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1 **Dissolution and hydrolysis of fibre sludge using hydroxyalkylimidazolium** 2 **hydrogensulphate ionic liquids**

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10

11 **Abstract**

12 The dissolution and hydrolysis of wet fibre sludge in ionic liquids (ILs) with different reaction
13 conditions are performed in this study. Novel types of hydroxyalkylimidazolium hydrogensulphate
14 ILs, [glymim]HSO₄, [hemim]HSO₄ and [hpmim]HSO₄, are especially designed and aimed to
15 combine the dissolution and hydrolysis of wet fibre sludge in a one-step pretreatment. The results
16 were obtained based on the analysis of total reducing sugars (TRS) with the DNS method. The
17 dissolution and hydrolysis of fresh wild horse chestnut seed (*Aesculus hippocastanum*) with the
18 same ILs were also carried out as a comparison reference. Since fibre sludge is cellulose based and
19 horse chestnut seed is starch based, a direct comparison of the difference in functions between these
20 ILs in one-step dissolution and hydrolysis were analysed based on the results.

21 *Keywords: Ionic liquid, Dissolution, Hydrolysis, Fibre sludge (Pinus sylvestris, Picea abies, Betula*
22 *pubescens and Betula pendula), Lignocellulose, Horse chestnut seed (Aesculus hippocastanum)*

23 **1 Introduction**

24 Solid residuals generate a continuous disposal problem for the forest and pulp industry. The rising
25 cost of landfill is driven by legislation to protect the environment and human health. The European
26 Council Waste Framework Directive (WFD) 2006/12/EC has been amended by the new WFD
27 Directive 2008/98/EC which came into force in December 2010. The aim of this waste policy is to
28 reduce resource usage and recover the waste, in order to promote sustainability. A significant
29 amount of research, therefore, has been conducted to convert solid residual materials towards other
30 useful materials [1] [2]. As a result, there is a growing tendency in the Finnish pulp and paper
31 industry to look for options for the reuse or recycling of solid residuals.

32 Fibre sludge is a by-product from a pulp mill in which the residuals from the chemical pulping
33 process in Finland totals approximately 300,000 tonnes as dry material annually [3] [4]. Depending
34 on the pulp mill, fibre sludge is either combusted for energy production and/or disposed at landfills.
35 However, fibre sludge is rich in cellulose and it is possible to be used as a raw material in the
36 production of more valuable products, such as biofuel [3].

37 Ionic liquids (ILs) have been viewed as remarkable environmental friendly solvents, compared to
38 other volatile organic compounds for biomass pretreatment due to their broad liquid region, high
39 thermal stability, negligible vapour pressure and that no formed toxic or explosive gases are
40 released during utilisation [5] [6] [7].

41

42 Most ILs consist of organic cation and inorganic anion. By varying the nature of the anion or cation
43 present in the IL, the resulting physical and chemical properties of the IL such as melting point,
44 viscosity, hydrophobicity and hydrolysis stability can be directly affected [8]. This means, ILs can
45 be tailored for a specific application. Due to this enormous potential, ILs have been put forward to
46 be used in various fields. For example, ILs can be used in biocatalysis, batteries, waste recycling
47 and cellulose processing [9].

48

49 In our previous study [3], a task-specific ionic liquid 1-(4-sulfobutyl)-3-methylimidazolium
50 chloride ([SBMIM]Cl) with a Brønsted –acid function has been used in a one-step dissolution and
51 hydrolysis of fibre sludge [3]. The study proved that it is possible to combine both dissolution and
52 hydrolysis in the pretreatment of lignocellulosic materials, but the levels of total reducing sugars
53 were not high enough. Therefore, a one-step pretreatment of fibre sludge with three novel types of
54 hydroxyalkylimidazolium hydrogensulphate ILs is of particular interest in this study. The
55 commonly used ILs in pretreatment of lignocellulosic materials often contain chloride anions and
56 since chloride has so many negative impacts on human health and the environment, the use of other
57 anions that are also effective in pretreatment should be considered.

58

59 The aim of this study is to combine the dissolution and acidic hydrolysis stages into one single fibre
60 sludge pretreatment step using hydroxyalkylimidazolium hydrogensulphate ILs. At the end of
61 pretreatment, a certain amount of fermentable sugars is expected to be produced.

62

63 In addition to fibre sludge, horse chestnut seeds (*Aesculus hippocastanum*, collected from
64 Germany) are also pretreated with the same method in this study. Since horse chestnut seed is a

65 starch based biomass compared to fibre sludge which is cellulose based, by the end of this study,
66 obtained results of these two types of feedstock in pretreatment can be directly compared.

67 **2 Experimental**

68 **2.1 Materials and characterization**

69 **2.1.1 Fibre sludge**

70 Fibre sludge, also known as a primary sludge, was provided by a Finnish pulp mill (UPM
71 Pietarsaari pulp mill) as a by-product from its chemical pulping process of Scots pine (*Pinus*
72 *sylvestris*), Norway spruce (*Picea abies*), downy birch (*Betula pubescens*) and silver birch (*Betula*
73 *pendula*). According to chemical analysis, fibre sludge contains mass fraction of approximate 93-
74 94% cellulose and 6-7% hemicelluloses of total carbon materials [3]. The fibre sludge that is
75 supplied by a pulp mill is dried by a roll press to obtain a high solid concentration, which has a
76 mass fraction of around 47% (See Figure 1).

77 Figure 1 Here

78 *Figure 1 Dried and wet fibre sludge used in this study are analysed by FTIR.*

79 The official standard method T 203cm-99 was used to determine α -, β - and γ -cellulose contents of
80 the dried fibre sludge sample. Undergraded, higher-molecular-weight cellulose is indicated by α -
81 cellulose, β -cellulose indicates degraded cellulose while γ -cellulose mainly consists of
82 hemicellulose [4]. In addition, the total carbon content (TC) of the dry sample was determined by
83 elementary analysis with a Perkin Elmer CHNS analyser [3] [4].

84 shows the characterization of fibre sludge that was used in the experiments and also some
85 literature values are given as a reference.

86 *Table 1 Elemental analysis and some physical properties of fibre sludge [3][4]*

87 Table 1 Here

88

89 **2.1.2 Horse chestnut seed**

90 Horse chestnut seed is low in protein (<5%) and fat but contain complex carbohydrates. As such,
91 starch is the main component of horse chestnut seed. In this investigation fresh wild edible horse

92 chestnut seeds were collect from a street in northern Germany due to the huge amount of this type
93 of chestnut seeds dropping beside the street each year. The characterization of horse chestnut seed is
94 presented in

95 *Table 2 Chemical composition of a horse chestnut seed [10][11]*

96 Table 2 Here

97 **2.2 Ionic liquids**

98 Three types of hydroxyalkylimidazolium hydrogensulphate ILs, [glymim]HSO₄, [hemim]HSO₄ and
99 [hpmim]HSO₄ that were used in this study, their chemical structures are illustrated in Figure 2.
100 These ILs are particularly designed for the combined application of dissolution and hydrolysis of
101 lignocellulosic materials in a one-step reaction.

102

103 **2.2.1 Ionic liquids preparation**

104 Hydroxyalkylimidazolium hydrogensulphate ILs were obtained from a two steps process in which
105 hydroxyalkylimidazolium chlorides were prepared by the following reported method described in
106 literature [12]. 3-Chloro-1-propanol 28,1 g (0,29 mol), 2-chloro-1-ethanol 23,7 g (0,29 mol) and 3-
107 chloro-1,3-propanediol 33,0 g (0,29 mol), were dissolved with N-methylimidazole 24,6 g (0,3 mol)
108 in a three-neck flask and stirred under mechanical agitation at 75°C for 48 h. The resulting mixture
109 was then cooled down to room temperature and washed repeatedly with small portions of ethyl
110 acetate. Solvent residue was then removed under a vacuum and the resulting crude ILs were
111 obtained as yellow, viscous oils except [hemim]Cl, which solidified after cooling. Crude
112 [glymim]Cl or [hpmim]Cl were dissolved in methanol (200 mL) and stirred with the addition of
113 activated charcoal (5 g) for 1 hour at 50°C. The suspension was then filtered and methanol was
114 evaporated under vacuum. Purified ILs were obtained as almost white, viscous oils and their
115 resulting yields are between 90% and 92%.

116

117 In the case of hydroxyalkylimidazolium hydrogensulphates, these were prepared based on the
118 method described in literature but with a small modification [13]. The solution of proper
119 hydroxyalkylimidazolium chloride (0.2 mol) in a mixture of methanol/acetonitrile (50 + 200 mL)
120 was placed in a two-neck flask in which potassium hydrogen sulphate (0.24 mol) was added and

121 stirred under mechanical agitation for 24 h at room temperature. After this time a precipitated white
122 solid of KCl was filtered out and solvents were evaporated under vacuum. Crude ILs were obtained
123 as yellow, viscous oils which were then subsequently dissolved in methanol (200 mL) and stirred
124 with the addition of active charcoal (5 g) for 1 hour at 50°C. Finally methanol was evaporated under
125 vacuum and the resulting purified ILs were obtained as light yellow, viscous oils.

126 Figure 2 Here

127 *Figure 2 Structures of [glymim]HSO₄, [hemim]HSO₄ and [hpmim]HSO₄.*

128

129 2.2.2 Ionic liquids characterization

130 The pH of these acidic ILs were between 2 and 3, and the viscosity of [glymim]HSO₄ was the
131 highest with an over range of 80% and a floating point of 13 Pa·s, compared to [hpmim]HSO₄
132 which was the lowest with an over range of 8.3% and a floating point of 1.7 Pa·s. Beside this, these
133 ILs were analysed by FTIR and the resulting spectra are presented in Figure 3. The results clearly
134 show that a small amount of water is present in these ILs, which is either due to the fact that the
135 original ILs contain a small amount of water or the ILs possibly absorb water from the air, or both.
136 Therefore, ILs with a water content of 9-13 dm³m⁻³ were determined by Karl Fischer titration and
137 further detailed analysis on their chemical structures by nuclear magnetic resonance (NMR) were
138 performed.

139 Figure 3 Here

140 *Figure 3 ILs used in this study were analysed by FTIR.*

141 ¹H NMR spectra of ILs were acquired using a Bruker DPX 200 instrument (200.13 MHz) in
142 deuterium dioxide, D₂O, at room temperature. Calibration of peaks is based on a solvent residual
143 peak (H₂O = 4.79 μL/L).

144 **[glymim]HSO₄** Yield 92.3%, IR (neat): 3275, 3238 (OH), ¹H-NMR (500 MHz, D₂O, μL/L): 8.77
145 (s, 1H), 7.48 (s, 1H); 7.43 (s, 1H); 4.28 (dd, 2H); 4.01 (m, 1H); 3.91; 3.94; 3.89 (s, 3H); 3.61 (m,
146 2H), ¹³C-NMR (120 MHz, D₂O, μL/L): 137.3, 123.2, 123.1, 69.8, 62.4, 51.7, 35.7 MS (ESI-M⁺)
147 *m/z* 83 [HIm⁺] (41%), 157.1 [M⁺] (100%)

148 **[hpmim]HSO₄** Yield 91.7%, IR (neat): 3276, 3241 (OH), ¹H-NMR (500 MHz, D₂O, μL/L): 8.65
149 (s, 1H); 7.49 (s, 1H); 7.43 (s, 1H), 4.20 (dd, 1H), 4.02 (dd, 1H); 3.98; 3.80 (s, 3H), 3.49 (m, 2H);

150 1.91 (m, 2H), ¹³C-NMR (120 MHz, D₂O, μL/L): 136.8, 123.2, 122.5, 58.2, 48.9, 36.6, 31.5 MS
151 (ESI-M⁺) *m/z* 83 [HIm⁺] (9%), 147.1 [M⁺] (100%)

152 [**hemim**]HSO₄ Yield 92.6%, IR (neat): 3277, 3241 (OH). ¹H-NMR (500 MHz, D₂O, μL/L): 8.64 (s,
153 1H); 7.40 (s, 1H); 7.35 (s, 1H); 4.19 (m, 2H); 3.79 (m, 2H); 3.78 (s, 3H), ¹³C-NMR (120 MHz,
154 D₂O, μL/L): 136.4, 123.6, 122.4, 59.8, 51.1, 35.8 MS (ESI-M⁺) *m/z* 83 [HIm⁺] (20%), 127.0 [M⁺]
155 (100%)

156

157 **2.3 Sample dissolution and hydrolysis in ionic liquid**

158 To analyse the dissolution and hydrolysis of wet fibre sludge in three different types of
159 hydroxyalkylimidazolium hydrogensulphate ILs, the following experimental procedure was
160 developed (See Figure 4).

161 Figure 4 Here

162 *Figure 4 Fractionation scheme in one-step dissolution and hydrolysis of fibre sludge.*

163

164 Wet fibre sludge sample (WFSSPS) and IL were heated in a flask that was partly submerged in an
165 oil bath at different temperatures (T), reaction times (RT) (100°C for 30min; 100 °C for 1h and 45
166 °C for 3h) and weight ratios (wet fibre sludge : ionic liquid) of 20%, 15%, 10% and 5%. 10 cm³ of
167 anti-solvent (hot distilled water) was added after the reaction, in order to reform the cellulose. The
168 horse chestnut seed sample (CNTS) pretreatment was performed with the same procedure and
169 parameters.

170 During dissolution and hydrolysis for every reaction observations showed that a gel was formed,
171 however, the amount of formed gel is related to the amount of fibre sludge in ILs. The more fibre
172 sludge presented, the more gel was formed. Due to the low amount of IL, fibre sludge was not
173 totally dissolved.

174 **2.4 Determination of total reducing sugars (TRS)**

175 The total amount of reducing sugars including the content of glucose, xylose and cellobiose were
176 measured according to the DNS method after one-step dissolution and hydrolysis. This method

177 provides a simple and rapid estimation of the sugar extent by simultaneous oxidation of functional
178 sugar groups, the reduction of DNS reagent and colour changes during the reaction. However, this
179 colour change reaction can be interfered by an additional reaction between dissolved oxygen and a
180 reagent.

181 In the determination of TRS, a 1% 3,5-dinitrosalicylic acid reagent was added into the sample
182 solution with a volume ratio of 1:1 and heated in a boiled water bath for 5min. The determination of
183 sugar concentration was performed with a UV spectrophotometer (Shimadzu UV-1800) at a
184 wavelength of 540nm which is based on the standardisation of glucose.

185

186 **3 Results and discussion**

187 Fibre sludge and horse chestnut seeds were pretreated with three hydroxyalkylimidazolium
188 hydrogensulphate ILs [glymim]HSO₄, [hemim]HSO₄ and [hpmim]HSO₄, as described in Section
189 2.3. The hydrogensulfate ion, HSO₄⁻, is a poor nucleophile and offered its acidic nature in further
190 hydrolysis reaction. In aqueous medium, HSO₄⁻ is a good hydrogen ion donor instead of acceptor.
191 These properties of HSO₄⁻ promoted the achievement of hydrolysis reaction. Since the pretreatment
192 process includes simultaneous dissolution and hydrolysis, the results of the pretreatment are based
193 on the yield of TRS in the final liquid phases (See Figure 5 and Figure 6).

194 Figure 5 Here

195 *Figure 5 TRS yields analysis for chestnuts and wet fibre sludge after pretreatment.*

196

197 Fibre sludge samples with different weight ratios in ILs were pretreated in the ILs and as a
198 reference comparison while horse chestnut seed samples were also pretreated with the same ILs. In
199 Figure 5, it clearly shows that the pretreatment of fibre sludge with a weight ratio of 10% in
200 [glymim]HSO₄, at 100°C for 30min (See Figure 5, S10) produced the highest TRS yield. Similar
201 observations were seen with the same fibre sludge sample in [glymim]HSO₄ at other weight ratios
202 (15%, 10% and 5%), demonstrating that among ILs, [glymim]HSO₄ had the most efficient
203 hydrolysis process. An exception to these observations was for a weight ratio of 20%. The
204 optimisation of dissolution and hydrolysis of wet fibre sludge in [glymim]HSO₄ can be considered

205 to be achieved with a sample weight ratio of around 10%. However, a too long reaction time leads
206 to a lowering in the TRS yield (See Figure 5, S13), likely due to the sugar degradation.

207 During the pretreatment process, a gel formed during the reaction and it is thought that the gelation is
208 possibly caused by methylcellulose that is a derivative of cellulose. There are presumably two
209 reasons to explain the appearance of methylcellulose in the reaction. (1) Methylcellulose is the side
210 product in the pulp mill which already exists in the fibre sludge samples. (2) In the pulp mill
211 industry, pulp is soaked and cooked in solution of sodium hydroxide (NaOH) for softening and the
212 resulting pulp goes to the further process. Fibre sludge, the residual from pulp mill, consists of
213 hydroxyl groups and it was rapidly dissolved in the hydroxyalkylimidazolium hydrogensulphate
214 ionic liquids, methylcellulose can be the by product in the substitution reaction by replacing
215 hydrophilic hydroxyl groups (-OH) with hydrophobic methoxide groups (-OCH₃) [14] [15] [16].
216 Methylcellulose has thermo-sensitive properties that allow it to be dissolved in water at low
217 temperature (approximately under 40°C) and it displays reversible gelation at a particular
218 temperature [17] [18]. The gelation of methylcellulose depends on the concentration of
219 methylcellulose, temperature and the type of salt solution used [19] [20]. Therefore, under the same
220 reaction conditions used in this study, the amount of gel formed can be affected by the type of IL
221 used. Figure 5 shows that the TRS yield of the fibre sludge sample S4, with weight ratio of 20% in
222 [glymim]HSO₄ is the lowest. A possible explanation for this could be that the [glymim]HSO₄ had a
223 greater effect on the gelation process than for other ILs and as a result, the formed gel blocked any
224 further reactions.

225

226 The results obtained from horse chestnut seed samples (S1, S2 and S3) are exactly the opposite to
227 fibre sludge of which horse chestnut seed sample S1 in [glymim]HSO₄ returned the lowest
228 production of TRS.

229

230 The major difference between cellulose and starch is that starch has its α -1,4 and α -1,6 glycosidic
231 bonds linked whereas for cellulose is β -1,4 glycosidic bonds linked. By having different glucose
232 molecule linkages, there are vast differences in properties. As can be seen from Figure 5, the
233 pretreatment in [hemim]HSO₄ and [hpmim]HSO₄ had a greater effect on the hydrolysis of horse
234 chestnut seeds, as opposed to the pretreatment of fibre sludge. It is possible that [hemim]HSO₄ and
235 [hpmim]HSO₄ worked in a similar way to amylases which are a good solvent at breaking α -1,4
236 glycosidic bonds. On the other hand, [glymim]HSO₄ is efficient at breaking β -1,4 glycosidic bonds
237 in cellulose.

238 Figure 6 Here

239 *Figure 6 TRS yields analysis after specific conditions for wet fibre sludge pretreatment.*

240 From Figure 6, sample S19 is of particular interest to the authors since it can be directly compared
241 to sample 16 (Figure 5) which was performed with similar reaction conditions. Both utilising wet
242 fibre sludge with a weight ratio of 5%, in [glymim]HSO₄, the major difference between the two
243 samples was that S19 was exposed in air for 2 hours, followed by pretreatment. The results show
244 that there was a higher TRS yield in S19 than in S16 which can be explained by the reaction that
245 took place in the pretreatment process. In both samples cellulose was dissolved and further
246 hydrolysed in the IL, but the mixture of S16 and IL did not contain much water. The small amount
247 of water that was present caused the uncompleted hydrolysis of S16 where on the other hand, the
248 mixture of S19 and IL was first exposed in the air which allowed moisture to be absorbed from the
249 air. Therefore, more water was available for the hydrolysis process and so more TRS was produced
250 in the pretreatment of S19.

251 Since fibre sludge samples pretreated with [glymim]HSO₄ produced the highest TRS yields in most
252 of the experimental cases, the authors also studied another [glymim]⁺ cation based IL, i.e.
253 [glymim]OH in the pretreatment of fibre sludge. Based on preliminary results, the TRS yield of
254 pretreatment of wet fibre sludge in [glymim]OH was significantly higher among the other three
255 hydroxyalkylimidazolium hydrogensulphate ILs. It appears that cation [glymim]⁺ has quite an effect
256 on the dissolution and hydrolysis of cellulose. The pretreatment of cellulose with [glymim]OH will
257 be carried out in further studies.

258 **4 Conclusion**

259 Fibre sludge is able to be dissolved and hydrolysed by a specific designed IL. In this study, the
260 highest TRS yield (28.96%) was produced in the pretreatment of wet fibre sludge in
261 [glymim]HSO₄. Results indicate that cation [glymim]⁺ based ILs are a good option for the
262 dissolution and hydrolysis of cellulose, since [glymim]HSO₄ is good for breaking down β -1,4
263 glycosidic bonds into glucose. For starch, [hemim]HSO₄ and [hpmim]HSO₄ are good for breaking
264 down α -1,4 glycosidic bonds.

265 The optimal wet fibre sludge weight ratio is around 10% while a greater weight ratio of fibre sludge
266 in an IL will cause gelation during the pretreatment resulting in the gel blocking any further
267 reactions. To achieve higher TRS yields, further optimisation of IL structures and dissolution

268 conditions is required. The amount of water (contained in ILs or samples) involved in the reaction
269 should be also considered and optimised. In the next study, we will test [glymim]OH in the
270 dissolution and hydrolysis of lignocellulosic materials and also the recycling of ILs.

271

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276

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Captions:

Figure 1 Dried and wet fibre sludge used in this study are analysed by FTIR.

Figure 2 Structures of [glymim]HSO₄, [hemim]HSO₄ and [hpmim]HSO₄.

Figure 3 ILs used in this study were analysed by FTIR.

Figure 4 Fractionation scheme in one-step dissolution and hydrolysis of fibre sludge.

Figure 5 TRS yields analysis for chestnuts and wet fibre sludge after pretreatment.

Figure 6 TRS yields analysis after specific conditions for wet fibre sludge pretreatment.

Figure 1

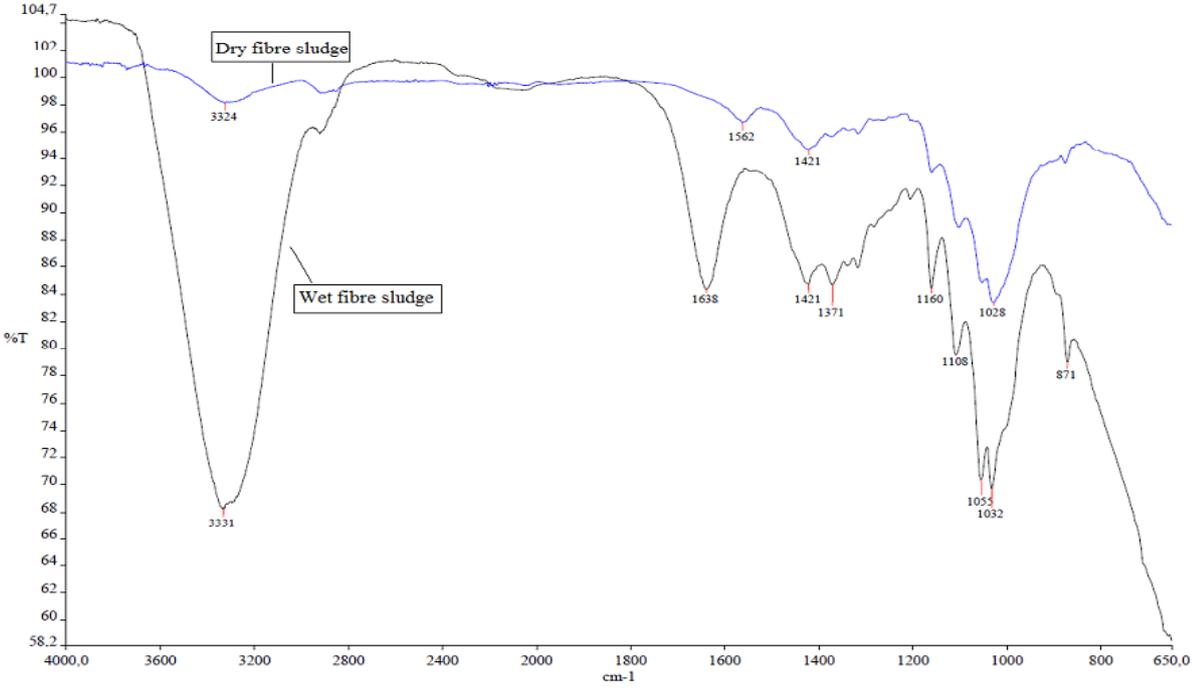


Figure 2

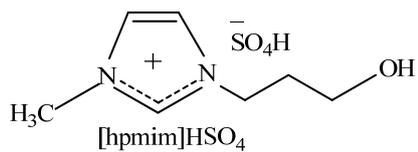
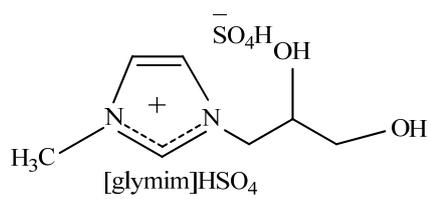


Figure 3

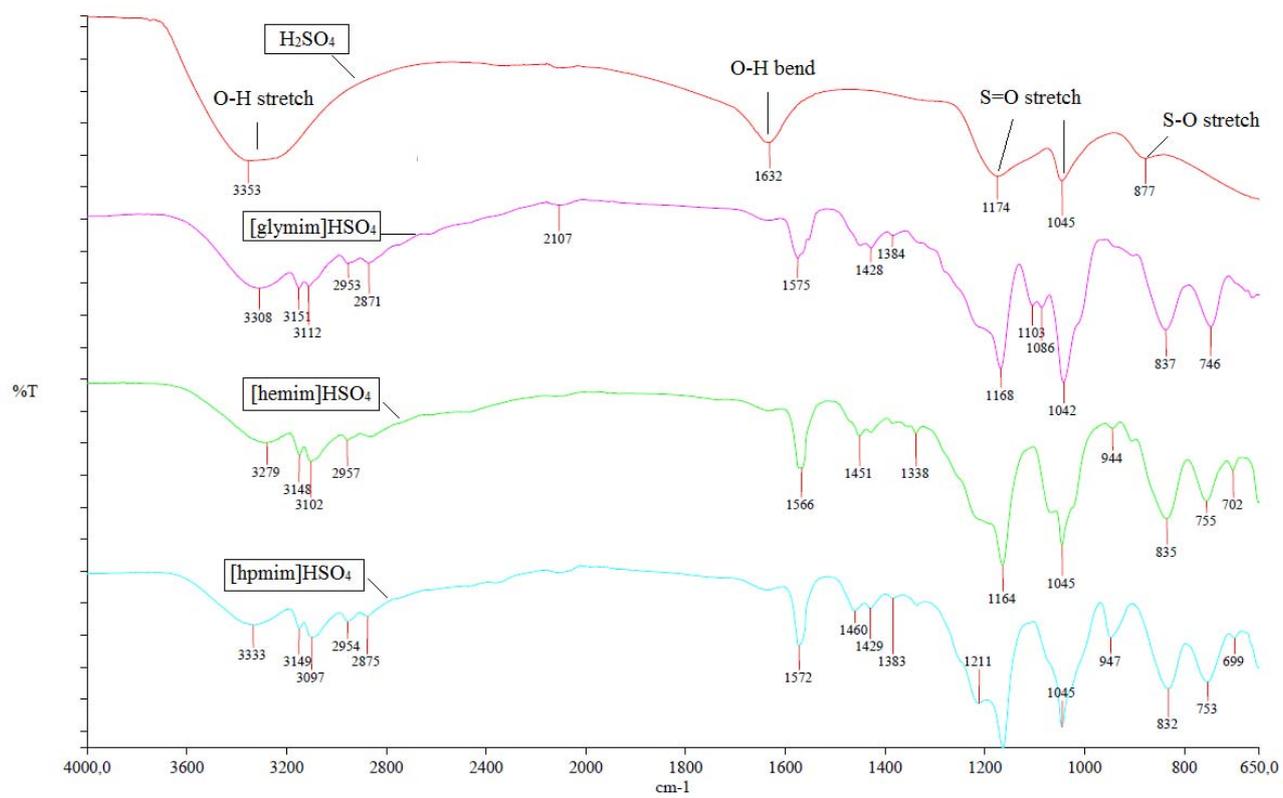


Figure 4

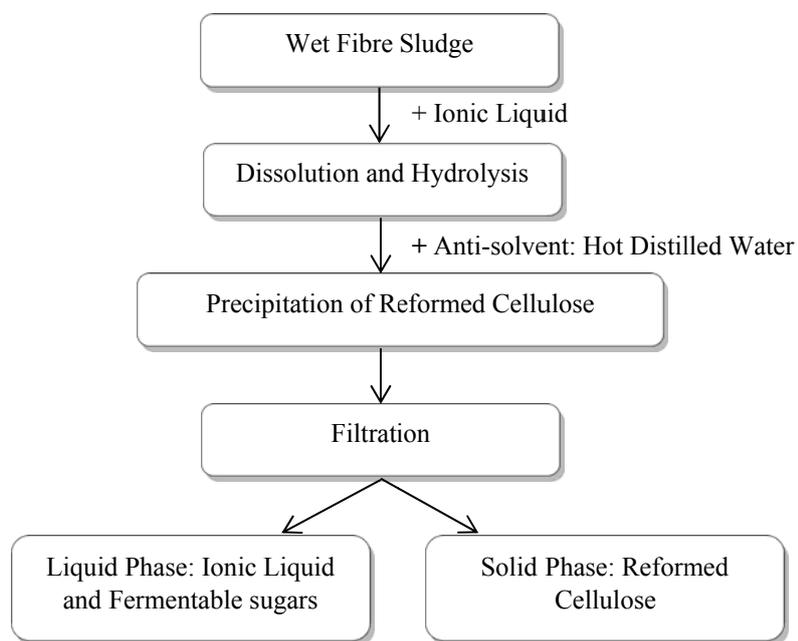


Figure 5

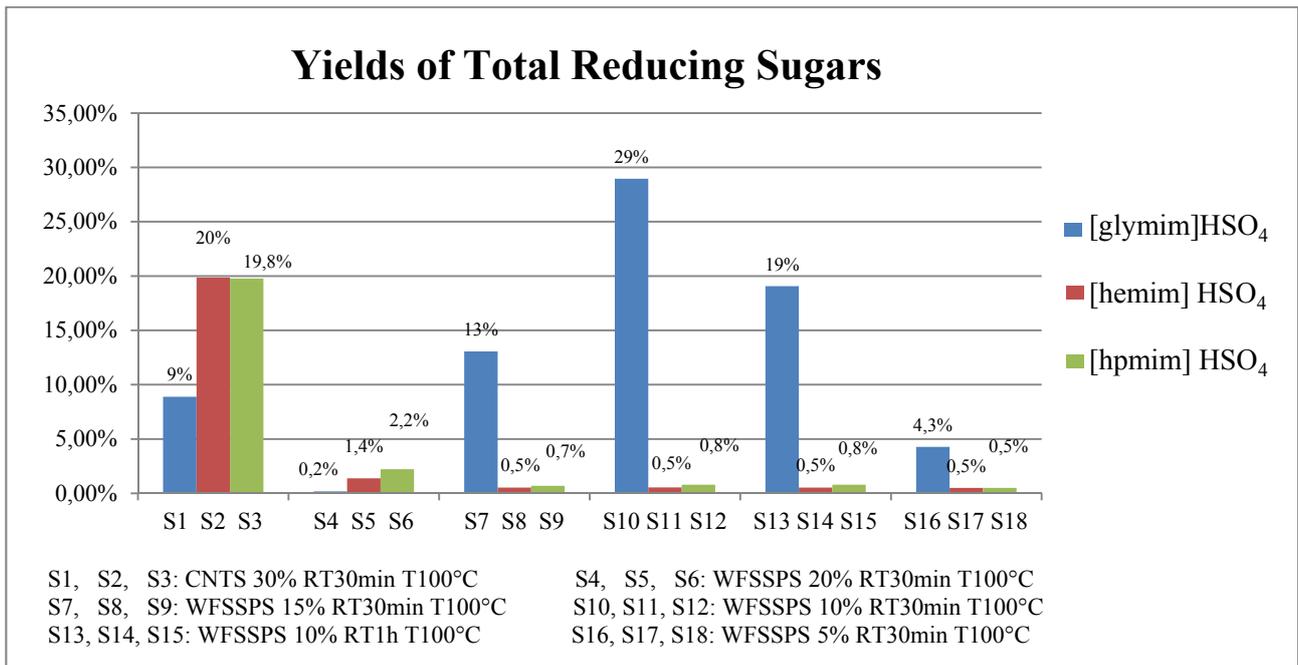
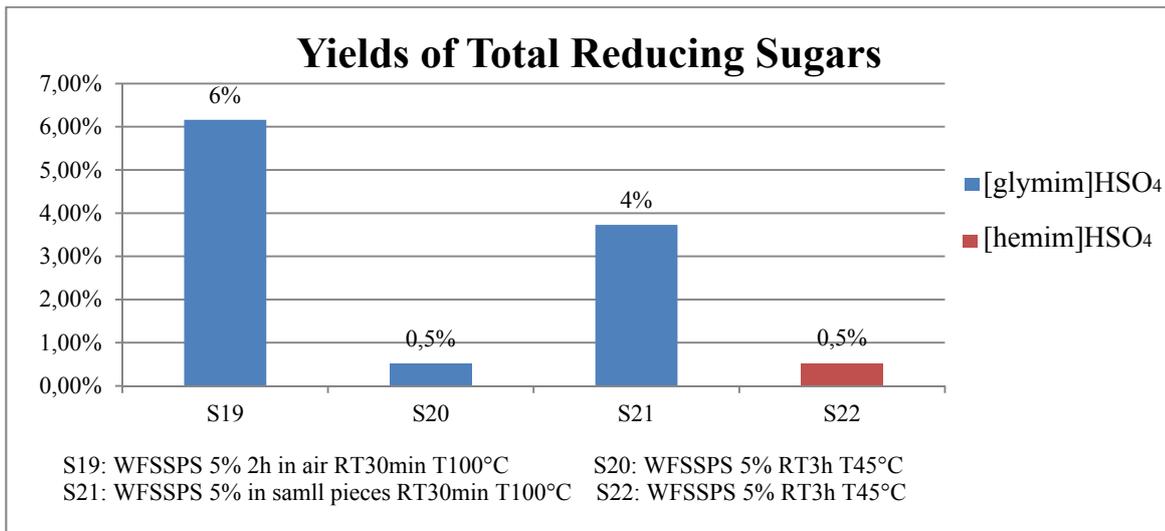


Figure 6



Captions:

Table 1 Elemental analysis and some physical properties of fibre sludge [3] [4].

Table 2 Chemical composition of a horse chestnut seed [10] [11].

Table 1

| | Fibre sludge | Literature value |
|---|---------------------|-------------------------|
| α-cellulose (%), d.s.* | 80 n.d. | |
| β- cellulose (%), d.s.* | 13 n.d. | |
| γ-cellulose (%), d.s.* | 7 n.d. | |
| Total carbon (%), d.s. | 38.4 23-45 | |
| Hydrogen (%), d.s. | 4.7 3-6 | |
| Oxygen (%) | n.d. 15-35 | |
| Nitrogen (%), d.s. | 0.3 0.5-4. | 5 |
| Sulphur (%), d.s. | <0.5 <0.5 | |
| Heat valued (MJ/kg), d.s. | 13 12-19 | |
| Moisture (%),d.s. | 53 50-60 | |
| Ash content (%), d.s. | 20.7 5-20 | |

% d.s. Mass fraction calculated from dry material (substance)

n.d. Not determined

* Calculated from the organic material in the sample

Table 2

| Component | Mass Fraction (%) |
|----------------------------------|--------------------------|
| Moisture, d.s. | 50 |
| Total carbohydrates, d.s. | 72-88 |
| Total sugar, d.s. | 10-23 |
| Starch, d.s. | >35 |
| Sucrose, d.s. | 9-21 |
| Crude cellulose, d.s. | 2-6 |
| Total Carbon, d.s. | 42 |

% d.s. Mass fraction calculated from dry material (substance)