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# Dissolution and hydrolysis of fibre sludge using hydroxyalkylimidazolium hydrogensulphate ionic liquids

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## Abstract

The dissolution and hydrolysis of wet fibre sludge in ionic liquids (ILs) with different reaction conditions are performed in this study. Novel types of hydroxyalkylimidazolium hydrogensulphate ILs, [glymim]$HSO_4$, [hemim]$HSO_4$ and [hpmim]$HSO_4$, are especially designed and aimed to combine the dissolution and hydrolysis of wet fibre sludge in a one-step pretreatment. The results were obtained based on the analysis of total reducing sugars (TRS) with the DNS method. The dissolution and hydrolysis of fresh wild horse chestnut seed (Aesculus hippocastanum) with the same ILs were also carried out as a comparison reference. Since fibre sludge is cellulose based and horse chestnut seed is starch based, a direct comparison of the difference in functions between these ILs in one-step dissolution and hydrolysis were analysed based on the results.

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

## 1 Introduction

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

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

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

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

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

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

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

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

# 2 Experimental

## 2.1 Materials and characterization

### 2.1.1 Fibre sludge

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

Figure 1 Here

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

The official standard method T 203cm-99 was used to determine α-, β- and γ-cellulose contents of the dried fibre sludge sample. Undergraded, higher-molecular-weight cellulose is indicated by α-cellulose, β-cellulose indicates degraded cellulose while γ-cellulose mainly consists of hemicellulose [4]. In addition, the total carbon content (TC) of the dry sample was determined by elementary analysis with a Perkin Elmer CHNS analyser [3] [4].
shows the characterization of fibre sludge that was used in the experiments and also some literature values are given as a reference.

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

Table 1 Here

### 2.1.2 Horse chestnut seed

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

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

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

Table 2 Here

## 2.2 Ionic liquids

Three types of hydroxyalkylimidazolium hydrogensulphate ILs, [glymim]$HSO_4$, [hemim]$HSO_4$ and [hpmim]$HSO_4$ that were used in this study, their chemical structures are illustrated in Figure 2. These ILs are particularly designed for the combined application of dissolution and hydrolysis of lignocellulosic materials in a one-step reaction.

### 2.2.1 Ionic liquids preparation

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

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

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

Figure 2 Here

***Figure 2 Structures of [glymim]$HSO_4$, [hemim]$HSO_4$ and [hpmim]$HSO_4$.***

### 2.2.2 Ionic liquids characterization

The pH of these acidic ILs were between 2 and 3, and the viscosity of [glymim]$HSO_4$ was the highest with an over range of 80% and a floating point of 13 Pa·s, compared to [hpmim]$HSO_4$ which was the lowest with an over range of 8.3% and a floating point of 1.7 Pa·s. Beside this, these ILs were analysed by FTIR and the resulting spectra are presented in Figure 3. The results clearly show that a small amount of water is present in these ILs, which is either due to the fact that the original ILs contain a small amount of water or the ILs possibly absorb water from the air, or both. Therefore, ILs with a water content of 9-13 $dm^3m^{-3}$ were determined by Karl Fischer titration and further detailed analysis on their chemical structures by nuclear magnetic resonance (NMR) were performed.

Figure 3 Here

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

$^1$H NMR spectra of ILs were acquired using a Bruker DPX 200 instrument (200.13 MHz) in deuterium dioxide, $D_2O$, at room temperature. Calibration of peaks is based on a solvent residual peak ($H_2O$ = 4.79 µL/L).

**[glymim]$HSO_4$** Yield 92.3%, IR (neat): 3275, 3238 (OH), $^1$H-NMR (500 MHz, $D_2O$, µL/L): 8.77 (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, 2H), $^{13}$C-NMR (120 MHz, $D_2O$, µL/L):137.3, 123.2, 123.1, 69.8, 62.4 , 51.7, 35.7 MS (ESI-$M^+$) *m/z* 83 [$HIm^+$] (41%), 157.1 [$M^+$] (100%)

**[hpmim]$HSO_4$** Yield 91.7%, IR (neat): 3276, 3241 (OH), $^1$H-NMR (500 MHz, $D_2O$, µL/L): 8.65 (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);

1.91 (m, 2H), $^{13}$C-NMR (120 MHz, $D_2O$, μL/L): 136.8,123.2, 122.5, 58.2, 48.9, 36.6, 31.5 MS (ESI-$M^+$) *m/z* 83 [$HIm^+$] (9%), 147.1 [$M^+$] (100%)

**[hemim]$HSO_4$** Yield 92.6%, IR (neat): 3277, 3241 (OH).$^1$H-NMR (500 MHz, $D_2O$, μL/L): 8.64 (s, 1H); 7.40 (s, 1H); 7.35 (s, 1H); 4.19 (m, 2H); 3.79 (m, 2H); 3.78 (s, 3H), $^{13}$C-NMR (120 MHz, $D_2O$, μL/L): 136.4, 123.6, 122.4, 59.8, 51.1, 35.8 MS (ESI-$M^+$) *m/z* 83 [$HIm^+$] (20%), 127.0 [$M^+$] (100%)

## 2.3 Sample dissolution and hydrolysis in ionic liquid

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

Figure 4 Here

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

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

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

## 2.4 Determination of total reducing sugars (TRS)

The total amount of reducing sugars including the content of glucose, xylose and cellobiose were 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]$HSO_4$, [hemim]$HSO_4$ and [hpmim]$HSO_4$, as described in Section
189 2.3. The hydrogensulfate ion, $HSO_4^-$, is a poor nucleophile and offered its acidic nature in further
190 hydrolysis reaction. In aqueous medium, $HSO_4^-$ is a good hydrogen ion donor instead of acceptor.
191 These properties of $HSO_4^-$ 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]$HSO_4$, at 100ºC for 30min (See Figure 5, S10) produced the highest TRS yield. Similar
201 observations were seen with the same fibre sludge sample in [glymim]$HSO_4$ at other weight ratios
202 (15%, 10% and 5%), demonstrating that among ILs, [glymim]$HSO_4$ 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]$HSO_4$ 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 pretratment 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 ($-OCH_3$) [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]$HSO_4$ is the lowest. A possible explanation for this could be that the [glymim]$HSO_4$ 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]$HSO_4$ 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]$HSO_4$ and [hpmim]$HSO_4$ 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]$HSO_4$ and
235 [hpmim]$HSO_4$ 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]$HSO_4$ is efficient at breaking β-1,4 glycosidic bonds
237 in cellulose.

Figure 6 Here

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

From Figure 6, sample S19 is of particular interest to the authors since it can be directly compared to sample 16 (Figure 5) which was performed with similar reaction conditions. Both utilising wet fibre sludge with a weight ratio of 5%, in [glymim]$HSO_4$, the major difference between the two samples was that S19 was exposed in air for 2 hours, followed by pretreatment. The results show that there was a higher TRS yield in S19 than in S16 which can be explained by the reaction that took place in the pretreatment process. In both samples cellulose was dissolved and further hydrolysed in the IL, but the mixture of S16 and IL did not contain much water. The small amount of water that was present caused the uncompleted hydrolysis of S16 where on the other hand, the mixture of S19 and IL was first exposed in the air which allowed moisture to be absorbed from the air. Therefore, more water was available for the hydrolysis process and so more TRS was produced in the pretreatment of S19.

Since fibre sludge samples pretreated with [glymim]$HSO_4$ produced the highest TRS yields in most of the experimental cases, the authors also studied another $[glymim]^+$ cation based IL, i.e. [glymim]OH in the pretreatment of fibre sludge. Based on preliminary results, the TRS yield of pretreatment of wet fibre sludge in [glymim]OH was significantly higher among the other three hydroxyalkylimidazolium hydrogensulphate ILs. It appears that cation $[glymim]^+$ has quite an effect on the dissolution and hydrolysis of cellulose. The pretreatment of cellulose with [glymim]OH will be carried out in further studies.

## 4 Conclusion

Fibre sludge is able to be dissolved and hydrolysed by a specific designed IL. In this study, the highest TRS yield (28.96%) was produced in the pretreatment of wet fibre sludge in [glymim]$HSO_4$. Results indicate that cation $[glymim]^+$ based ILs are a good option for the dissolution and hydrolysis of cellulose, since [glymim]$HSO_4$ is good for breaking down β-1,4 glycosidic bonds into glucose. For starch, [hemim]$HSO_4$ and [hpmim]$HSO_4$ are good for breaking down α-1,4 glycosidic bonds.

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

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

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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]$HSO_4$, [hemim]$HSO_4$ and [hpmim]$HSO_4$.***

***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

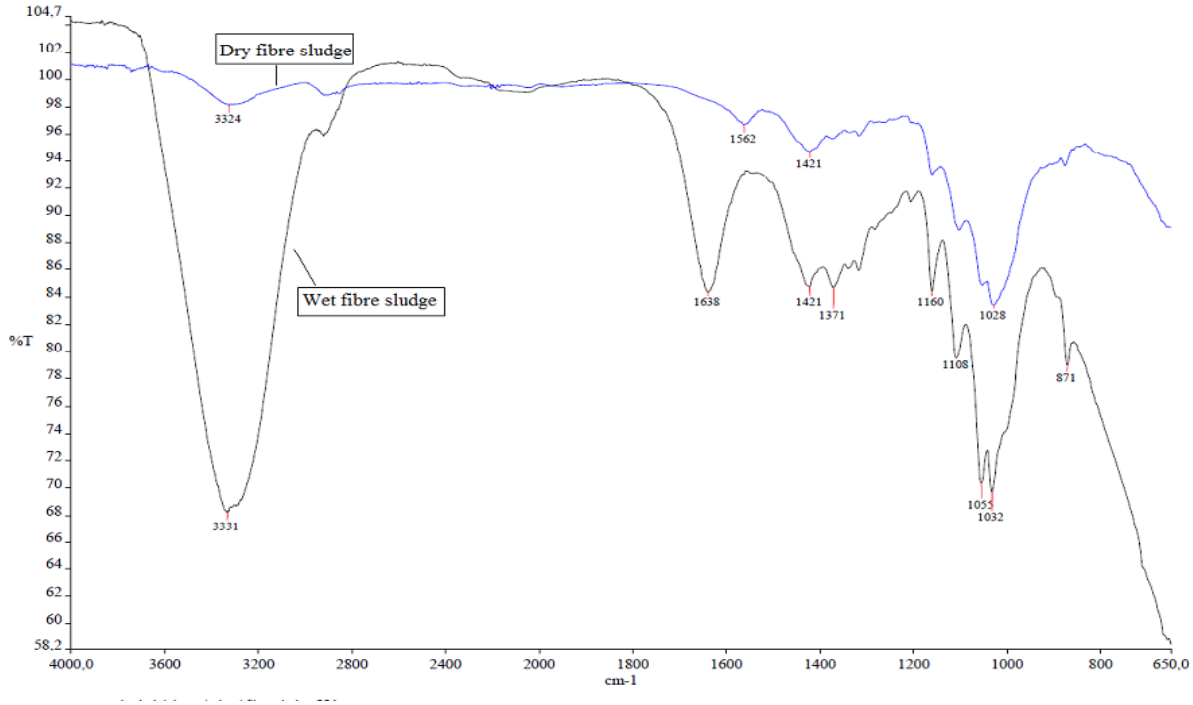
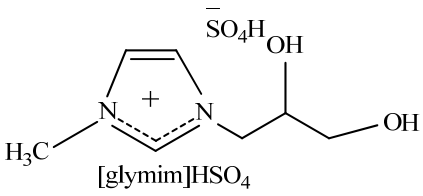
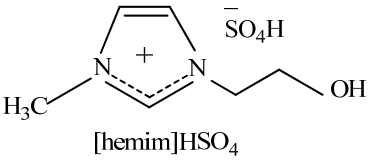

Dry fibre sludge
Wet fibre sludge
%T
cm-1
3324
3331
1562
1421
1638
1421
1371
1160
1028
1108
871
1055
1032

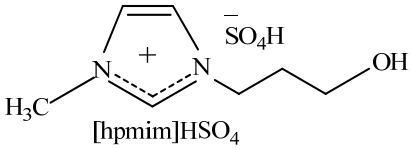
Figure 2




[glymim]$HSO_4$




[hemim]$HSO_4$




[hpmim]$HSO_4$

Figure 3

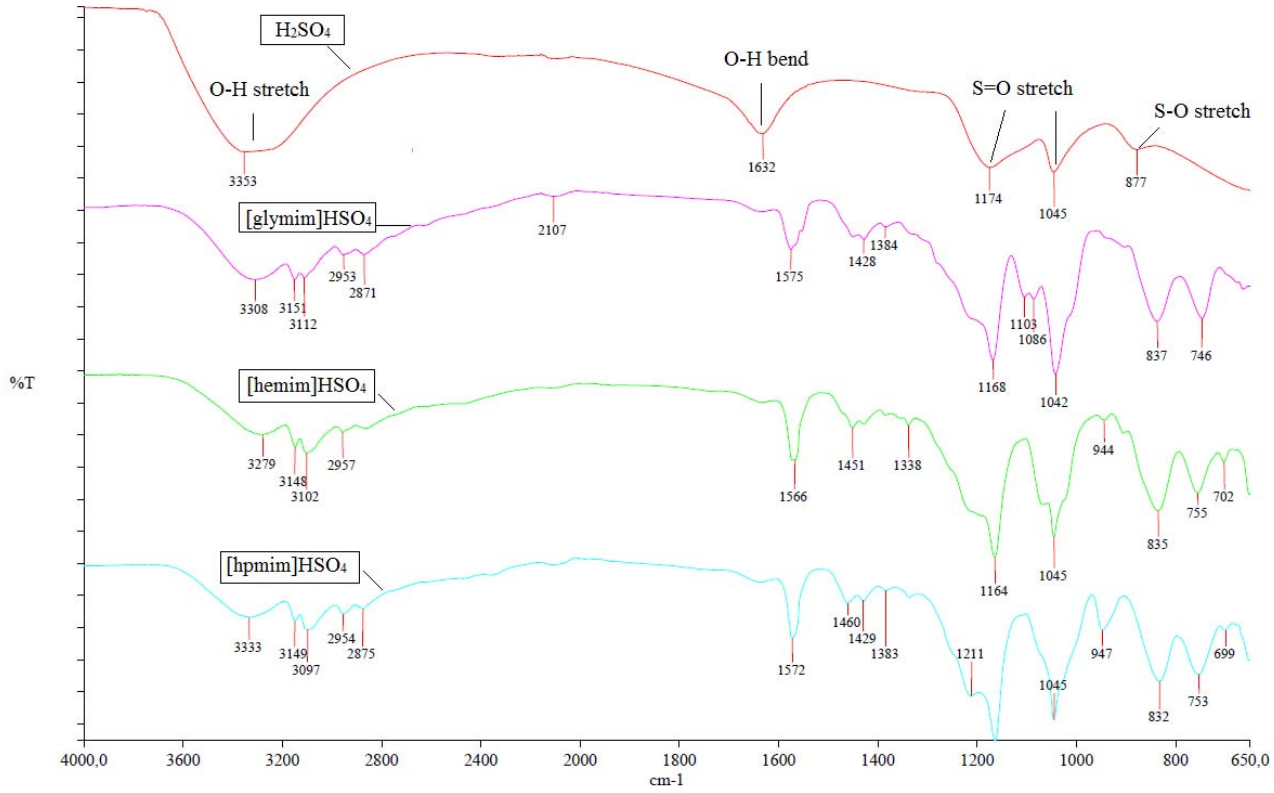

H2SO4
O-H stretch
3353
O-H bend
1632
S=O stretch
1174
1045
S-O stretch
877
[glymim]HSO4
3308
3151
3112
2953
2871
2107
1575
1428
1384
1168
1103
1086
1042
837
746
[hemim]HSO4
3279
3148
3102
2957
1566
1451
1338
1164
1045
944
835
755
702
[hpmim]HSO4
3333
3149
3097
2954
2875
1572
1460
1429
1383
1211
1045
947
832
753
699
%T
4000,0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
650,0
cm-1

Figure 4

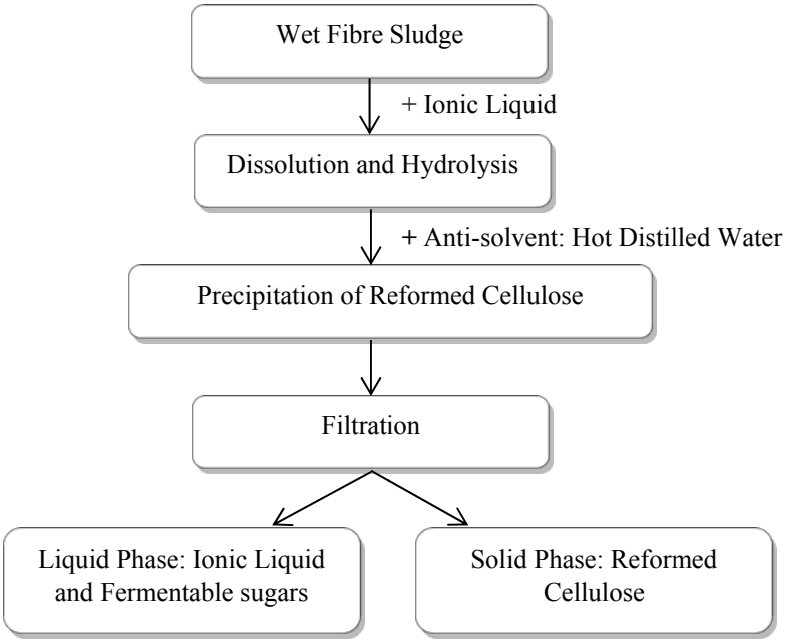
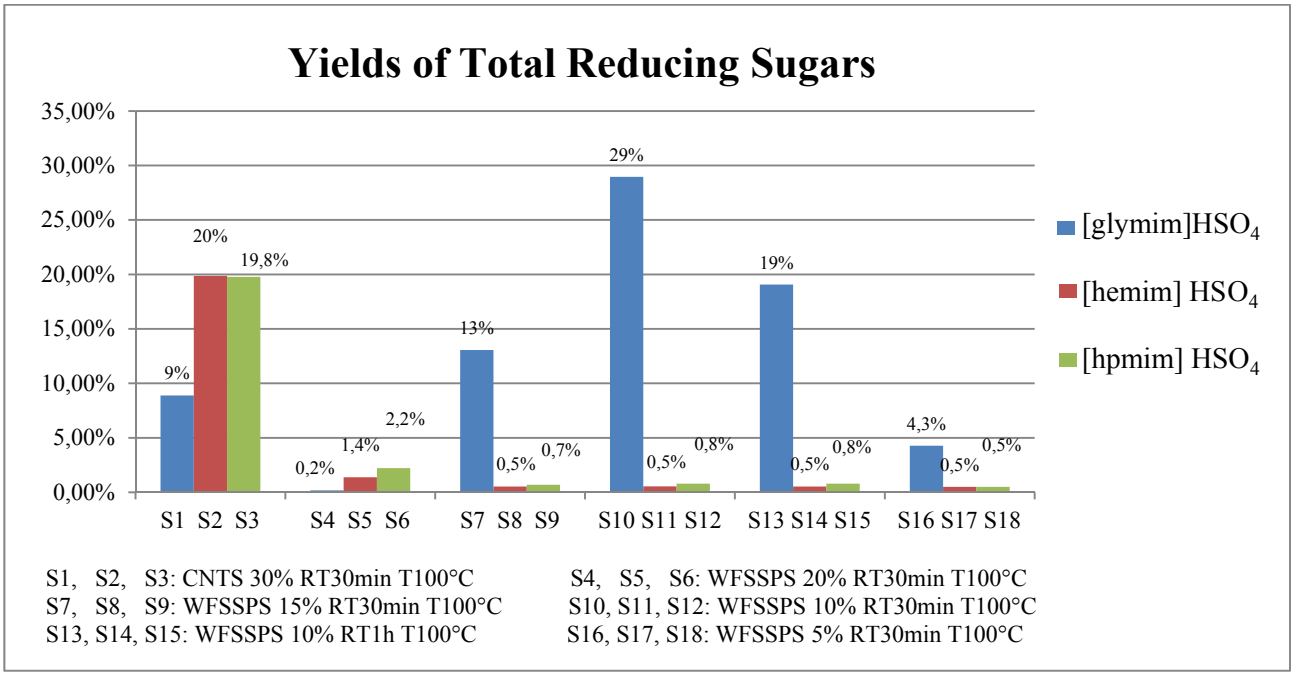
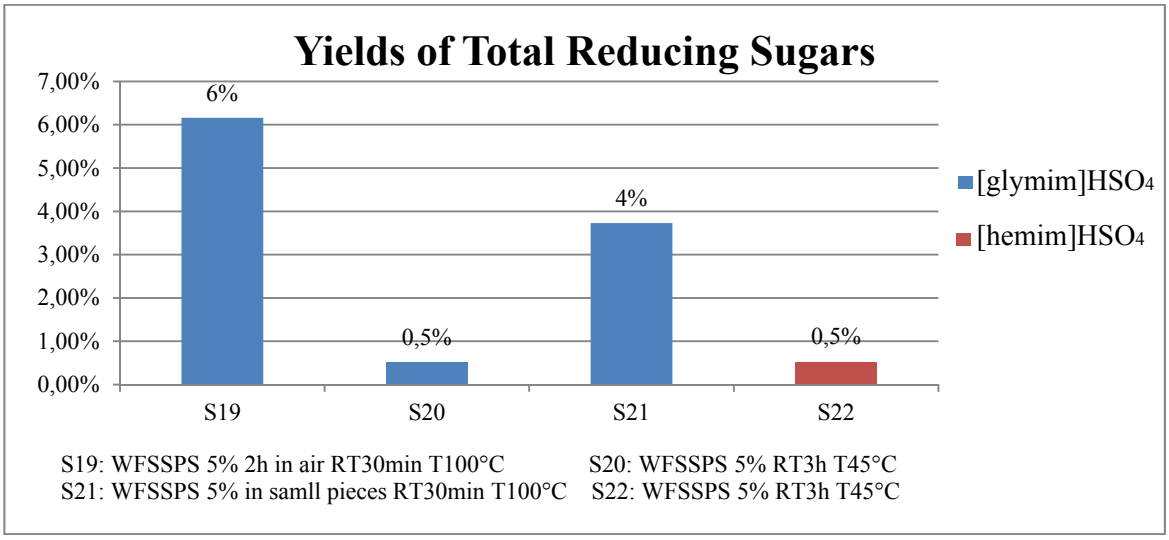

Wet Fibre Sludge
+ Ionic Liquid
Dissolution and Hydrolysis
+ Anti-solvent: Hot Distilled Water
Precipitation of Reformed Cellulose
Filtration
Liquid Phase: Ionic Liquid and Fermentable sugars
Solid Phase: Reformed Cellulose

Figure 5




S1, S2, S3: CNTS 30% RT30min T100°C
S4, S5, S6: WFSSPS 20% RT30min T100°C
S7, S8, S9: WFSSPS 15% RT30min T100°C
S10, S11, S12: WFSSPS 10% RT30min T100°C
S13, S14, S15: WFSSPS 10% RT1h T100°C
S16, S17, S18: WFSSPS 5% RT30min T100°C

Figure 6


Yields of Total Reducing Sugars
7,00%
6,00%
5,00%
4,00%
3,00%
2,00%
1,00%
0,00%
6%
0,5%
4%
0,5%
S19
S20
S21
S22
[glymim]HSO4
[hemim]HSO4
S19: WFSSPS 5% 2h in air RT30min T100°C
S20: WFSSPS 5% RT3h T45°C
S21: WFSSPS 5% in samll pieces RT30min T100°C
S22: WFSSPS 5% RT3h T45°C

**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)**