

Yufan Wang

**ENHANCING TOTAL REDUCING SUGARS OF FIBRE SLUDGE
USING IONIC LIQUIDS AND CO-SOLVENTS**

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ABSTRACT

Centria University of Applied Sciences	Date May 2017	Author Yufan Wang
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Name of thesis ENHANCING TOTAL REDUCING SUGARS OF FIBRE SLUDGE USING IONIC LIQUIDS AND CO-SOLVENTS		
Instructor Jana Holm	Pages 24	
Supervisor Yue Dong		
<p>The aim of this thesis work is to study the effect of ionic liquid [AzepSO₃H] HSO₄ on dissolution and hydrolysis of lignocellulosic waste-based fibre sludge. An efficient method to enhancing the total reducing sugar (TRS) yield was achieved by addition of co-solvents. The yield of TRS was measured by DNS method. The Fourier transformation infrared spectroscopy (FTIR) was used to investigate changes of fibre sludge sample after reaction.</p> <p>As a result, the highest TRS yield 14 wt % was obtained by THF as co-solvent at 100 °C for 30 min. The good performance of conversion rate provided when the proportion of co-solvent to ILs is 50:50 wt %. The water amount plays an important role in TRS yield of fibre sludge conversion, and an appropriate amount of water should be considered to hydrolysis in ionic liquid. The total reducing sugar and conversion rate can significantly increase between fibre sludge and solvent system by using the mixture of ILs and co-solvents.</p>		

Key words

Ionic liquids, co-solvent, dissolution, hydrolysis, lignocellulosic biomass, fibre sludge, total reducing sugars

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CONCEPT DEFINITIONS

[BMIM]Cl	1-Butyl-3-methylimidazolium chloride
[EMIM]Cl	1-Ethyl-3-methylimidazolium chloride
DMA	Dimethylacetamide
DMI	1,3-dimethyl-2-imidazolidinone
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DNS	Dinitrosalicylic acid
FTIR	Fourier-Transform Infra-Red Spectroscopy
ILs	Ionic liquids
TRS	Total reducing sugar
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-Visible Spectroscopy
wt %	Weight percentage
w/w	Weight per weight

ABSTRACT
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1 INTRODUCTION

As populations continue to grow, resource demand is on the rise virtually, and the world will need 50 % more food, 45 % more energy, and 30 % more water by 2030. Nowadays, facing the pressure of energy shortage and environmental pollution, it is imperative to develop clean and renewable energy. Lignocellulosic biomass is one of the most valuable and renewable feedstocks as an alternative source for fossil fuels. The data shows that worldwide production of the lignocellulosic biomass can obtain an approximately 1.1×10^{11} tons in annual value through natural plants such as woody trees, shrubs, and grasses, etc. Moreover, lignocellulosic wastes has come mainly from agricultural and forestry industries such as corn stover, grain straw, and woody crops, which it have the potential to be another raw material source for conversion into biofuels and other valuable products (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 253).

Fibre sludge is wood-based residues from the chemical pulping process, which an estimated approximately 300,000 tons of a dry mass are produced each year in the Finnish pulping industry. The standard waste disposal methods are landfilling and energy production by combusting. Fibre sludge makes up cellulose 93-94 % and hemicellulose 6-7 % of the dry matter (Holm, Lassi & Hernoux-Villiere 2013, 432-433). If large amounts of industrial fibre sludge can be converted cost-effectively by hydrolysis into fermentable sugars, and further used for the production of biofuels, which will help improve the current situation of resource constraint and environmental degradation.

However, there are difficulties in pretreatment process of lignocellulosic biomass that should be removed of lignin and hemicellulose, and reduced of crystalline cellulose to improve the efficiency of cellulose hydrolysis (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 254). Ionic liquid (ILs), as green solvents, attracted more attention in recent years due to its several unique properties such as low vapor pressure, low operating temperature, better chemical stability, and better dissolving capacity, in comparison to conventional solvents (Badgujar & Bhanage 2014, 3). It has been proved that ILs is able to dissolve lignocellulosic biomass, which lignin and hemicellulose could be removed and the crystalline structure of cellulose is disrupted in varying degrees depending on the features of ILs (Mäki-Arvela, Anugwom, Virtanen, Sjöholm & Mikkola 2010, 192-195).

This study focuses specifically on the effects of ILs, [AzepSO₃H] HSO₄, and co-solvents mixture on dissolution and hydrolysis of fibre sludge. The co-solvents selected organic solvent including 1,4-dioxane, tetrahydrofuran (THF), dimethylformamide (DMF), and toluene. The influence of the co-solvent ratio and different water content were also investigated, which promote the conversion into fermentable sugars. The total reducing sugar (TRS) was estimated by 3,5-dinitrosalicylic acid (DNS) method. The Fourier transformation infrared spectroscopy (FTIR) was used to investigate changes of fibre sludge sample after reaction.

2 LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass is the most abundant and the cheapest renewable resources on Earth, which is estimated that annual production up to 1.1×10^{11} tons on a global scale (Badgujar & Bhanage 2014, 3). Lignocellulosic biomass is mainly composed of 30%-50% cellulose, 15%-35% hemicellulose, and 10%-30% lignin. The remaining fraction includes a few pectins, extractives, inorganic compounds and proteins (Dong, Holm & Lassi 2015, 367). As shown in TABLE 1, the proportion of three components varies in plant species, hardwood and softwood contain more amount of cellulose, while the grasses contain more hemicellulose than other plant species.

TABLE 1. Cellulose, hemicellulose, and lignin content in types of lignocellulosic biomass (adapted from Isikgor & Becer 2015, 4).

		Cellulose (%)	Hemicellulose (%)	Lignin(%)
Hardwood	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Softwood	Pine	42-50	24-27	20
	Spruce	45.5	22.9	27.9
Agricultural	Wheat straw	35-39	23-30	12-16
	Rice straw	29.2-34.7	23-25.9	17-19
Waste	Corn stalks	35-39.6	16.8-35	7-18.4
	Grasses	25-40	25-50	10-30
Grasses	Switchgrass	35-40	25-30	15-20

2.1 Cellulose

Cellulose, as the main component of the plant cell walls, is one of the most widely distributed organic polymers in nature (Dong, Holm & Lassi 2015, 367). It is made up of glucose units linked by β -1,4-glycosidic bonds (FIGURE 1). The cellulosic molecules are arranged together in an aggregated state, with each cellulosic molecule consisting of about more than 10 000 glucose units. Cellulose has highly

crystalline structure and intra- and inter- molecular hydrogen bonds interact with Van der Waals forces, which resulted in cellulose insolubility in water and most solvents (Brandt, Gräsvik, Hallett, & Welton, 2013, 552; Quiroz-Castañeda & Folch-Mallol 2013, 121-122).

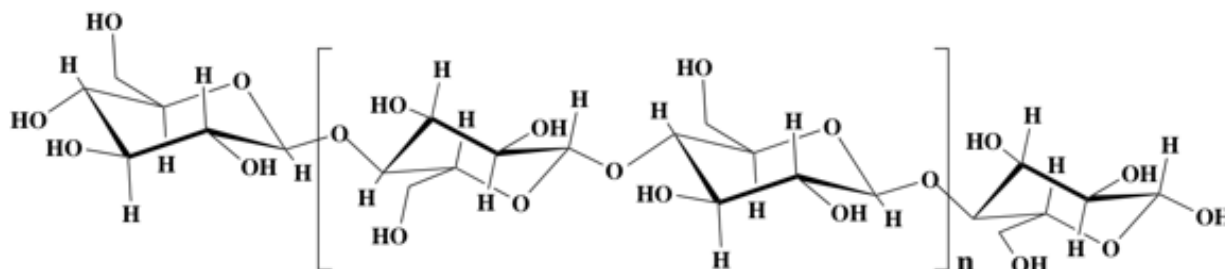


FIGURE 1. The structure of cellulose polymer chain (Kambo & Dutta 2015).

2.2 Hemicellulose

Hemicellulose is a group of polysaccharides on the cell wall, which consist pentoses (xylose and arabinose) and hexoses (glucose, mannose, and galactose) (FIGURE 2). Hemicellulose surrounds the cellulose fibres in the cell wall of plants to form a network of cross-linked (Brandt, Gräsvik, Hallett, & Welton, 2013, 552). Hemicellulose varies greatly in structure and composition, generally composed of shorter chains of polysaccharides with 500-3000 sugar units with acidic groups. Hemicellulose includes xylans, xyloglucans, glucomannans and galactoglucomannans (Gibson 2012). Xylose is the major hemicellulose sugar in hardwood, while in soft wood present abundant mannose. Comparing to cellulose, hemicellulose is easier hydrolyzed and more susceptible to depolymerisation due to its non-crystalline structure (Brandt, Gräsvik, Hallett, & Welton, 2013, 552-553).

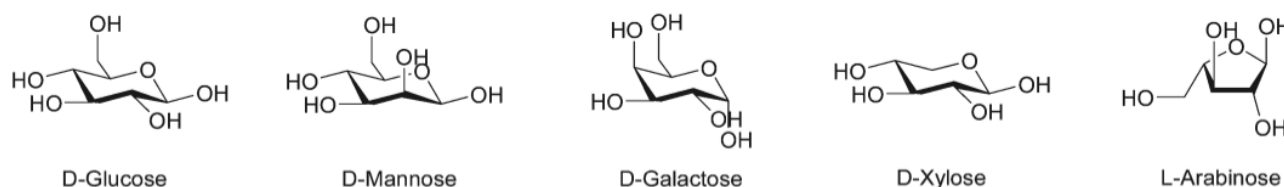


FIGURE 2. Typical pentose and hexose sugars in hemicellulose (Brandt, Gräsvik, Hallett, & Welton, 2013, 553).

2.3 Lignin

Lignin is a complex aromatic polymer formed by three monomers: coniferyl, sinapyl and p-coumaryl alcohols which form phenolic subunits such as guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) (FIGURE 3). The various composition and structure of lignin depend on the types and species of lignocellulosic plant. Softwoods contain mostly guaiacyl units, while guaiacyl and syringyl units exist in hardwoods (Abdullah, Muhammad & Mahmood 2017, 294).

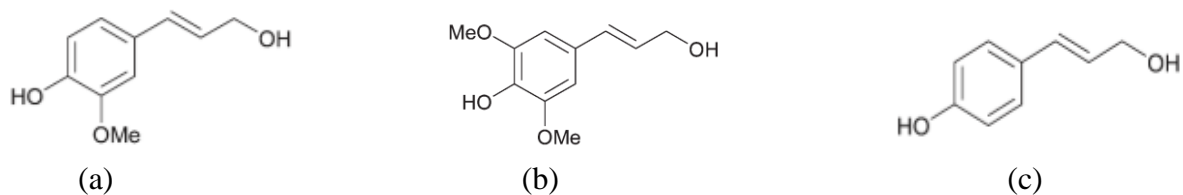


FIGURE 3. Lignin monomers: (a) coniferyl alcohol, (b) sinapyl alcohol, and (c) p-coumaryl alcohol. (Brandt, Gräsvik, Hallett, & Welton, 2013, 554).

Lignin is one of the major obstacles in the conversion and utilization of lignocellulosic biomass. It present in the cell wall of plant tissues, which the primary function to strengthen the cell wall by forming an interlaced network. The lignin polymer is a complex structure with a broad range of linkages that connected by various C-C and C-O linkages. Besides, lignin forms a protective layer around the cellulose and hemicellulose that affects decomposition of lignocellulosic biomass and inhibits the hydrolysis of cellulose and hemicellulose (Brandt, Gräsvik, Hallett, & Welton, 2013, 553-555).

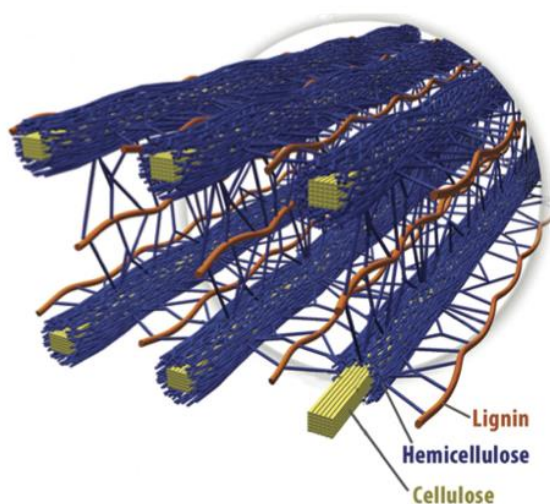


FIGURE 4. The network of cellulose, hemicellulose, and lignin in the cell wall of lignocellulosic biomass (Brandt, Gräsvik, Hallett, & Welton, 2013, 552).

2.4 Fibre sludge in pulping

Fibre sludge is lignocellulosic waste-based materials from the chemical pulping process. It is also called primary sludge and consists of organic solid materials and water. In chemical pulping, fibre sludge is produced from wastewater stream of mechanical treatment and is separated by primary clarification process (FIGURE 5). Wet fibre sludge was dewatered to higher solid concentration by a roll press at the pulp mill (Holm, Lassi & Hernoux-Villiere 2013, 433). In previous research, dry fibre sludge has shown more valuable than others sludge in pulping for further study (Holm 2013, 26).

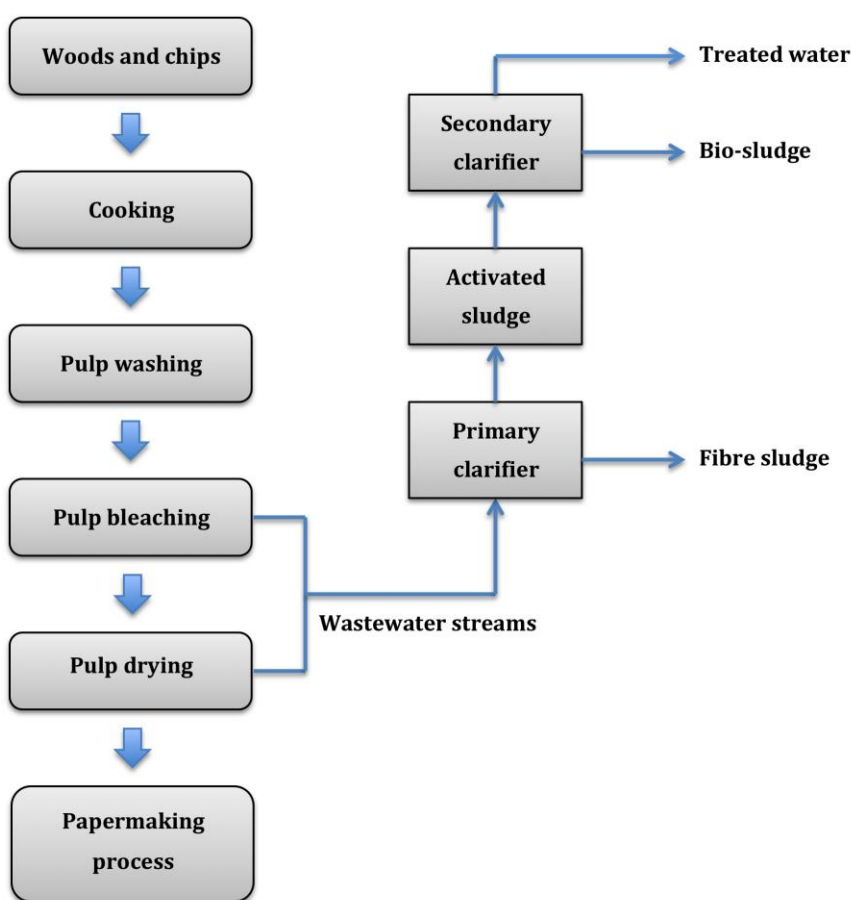


FIGURE 5. Chemical pulping flow and wastewater treatment stream at the pulp and paper mill (adapted from Holm, Lassi & Hernoux-Villiere 2013, 433; Larsson, Jansson, Grönkvist & Alvfor 2015, 462-463).

Currently, lignocellulosic biomass was developed mainly in the field of pulping and papermaking production. In chemical pulping, Kraft process converts wood into wood pulp, which wood chips are

cooked with the aqueous mixture of white liquor to break down the complicated structure of lignocellulosic biomass. It can remove most of the lignin and part of the hemicellulose and release the cellulose (Brandt, Gräsvik, Hallett, & Welton, 2013, 556; Holm 2013, 25). Fibre sludge, as the by-product of chemical pulping, is cellulose-enriched with approximately 93-94 wt % cellulose and 6-7 wt % hemicellulose (Holm, Lassi & Hernoux-Villiere 2013, 433).

3 IONIC LIQUIDS CHARACTERIZATION

ILs are compounds that consist of organic cations and organic or inorganic anions. ILs are molten salts existing in the liquid state in room temperature which melting points below 100 °C. ILs have recognized environmental friendly solvent due to their unique properties, such as low vapor pressure, low operating temperature, chemical stability, high ionic conductivity, recyclability, non-volatile and non-flammability, which make ILs as potential candidates to replace to volatile organic compounds. (Badgujar & Bhanage 2014, 3).

The common cations are organic compounds such as imidazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, ammonium, and sulfonium. The heterocyclic aromatic based cations, like imidazolium and pyridinium, has shown that better dissolution capacity than non-heterocyclic ammonium-based cations in dissolving cellulose. Ionic liquid composes of non-aromatic cyclic cations based, for instance, pyrrolidinium or piperidinium, which are not able to dissolve cellulose (Badgujar & Bhanage 2014, 5). Some examples of common cations used in most studied are presented in FIGURE 6.

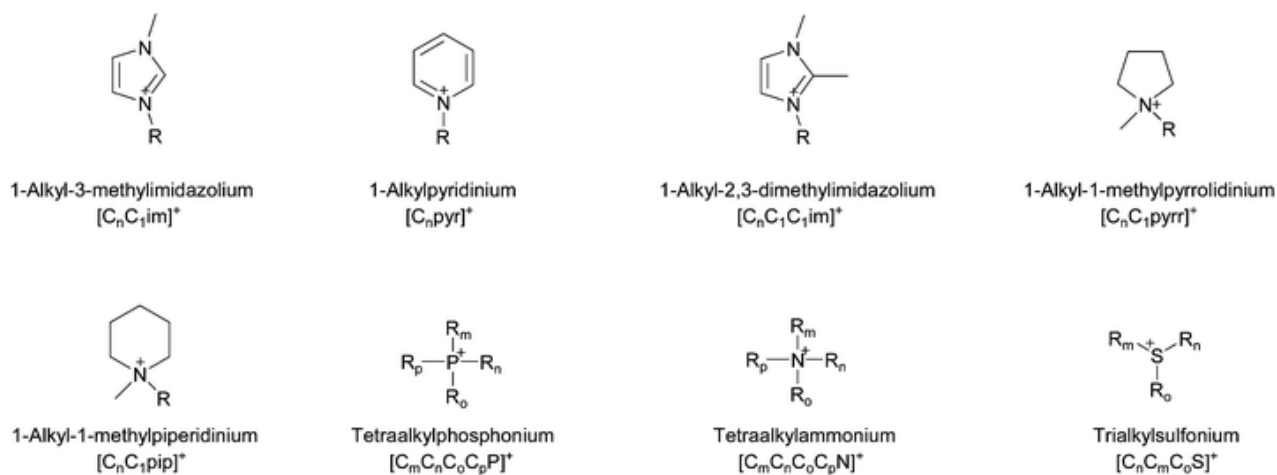


FIGURE 6. Common cations used in ionic liquids. (Brandt, Gräsvik, Hallett, & Welton, 2013, 558)

As for the anions, are based on halogens, carboxylates, amides, imides, sulfate, sulfonate, and phosphate compounds, have shown in FIGURE 7. In the most study, chloride anion was considered the decent option in the pretreatment of lignocellulosic biomass because of it has good dissolution ability that increases hydrogen bonds acceptability of the anions and results in efficient ability of hydrogen

bonds formation between the hydroxyl protons of cellulose and anion. Therefore, anions play a significant role in swelling and dissolution of lignocellulosic biomass. Moreover, the anions are related to the melting points and viscosity of ILs, such as carboxylic acid anions (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 258). The cation and anion have a significant influence ILs performance on dissolving lignocellulosic biomass. However, ILs can be designed by modification or combination of functional cations and anions for specific requirements in applied industrial fields, so-called ‘‘Designer Solvents’’ (Badgajar & Bhanage 2014, 3).

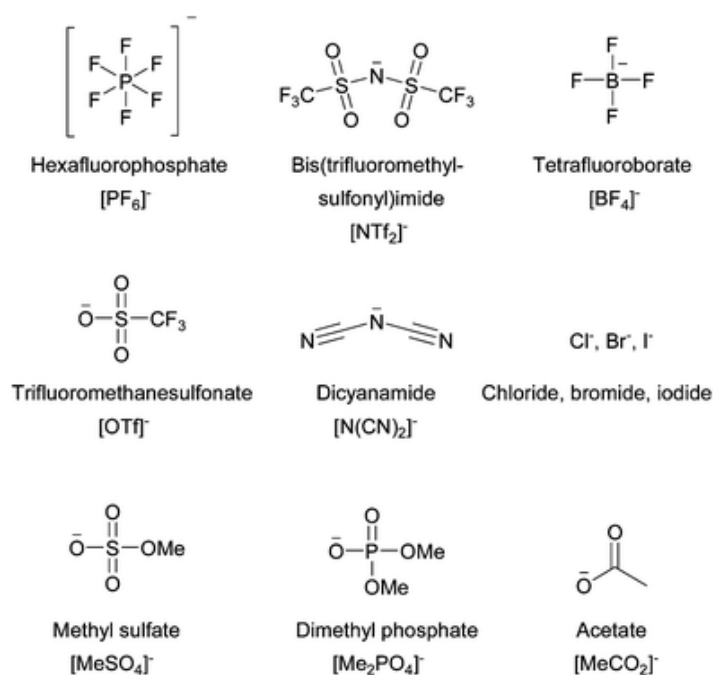


FIGURE 7. Typical anions used in ionic liquids. (Brandt, Gräsvik, Hallett, & Welton, 2013, 558)

3.1 Dissolution and hydrolysis of lignocellulosic biomass with ionic liquids

In order to achieve efficient conversion and utilization of lignocellulosic biomass, it must be overcome that exists covalent bonds between lignin and carbohydrates and leads to limit the release of carbohydrates. On the other hand, the most barriers in the complex structure of lignocellulosic biomass, to expose and enhance the accessibility of cellulose that hemicellulose-lignin protective layer must be broken up (Brandt, Gräsvik, Hallett, & Welton 2013, 556; Joao 2013, 13). Cellulose has amorphous and crystalline structure, so that also inhibit chemical and biological hydrolysis. Compare to conventional methods, and ionic liquids have the ability to achieve more efficient pretreatment in dissolution and

hydrolysis processes (Dong, Holm & Lassi 2015, 374, 377). It has described that the use of ionic liquid as pretreatment can reduce cellulose crystallinity, increase the surface area of cellulose, and remove hemicellulose and lignin due to disrupting intra- and inter- molecular hydrogen bonds of lignocellulose biomass (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 254-256).

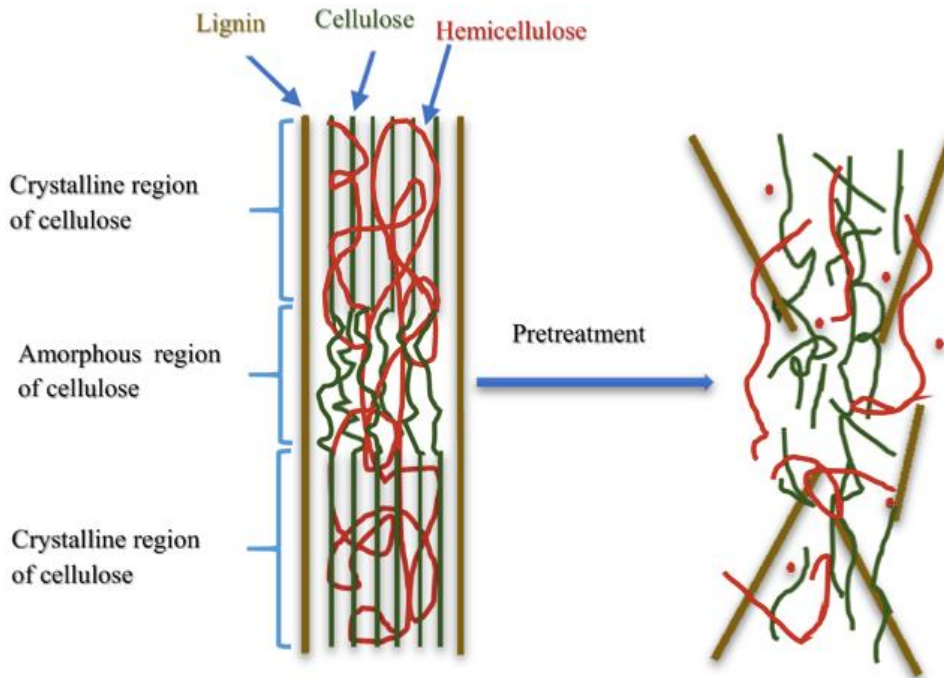


FIGURE 8. The disruption structure of lignocellulosic biomass in pretreatment. (Dong, Holm and Lassi 2015, 374)

Anion influences significantly on the capability of ionic liquids, which is essential to break down intra- and inter- molecular hydrogen bonds of lignocellulose biomass. Gracia et al. has reported that cork powder was not dissolved in both [EMIM]Cl and [BMIM]Cl in same reaction conditions. However, by replacing chloride anion to lactate or acetate anion can gain the dissolution significantly increased. (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 258). The anion with good basicity has better dissolution capacity than those with low-basicity anions. The large anion size has an adverse effect on the hydrogen-bond formation. Therefore, the decreasing of solubility of lignocellulosic biomass was affected by increasing the size of anion (Badgajar & Bhanage 2014, 5).

Furthermore, the efficient dissolving lignocellulosic biomass depends on different conditions including viscosity, melting point, water content, reaction temperature, and time etc. The studies have indicated

that the ionic liquid with high viscosity decrease the reaction rate and further reduce dissolving capacity of cellulose, which is due to strong cation-anion interaction of the ILs (Li & Luterbacher 2015, 138). Lignocellulosic biomass dissolving in ILs leads to swelling and increasing viscosity of ILs that inhibit mass transfer and reduce the ability of dissolution process. In generally, the advantages of low viscosity ILs provide feature such as better solvation, better cellulose solubility, and easy operating. (Badgular & Bhanage 2014, 8, 11). The higher temperature and longer time decrease the viscosity of ILs, while too long reaction time and high temperature causes degradation (Dong, Holm and Lassi 2015, 378).

4 MATERIALS AND METHODS

4.1 Fibre sludge

Fibre sludge was used as raw material for conversion of lignocellulosic waste-based biomass into reducing sugars. The sample was provided from chemical pulping process by UPM Finnish pulp mill. The TAPPI's official standard method T 203 cm-99 was used to determine the α -, β -, γ -cellulose content of dried fibre sludge sample (Dong, Schneider, Hu, Jaakkola, Holm, Leveque & Lassi 2016, 37). TABLE 2, shows that the composition and properties of the dried fibre sludge has been characterized by elemental analysis. The α -cellulose and β -cellulose refer to undegraded celluloses and degraded celluloses respectively, while γ -cellulose indicates the hemicellulose content of fibre sludge.

TABLE 2. Elemental analysis and some physical properties of fibre sludge (adapted from Dong, Schneider, Hu, Jaakkola, Holm, Leveque & Lassi 2016, 37).

Fibre sludge	
α-cellulose, d.s.^a (%)	72
β-cellulose, d.s.^a (%)	3
γ-cellulose, d.s.^a (%)	11
Klason lignin, d.s.^a (%)	14
Carbon, d.s. (%)	41.9
Hydrogen, d.s. (%)	6.0
Oxygen, d.s. (%)	n.d.
Nitrogen, d.s. (%)	0.88
Sulphur, d.s. (%)	n.d.

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

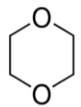
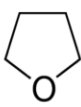
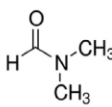
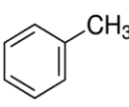
^a = Calculated from the organic material in the sample

n.d. = Not determined

4.2 Ionic liquid and co-solvents

Organic solvent can be further classified into four types: non-polar solvents, polar aprotic solvents, polar protic solvents and ILs. The co-solvents were investigated in this study including polar aprotic solvents 1,4-dioxane, THF and DMF, and non-polar solvent toluene. Generally, non-polar solvents do not have an electric dipole and are unable to create hydrogen bonds. Polar aprotic solvents have an electric dipole with lone electron pair that can accept by hydrogen bonds. (Li & Luterbacher 2015, 136). The structure and properties of co-solvents used in this study are summarized in TABLE 3.

TABLE 3. Properties of four types of solvent (Sigma-Aldrich, 2017).

	1,4-Dioxane	THF	DMF	Toluene
Structure				
Molecular formular	C ₄ H ₈ O ₂	C ₄ H ₈ O	C ₃ H ₇ NO	CH ₃ C ₆ H ₅
Molecular weight	88.11 g/mol	72.11 g/mol	73.10 g/mol	92.14 g/mol
Density	1.033 g/ml	0.8892 g/ml	0.948 g/ml	0.87 g/ml
Water solubility	Miscible	Miscible	Miscible	0.52 g/L (20 °C)
Melting point	11.8 °C	-108.4 °C	-60.5 °C	-95 °C
Boiling point at 760 mm Hg	101.1 °C	66 °C	152 °C	111 °C
Vapor pressure at 20 °C	29 mm Hg	132 mm Hg	2.7 mm Hg	22 mm Hg
Viscosity at 20 °C	1.37 cP	0.55 cP	0.92 cP	0.59 cP

The ILs [AzepSO₃H]HSO₄ used in the study was designed and synthesized by my instructor Yue Dong. The structure of [AzepSO₃H]HSO₄ has shown in FIGURE 9

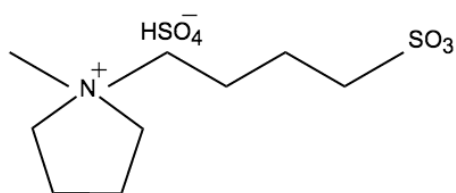


FIGURE 9. Structure of [AzepSO₃H] HSO₄.

4.3 Procedure for dissolution and hydrolysis of fibre sludge

In each reaction, 50 mg of fibre sludge was mixed with the different weight ratio of ionic liquid to co-solvent on a 25 ml round-bottom flask. Each reaction included various amounts (up to 30%) of water. The mixture was heated at 100 °C in an oil bath with stirring 100 rpm for 30 min. For dissolved cellulose to regenerate 10 ml of distilled hot water was added after the reaction. The mixture precipitate reformed cellulose after a certain time. The liquid phase was separated from mixture solution by filtration. The solution was analyzed for total reducing sugar using DNS method. The solid materials were washed with water to remove the ionic liquids and were dried at room temperature for 24 h.

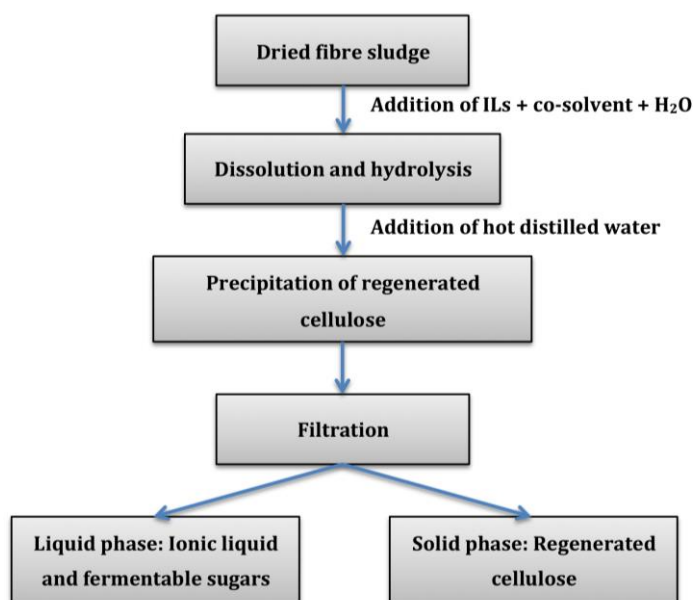


FIGURE 10. Fractionation procedure dissolution and hydrolysis of fibre sludge using ionic liquid (Dong, Holm, Kärkkäinen & Nowicki 2014, 464).

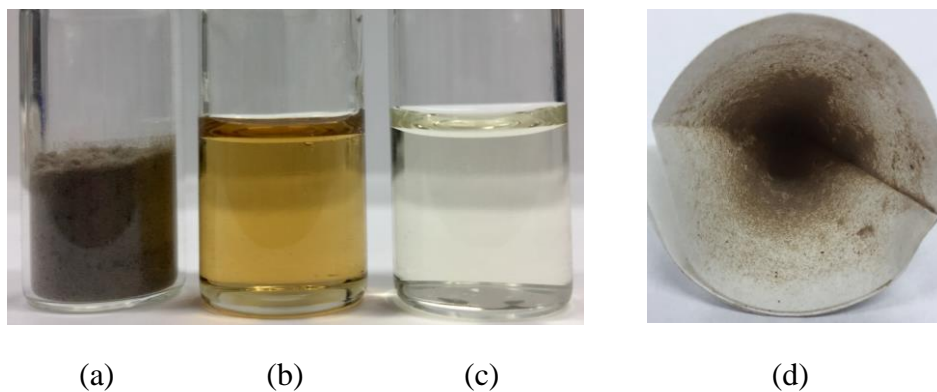


FIGURE 11. Fibre sludge sample (a), $[\text{AzepSO}_3\text{H}]\text{HSO}_4$ (b), mixture solution of ILs and fermentable sugars (c), and regenerated cellulose (d).

4.4 Estimation of total reducing sugar

The total reducing sugar was estimated by DNS method. DNS reagent was prepared by mixing 125 ml of hot deionized water (50 °C) with 45,5 g potassium sodium tartrate and adding 1,575 g 3,5-dinitrosalicylic acid, 65,5 ml of 2 M sodium hydroxide, 1,25 g of phenol and 1,25 g of sodium sulfite in the solution. The solution was dissolved by stirring and diluted it with distilled water up to 250 ml.

Each tube contains the 0,2 ml sample and 0,2 ml DNS reagent. The test tubes placed in boiling water for exactly 5 min and colors changed during the heating process. After that, the 2,6 ml distilled water added to the sample and cooled to room temperature. Glucose concentration draws the standard curve. The absorbance was determined at 540 nm using a UV-Vis spectrophotometer (Shimadzu UV-1800). The TRS yields of fibre sludge were calculated by the equation (1):

$$\text{TRS yield \%} = \frac{\text{redcing surgars weight}}{\text{fibre sludge weight}} \times 100\% \quad (1)$$

5 RESULTS AND DISCUSSION

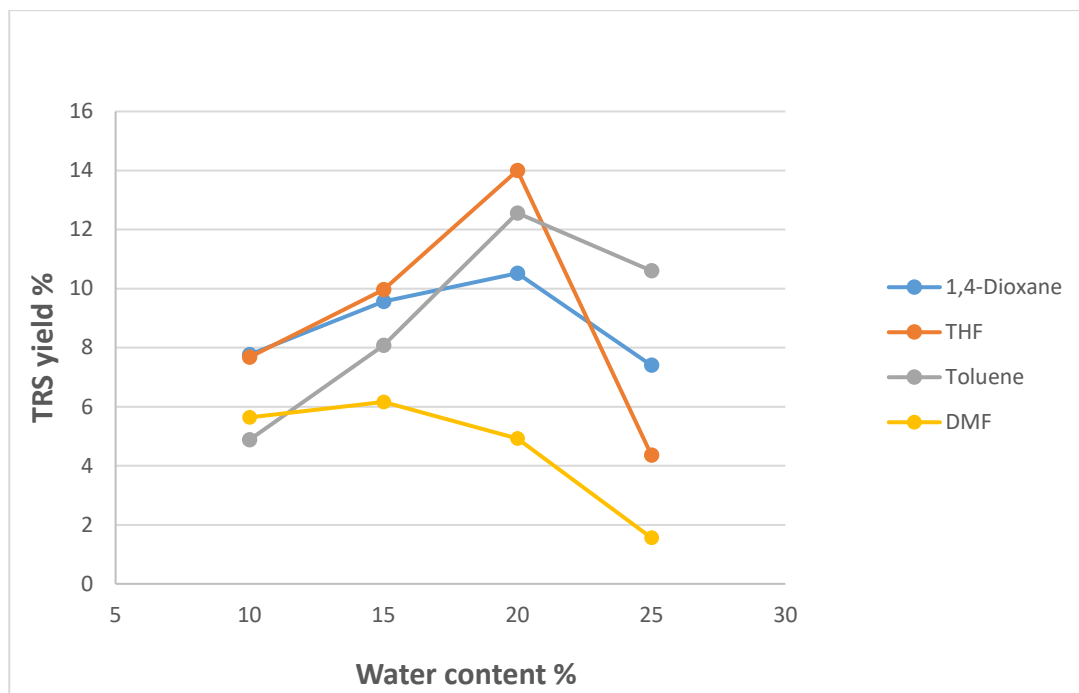
Fibre sludge was treated with the addition of co-solvents to [AzepSO₃H]HSO₄ that to determine the effect dissolution and hydrolysis. The hydrogensulfate ion, HSO₄, has mentioned in the previous study by Dong et al. that HSO₄ is an efficient anion play a vital role in hydrolysis process (Dong, Holm, Kärkkäinen & Nowicki 2014, 465). The use of the organic solvent as co-solvent could improve the solubility of cellulose and the solvent power of ionic liquid (Holding 2016). Water was added to contribute in an increase of hydrolysis rate. Moreover, the ratio of co-solvent to ILs and different water content also were studied.

5.1 Effect of water amount on TRS yield

Hydrolysis of fibre sludge in ionic liquid [AzepSO₃H]HSO₄ was significantly affected by the amount of water. The hydrolysis procedure was tested with different co-solvents in [AzepSO₃H]HSO₄ by adding water with total amount (1 g) of 10 wt %, 15 wt %, 20 wt %, and 25 wt %. It can be seen in GRAPH 1 that water plays a significant role on TRS yield, which TRS yield was controlled by water content. The TRS yield of four co-solvents was raised gradually with an increase of water amount. Some researchers have proved that addition of water can reduce the viscosity of ILs and the increasing of cellulose solubility was affected by the raising of water content (Elgharbawy, Alam, Moniruzzaman & Goto 2016, 261). Also, Brandt et al. demonstrated that the presence of water guarantees the swelling and dissolution of lignocellulosic biomass (Li & Luterbacher 2015, 141).

However, the TRS yields of 1,4-Dioxane, THF and Toluene were decreased with water content over 20 wt %, while the DMF was declined in 15 wt %. The excessive amount of water reduces likely the solubility of fibre sludge and leads to the decrease of TRS yield. Swatloski and co-workers mentioned that water molecules compete with cellulose to form hydrogen bonds with ILs anions, hence inhibit the dissolution of cellulose in ionic liquid (Swatloski, Spear, Holbery & Roger 2002, 4975).

According to studies have shown, water describes two-sided influence on dissolution and hydrolysis of cellulose, which may depend on the type of ILs and biomass. Additionally, it is necessary to control an appropriate amount of water in each reaction. (Li & Luterbacher 2015, 141).



GRAPH 1. The influence of increasing water content on the TRS yield.

5.2 Effect of different co-solvents on TRS yield

Four selective co-solvents, 1,4-dioxane, THF, DMF, and toluene, were used to determine that effects of the mixing organic solvents with ionic liquids on conversion of fibre sludge into reducing sugars. The mixtures of ionic liquid with organic solvents has been defined as organic electrolyte solutions (Brandt, Gräsvik, Hallett, & Welton 2013, 562). It has been successfully applied in lignocellulosic biomass conversion for improving the yield of multiple processes (Li & Luterbacher 2015, 136). Many studies show that addition of polar aprotic solvent enhances dissolution capacity of cellulose and accelerates dissolution rate in ionic liquids because of decreasing viscosity and raising thermal stability. Rinaldi et al. reported that mixtures of aprotic polar solvent and ionic liquid as solvent system, such as DMF, DMSO, DMA and DMI, were contributed to dissolve instantaneously cellulose at the relative low temperature (50 °C). However, to dissolve of cellulose in pure ionic liquid at same reaction conditions requires higher temperature and longer time than solvent system consisting co-solvent (Hou, Ju, Li, Liu, Chen & Yang 2017, 3)

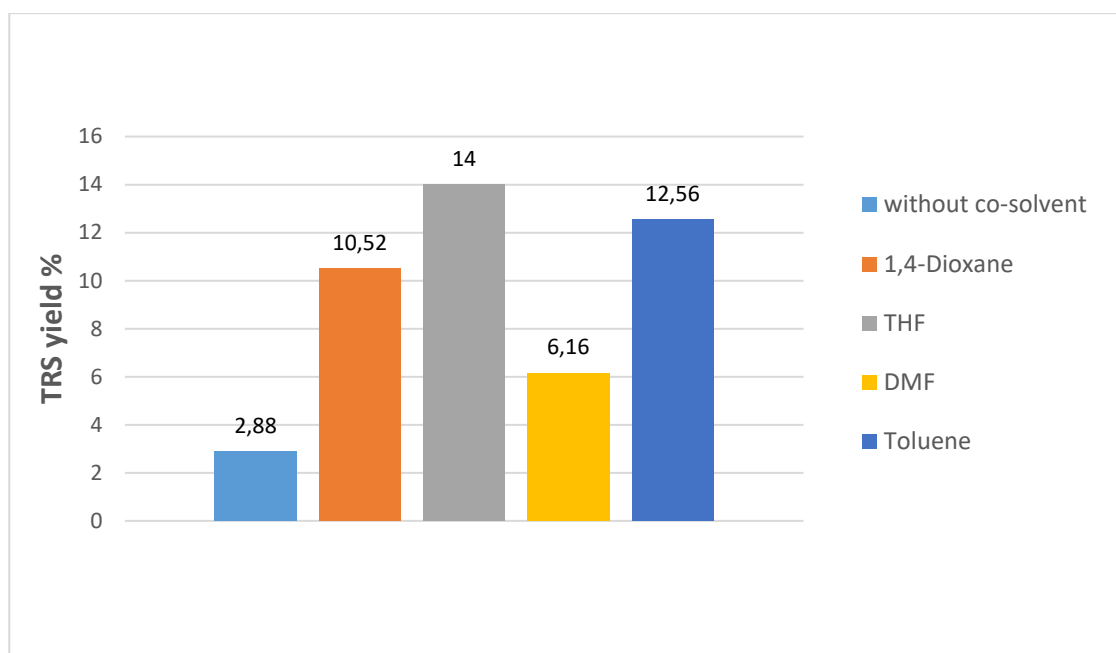
In TABLE 4, has shown that the TRS yield increase along with raising the ratio of solvent to ionic liquid in water proportion both 10 % and 15 %. Due to co-solvent effects the viscosity reducing and

conductivity increasing of solution mixture, hence it accelerate mass transfer rates between solvent system and fibre sludge (Holding 2016). As the amount of co-solvent up to 70 %, the yield of TRS declined gradually in each case, it might be by reason that decreased ability of [AzepSO₃H]HSO₄ to form hydrogen bonds with fibre sludge (Hou, Ju, Li, Liu, Chen & Yang 2017, 3).

TABLE 4. The increase of TRS yield with different weight ratios of co-solvent to ILs in various water content

Solvent:ILs (w/w)	H ₂ O 10 wt %			H ₂ O 15 wt %		
	10:90	30:70	50:50	10:90	30:70	50:50
1,4-Dioxane	1.72	5.44	7.76	3.32	6.44	9.56
THF	1.32	4.96	7.68	2.88	7.64	9.96
DMF	1.24	5.64	2.16	1.28	6.16	2.96
Toluene	0.96	3.76	4.88	2.53	7.16	8.08

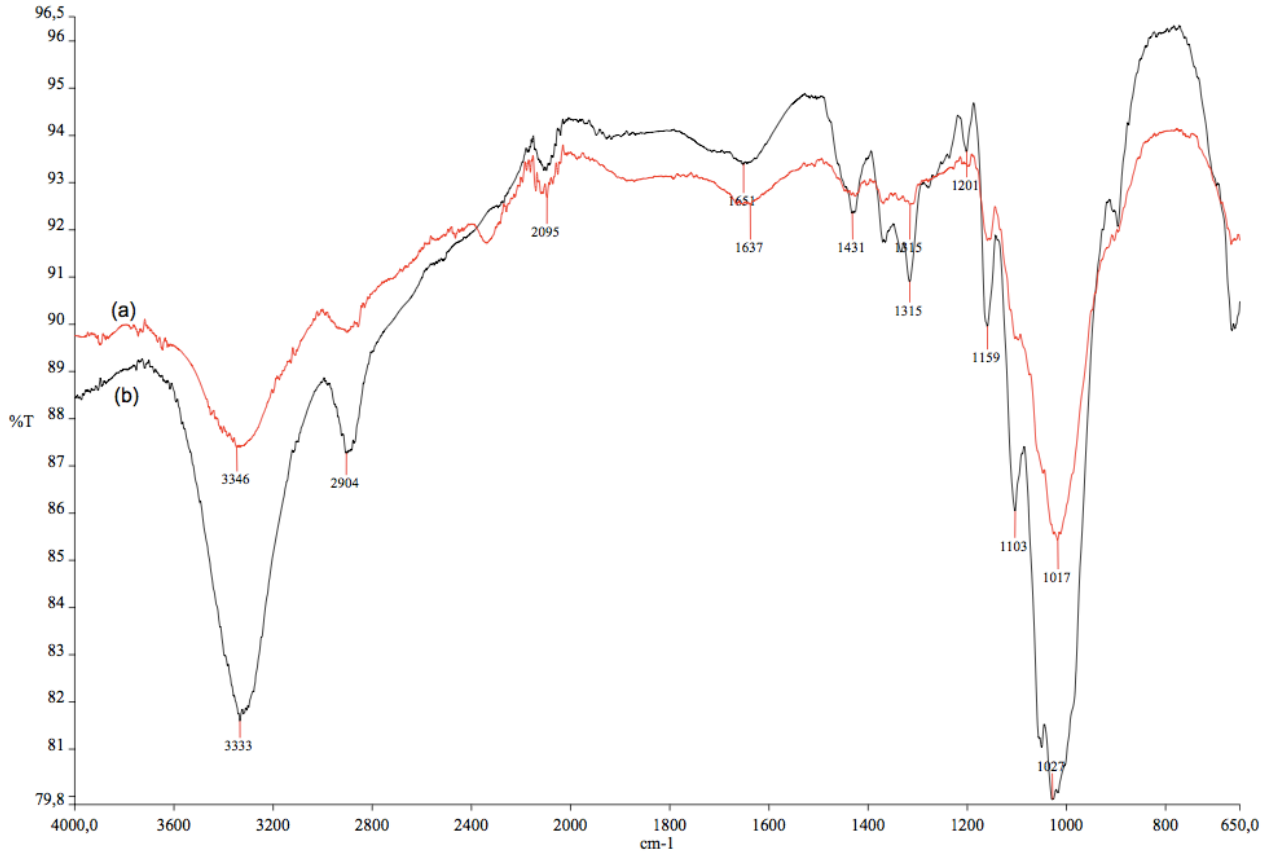
Based on the results, Fibre sludge used [AzepSO₃H]HSO₄ with different co-solvents obtaining higher reducing sugar yields than the test of pretreated without co-solvents. In this study, the highest TRS yield 14 wt % was achieved by THF as co-solvent at the proportion 50:50 wt % to ILs with water percent 20 wt %, the total weight of mixtures is 1 g. The toluene and 1,4-dioxane have a good performance with the TRS yield of 12.56 wt % and 10.52 wt %, respectively, while DMF has obtained 6.16 wt % TRS yield (GRAPH 2). Hardelin reported that various dissolution power of co-solvents depends on varying co-solvent molecular structure in the mixture of ILs and co-solvent. Therefore, co-solvents have an indirect influence on TRS yield with ILs, [AzepSO₃H]HSO₄, which polar aprotic solvent disrupt the interaction of ILs between solvated cations and ‘free’ anions that promote the interaction of anions with cellulose, hence increasing the dissolution and hydrolysis of fibre sludge. (Mai, Ha & Koo 2014, 1146)



GRAPH 2. The effect of TRS yields with various co-solvents.

5.3 FTIR analysis

As shown in FIGURE 13, describes the infrared spectrum of untreated fibre sludge and treated fibre sludge with [AzepSO₃H]HSO₄ and THF. All band positions of original fibre sludge peak at 3346 cm⁻¹, 2095 cm⁻¹, 1637 cm⁻¹, 1315 cm⁻¹, 1017 cm⁻¹. After chemical pulping, fibre sludge consists mainly cellulose, a small amount of cellulose and lignin, and chemical residuals. The broad band at 3333 cm⁻¹, assigned to OH-stretching vibration that is related to hydrogen bonds. Compared to the untreated fibre sludge (3346 cm⁻¹), the peak becomes sharper and with lower intensity, which the intra- and intermolecular hydrogen bonds was interrupted. The peak at 2904 cm⁻¹, is the C-H stretching vibration (Ciolacu, Ciolacu & Popa 2010, 17). The infrared spectrum of the amorphous and crystalline celluloses appears between 1200 cm⁻¹ and 1500 cm⁻¹ (Liu 2013, 307). The sharp peak at 1159 cm⁻¹ assigned to C-O-C asymmetrical stretching. There are no significant changes at peak position 1315 cm⁻¹ both original fibre sludge and treated fibre sludge with ILs and co-solvent that allocated to CH₂ rocking vibration at C6. The strong vibration 1027 cm⁻¹ is associated to C-O stretching characteristic of cellulose (Pandey 1998, 1974).



GRAPH 3. FTIR analysis structure of original fibre sludge (a) and treated fibre sludge (b)

The FTIR spectra of fibre sludge after reaction indicates that the bands do not appear position variation and the intensity of these bands become stronger and sharper than original fibre sludge, which might be $[AzeP\text{SO}_3\text{H}]\text{HSO}_4$ and co-solvent interaction with cellulose that diffuse the arrangement of cellulose chain. (Liu 2013, 307)

6 CONCLUSION

This study results confirmed that fibre sludge can be dissolved and hydrolyzed by ionic liquid, [AzepSO₃H]HSO₄. Addition of co-solvents, the total reducing sugars (TRS) have enhanced significantly from 2.88 wt % without co-solvent to 6.16 wt % with DMF, 10.52 wt % with 1,4-dioxane, 12.56 wt % with toluene, and 14 wt % with THF. Also, the ratio of co-solvents to ionic liquid influences the TRS yield has been studied. The results show a good performance of TRS yield when the proportion of co-solvent to ILs is 50:50 wt %. Ionic liquid are generally with high viscosity, which use of organic solvent as co-solvents minimize the usage amount and decrease the viscosity as well. Besides, the presence of water gives a positive effect on the increase of TRS yield with raising the water content until 20 wt %. Water is the most economical solvent that is particular green solvent with attractive properties such as low cost, non-toxic and environmental friendly. The water amount plays an important role in TRS yield of fibre sludge conversion, and an appropriate amount of water should be considered to hydrolysis in ionic liquid.

In conclusion, the total reducing sugar and conversion rate can be increased significantly by using the mixture of ILs and co-solvents. ILs offers greatly potential for pretreatment of lignocellulosic biomass and widely applied in bioenergy and biofuels production. The impact of composition of ILs and suitable reaction conditions, like reaction time and temperature play a key role in lignocelulosic biomass conversion. Furthermore, organic co-solvents plays an important role in lignocellulosic biomass conversion that several properties of co-solvent should be considered such as boiling point, solubility, properties of solvents, economical efficiency and recyclability. The most important opportunity and challenges in use of ILs and co-solvent in lignocellulosic biomass conversion on industrial scale is should be accompanied by economic and environmental solutions.

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