the baseline spectra. Untreated WS or untreated WSN was used as reference in every run. AcBr soluble lignin can be calculated according to the following equation using the absorbance reading,

$$\text{Lignin content (\%)} = 100\% \times V A / (17.54 m L)$$

where  $V$  is the volume of the sample (100 mL),  $A$  is the absorbance, 17.54 is the absorptivity for wheat straw (Fukushima and Hatfield 2004),  $m$  is the mass of sample (4 to 6 mg), and  $L$  is the path-length (1 cm).

The improved acetyl bromide method (Iiyama and Wallis 1988; 1990) was chosen to analyse lignin contents because it allows the use of very small samples, yet gives reasonable accuracy when performed consistently. The procedure was performed according to the Hatfield *et al.* (1999) method. They suggested that perchloric acid should not be used and that the temperature should be lowered to 50 °C and compensated for by increasing the reaction time from 30 min to 2 to 4 h. Without the addition of perchloric acid, the procedure gave slightly lower lignin content but the solubilisation of the sample was not complete. However, Hatfield *et al.* show that perchloric acid reacts with xylan, which gives unwanted absorption in the 280 nm region. The present results for lignin contents in wheat straw before cooking are in agreement with those of Fukushima and Hatfield (2004).

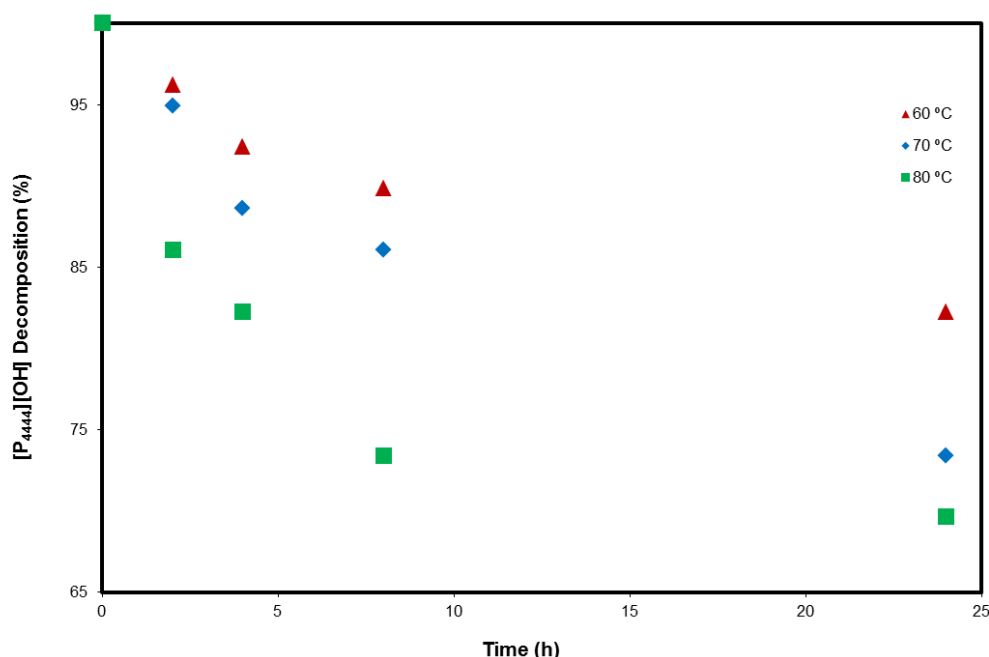
## Ash Content Determination

Ash contents were determined by accurately weighing 5 to 20 mg of the sample into pre-weighed oven dried TGA vessels. The vessel was placed in a muffle oven. The oven was heated directly to 600 °C and left to heat for 30 min at 600 °C. The vessel was removed from the oven when the temperature of the oven had cooled to below 250 °C. The vessel was weighed again to determine weight loss of the sample. In the present work, the TGA oven balance was used to obtain the most accurate results.

## RESULTS AND DISCUSSION

### Stability of $[P_{4444}][OH]_{(aq)}$

After initially testing the system, it was found that 60 wt%  $[P_{4444}][OH]_{(aq)}$  may not be as stable as required for continuous processing (Abe *et al.* 2012). Therefore, it was necessary to thoroughly investigate the stability before continuing biomass treatment experiments. In the present experiments,  $[P_{4444}][OH]$  decomposed completely if water was continuously removed. In dilute solution, decomposition occurred only partially, depending on concentration and heating.



**Fig. 3.** Decomposition of 60 %  $[P_{4444}][OH]$  in water at various temperatures

Results of the decomposition concentration limits from initial experiments are shown in Table 1. These results showed that the commercial solution (40 wt%, run 1) was stable at least up to 90 °C and was 50 wt% composition. Above this, it seems that concentration is critical, as the decomposition occurred slowly even at 40 °C, with the 60 wt% solution (Table 1 run 3). This is unfortunate, as Abe *et al.* (2012) reported that it was the 60 wt% concentration specifically that was capable of dissolving cellulose. This seems to correspond both to a critical salt hydration level necessary for cellulose dissolution and salt stability. This concentration is an approximate molar ratio of 10:1 for

H<sub>2</sub>O:[P<sub>4444</sub>][OH]. Below this ratio, degradation is rapid. Above this concentration degradation is slow, even at elevated temperatures. In essence, [P<sub>4444</sub>][OH]<sub>(aq)</sub> stability is highly concentration dependent. Further stability experiments were performed for 60 % composition at different temperatures (Fig. 3). These show rapid degradation as the temperature was increased. In Fig. 3, the initial decomposition plateau time is different for each temperature. This is due to the differing heating rates of the solutions, which depend on the temperature inside the oven.

**Table 1.** Decomposition Limits of [P<sub>4444</sub>][OH] (40-70 wt%) Determined using <sup>31</sup>P NMR

Run	[P <sub>4444</sub> ][OH]:H <sub>2</sub> O (w/w)	Temp. (°C)	Time (h)	Conclusion
1	40:60	90	24h	Stable
2	50:50	90	24h	Stable
3	60:40	40	24h	Unstable
4	70:30	-	-	*
* 70:30 w/w cannot be reached due to decomposition at this concentration.				

### Biomass Pretreatment

After determining the stability of the electrolyte solutions, it was decided to test the usable concentration ranges for extraction of wheat straw. It became obvious that if the straw was not pulverised to smaller particle size, then removal of the phosphonium salt electrolyte solution from the biomass becomes difficult and only achievable after repeated washing. It was found that, in the absence of high-shear mixing, preparatory ball-milling to 45 mesh was not time consuming, and it produced small enough particle sizes to permit rapid diffusion in and out of the biomass particles.

Extractives can be removed by, *e.g.*, Soxhlet extracting (toluene:ethanol 2:1) the straw for several hours (Sun and Tomkinson 2003). Deswarte *et al.* (2007) have developed a method to extract wheat straw with super critical CO<sub>2</sub>. They also made calculations of the economics of collecting extractives from wheat straw. In the present work the extractives were removed by simply washing the milled straw with common laboratory solvents (Foster *et al.* 2010) to permit accurate lignin analysis as extractives can have considerable UV absorptivity. Most of the extractives from the straw can be extracted rapidly by vortexing the straw twice with 70% (v/v) ethanol and once with a mixture of chloroform:methanol 1:1 (v/v) in the liquid to solid ratio of 25:1 (mL/g).

### Biomass Extraction with 40 % [P<sub>4444</sub>][OH]<sub>(aq)</sub>

The extractions were implemented with [P<sub>4444</sub>][OH]<sub>(aq)</sub> for two different types of straw. The first variety was WS. The second was a mixture of wheat straw and bran in ratio 6.2:1 (WSN). This material was prepared as follows, according to a previous publication (Jacquemin *et al.* 2012). The bran was treated with aqueous alkali for an hour. After alkali treatment, the bran was introduced to wheat straw and the mixture was extruded by using a twin-screw extruder. The goal of this was to extract hemicelluloses from the bran and valorise the remaining material as a mixture with straw.

The conditions for extracting wheat straw were optimized using [P<sub>4444</sub>][OH]<sub>(aq)</sub> by taking four factors into account. These factors are: concentration of the electrolyte solution, weight percent of straw in the mixture, temperature, and time of the treatment. Lignin content analysis of S1 was used as a quick measure of fractionation efficiency (Table 2).

**Table 2.** Constituents of the Solids Obtained from Treating WSN with Various Concentrations of [P<sub>4444</sub>][OH] and WSN

[P <sub>4444</sub> ][OH]:H <sub>2</sub> O (w:w %)	WSN loading (wt %)	Temp. ( °C)	Time (h)	Lignin (wt %)*
Untreated	-	-	-	22.7
40:60	5	RT	2	15.5
40:60	5	50	2	12.3
40:60	5	70	2	9.3
40:60	5	RT	4	14.3
40:60	5	50	4	8.6
40:60	5	70	4	9.1
40:60	2.5	RT	4	12.3
40:60	2.5	50	4	11.0
40:60	2.5	70	4	8.4
60:40	5	RT	4	14.0

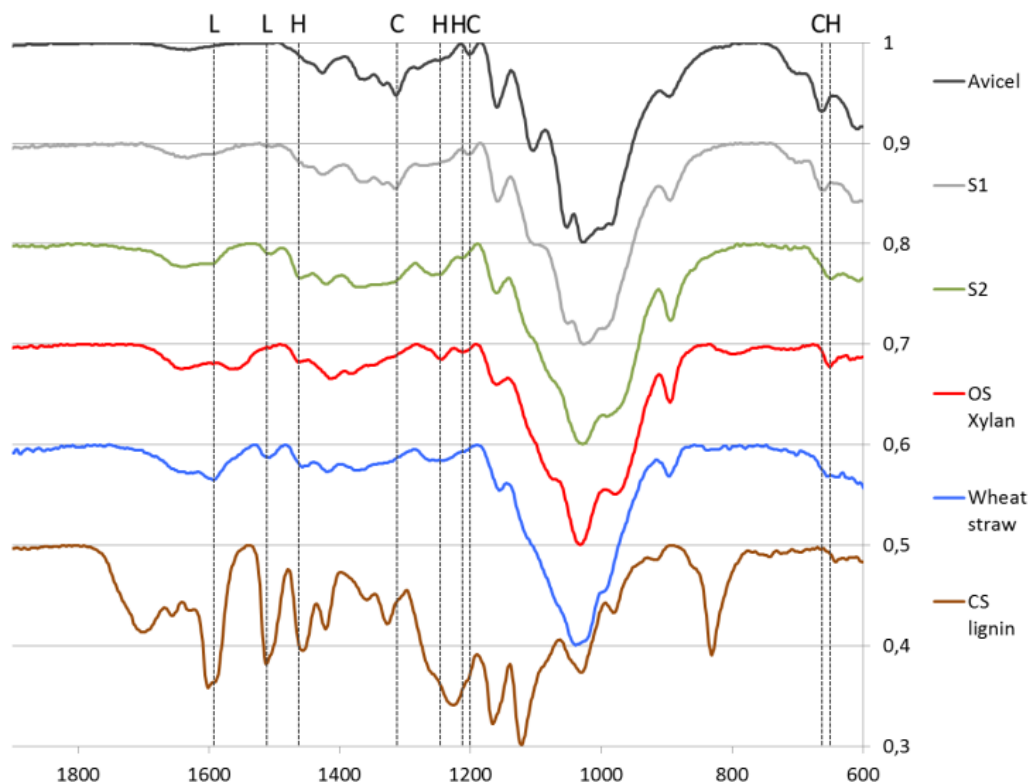
\* Yields were approximately 40% in each case, but due to the small scale, we were unable to measure accurate yields.

In the initial optimisation step, only the lignin contents were analysed because the removal of lignin at low phosphonium salt compositions was only expected (*i.e.*, cellulose is not soluble at 40:60 compositions). It can be seen that the lignin content was reduced significantly already after 2 h at 70 °C with the 40:60 solution. According to Table 2, the temperature was identified to be the most important factor; therefore, the temperature 90 °C was selected for further experiments. In fact, the unstable cellulose-dissolving mixture (60:40) performs relatively poorly as it cannot be heated, although it does not offer that much extra lignin removal for the lower salt concentrations at the same temperature. Time was fixed at 2 h.

The optimum condition results for wheat straw treatment are shown in Table 3. The scale was increased to allow for isolation of measurable amount of S2 to allow for lignin content analysis and ATR-IR analysis against standard samples (Fig. 4). These included microcrystalline cellulose (Avicel), oat spelt xylan, and cornstover enzymatic mild acidolysis lignin (EMAL) (Guerra *et al.* 2006a; 2006b). S1 was determined to be a carbohydrate-rich material with low lignin (7.2%) and ash (0.8%) contents. The lignin content of S1 was slightly lower but in the same range compared to those of Fu *et al.* (2010) and da Costa Lopes *et al.* (2013b). The IR spectrum of S1 is in general very similar to that of microcrystalline cellulose. As expected, it only contains small resonances similar to that of lignin (most characteristic peaks: aromatic ring ~1500 cm<sup>-1</sup>, acetyl or carboxylic acid groups ~1600 cm<sup>-1</sup>), and does not resemble that of xylan. There is an excellent summary of characteristic FTIR absorption bands for cellulose, hemicellulose and lignin (da Costa Lopes *et al.* 2013b).

Based on the findings described above, S1 is considered to be majority cellulose and potentially bleachable to high purity. S2 is a dark-coloured carbohydrate-rich solid with lignin content of 13.2 %. After drying, Solid 2 is similar to a hemicellulose-rich film-like solid that Bahcegul *et al.* (2012) obtained by acidifying the NaOH solution used in biomass extraction. The IR spectrum of S2 is compared to oat spelt xylan. S2 is also soluble in aqueous NaOH solutions, facilitating further processing.





**Fig. 4.** ATR-IR spectra of fractions (S1, S2) and reference materials (microcrystalline cellulose, xylan from oat spelts, ball-milled wheat straw, cornstover EMAL lignin) (Assignments: L = Lignin, H = Hemicelluloses, C = Cellulose)

The results in Table 3 show that  $[P_{4444}][OH]_{(aq)}$  reduced lignin and ash content efficiently in the high-yielding S1 fraction. The reduced yield can be explained by removal of ash, further hemicelluloses, and lignin. It is also apparent from Table 3 that much material was not recovered in S1 and S2. The mass balances were not complete. The S1 yield was, however, comparable to NaOH extracted straw, but with a reduced lignin content.

**Table 3.** Composition of the Solids from Optimised Extraction of Wheat Straw (Conditions: 2 h at 90 °C with 5 wt% WS Loading)

Treatment	Lignin (wt %) S1 (/ S2)	Ash (wt %) S1 (/ S2)	Yield (%) S1 (/ S2)
Untreated	22.4	5.6*	-
1.5 M NaOH	10.3	0.7	44
$[P_{4444}][OH]**$	7.2 / 13.2	0.8 / 1.0	39 / 3

\* More than half of the ash is soluble in boiling water.  
\*\* Performed in slightly larger scale in a round bottom flask.

Unfortunately, as we were not able to recover either ash or lignin rich precipitates during the process, it seems that lignin and silicates may accumulate in the used electrolyte solution, requiring further purification steps. More than half of the material remained dissolved and could not be precipitated with the two-step precipitation method. This may be due to cleavage or partial depolymerisation of the biopolymers to oligomeric

materials. However, it may be possible to recover more solids with different anti-solvents or using lower temperature in the treatment.

### Recycling of $[P_{4444}][OH]_{(aq)}$

Recycling the used electrolyte solution with addition of antisolvent to precipitate, followed by re-concentration to initial concentrations, was rejected at an early stage because it did not work efficiently enough in preliminary testing. In the present case there was always residual biomass trapped in the electrolyte solution preventing recycling by this method. It is likely that lignin was present in solution as phenolates with phosphonium counter ions, as the aqueous pKa of the phenols is lower than for aqueous hydroxides. Therefore, antisolvents may only open the opportunity to reuse the solution but not genuinely recycle *via* purification of the residual electrolyte or IL. To achieve more efficient precipitation of biomass, acidification was necessary, which results in anion metathesis. If sufficient biomass could be removed continuously, with the correct choice of acid to allow for reasonable process efficiencies, then metathesis back to hydroxide would be necessary. This could be achieved in a number of ways, *i.e.*, ion exchange (Umeno and Takita 1988).

## CONCLUSIONS

1. The relatively stable aqueous 40 wt% tetra-*n*-butylphosphonium hydroxide solution can be used to produce enriched cellulose and hemicellulose fractions *via* lignin and silicate extraction from wheat straw.
2. 40% tetra-*n*-butylphosphonium hydroxide aqueous solutions were slightly more effective for delignification of wheat straw than the reference aqueous 1.5 M NaOH solution.
3.  $^{31}P$  NMR decomposition studies showed that 60% aqueous tetra-*n*-butylphosphonium hydroxide decomposes rapidly within the processing temperatures.
4. Aqueous tetra-*n*-butylphosphonium hydroxide solutions cannot be concentrated to 70%, as the salt irreversibly decomposes at this concentration at low temperatures.
5. Purification of the electrolyte solution for continuous cycling is problematic. It was found that half of the treated straw remains in the used electrolyte solution.
6. Due to the high cost and low stability of the salt, recycling of soluble biomass and salt should be performed to make the process economical. This could be achieved through anion metathesis.

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