

**Gamma-Valerolactone and Ionic Liquid-Based Separation Processes of Cellulose  
and Hemicelluloses, and Its Associated Green/Sustainable Biorefinery Processes**

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## ABSTRACT

Biomass is one of the abundant renewable resources on earth, and a promising feedstock for the production of energy, chemicals, and materials. Paper-grade bleached pulp consisting of cellulose and hemicelluloses is very suitable to use to produce high-purity cellulose and other hemicellulose-based products. gamma-valerolactone (GVL) and ionic liquid (IL)-based separation processes were developed to separate hemicelluloses from cellulose in this work.

Three separation processes including GVL/water/dilute acid, IL/water, and IL/GVL (also IL/GVL/water) were investigated. In the GVL/water process, the CHM (cellulose/hemicelluloses matrix) was treated with binary mixtures having a sulfuric acid concentration of 0.007N at 135-150°C for 30 to 120 min. The purified cellulose produced was characterized by a cellulose content of 96-98 wt% at yields of 41-55 wt% and a CrI (crystalline index) of around 72%, under optimized conditions. The acid concentration was proved to be critical, and temperature also very important, as the two dictated the hydrolysis rate of the carbohydrates.

IL/water, IL/GVL, and IL/GVL/water systems demonstrated as effective separation mediums for the production of high-purity cellulose. CHM were treated with these mixtures at 60°C for 2h, the purified cellulose products were characterized by cellulose contents of 92 wt%, 95 wt%, and 95 wt%, with yields of 78 wt%, 76 wt%, and 77 wt% respectively, under their optimized mixture ingredient and operational conditions. The ionic liquid involved processes had advantages in gaining high purity at higher yields

but tended to disturb the original cellulose crystalline structures (CrIs were around 62%) when compared with the GVL/water/dilute acid process.

Extraction liquor recovery strategies were also proposed, including the recovery of hemicellulose, ionic liquid, GVL, and soluble sugars in sequence.

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## List of symbols

CHM: Cellulose/hemicellulose matrix

CNC: Cellulose nano-crystals

SA: Sulfuric acid

GVL:  $\gamma$ -valerolactone

IL: Ionic liquid

EmimAc: 1-Ethyl-3-methylimidazolium acetate

OES: Organic electrolyte solutions

IGW: IL/ GVL/ water mixtures

AS: Acid sulphite

PHK: Prehydrolysis kraft

CCE: Cold caustic extraction

HCE: Hot caustic extraction

XRD: X-ray Diffraction

HPLC: High-performance liquid chromatography

GPC: Gel permeation chromatography

IC: Ion-exchange chromatography

$[\eta]$ : Intrinsic viscosity, a measure of a solute's contribution to the viscosity  $\eta$  of a solution. It is used to characterize the DP of cellulose in this work.

Mw: Weight average molecular weight

Mn: Number average molecular weight

MWD: Molecular weight distribution

PDI: Polydispersity index

DP: Degree of polymerization

FT-IR: Fourier-transform infrared spectroscopy

SEM: Scanning electron microscopy

CrI: Crystalline index

UCST: Upper critical solution temperature

CSF: Canadian standard freeness, gives a measure of the rate at which a dilute suspension of pulp (3 g of pulp in 1 L of water) may be drained

Fock reactivity: A method for assessing the reactivity of dissolving pulps toward CS<sub>2</sub> in the downstream process

DMSO: Dimethyl sulfoxide

DMF: Dimethylformamide

DMI: 1,3-dimethyl-2-imidazolidinone

# **CHAPTER 1**

## **INTRODUCTION**

## **1.1 Background**

Demand from the general public for sustainable development calls for more research on technologies for energy, chemicals, and materials from renewable sources. Inexpensive biomass is geographically evenly distributed, thus can potentially be the feedstock for energy, chemicals and materials [1-7]. This concept is known as integrated forest biorefinery, which has received much attention recently and will continue to do so in the near future [8-11]. High-purity celluloses, also known as dissolving pulp, have been in high growth mode over the past 10 years. This pulp can be used for the production of cellulose rayon, cellulose esters, cellulose ethers [12-14]. Furthermore, they are superior raw materials for the production of nanofibrillation cellulose, nanocrystalline cellulose and microcrystalline cellulose [13, 15-17].

Acid sulphite (AS) and prehydrolysis kraft (PHK) are the main commercial processes for the production of dissolving pulp. Hemicelluloses such as xylans will cause operational and quality issues during downstream processes associated with the end-use of dissolving pulp [12, 18, 19]. Therefore, removal of hemicellulose for the production of dissolving pulp is imperative.

## **1.2 Paper-grade pulp as material to produce high purity cellulose**

Market paper-grade pulp contains cellulose and hemicelluloses. In recent years, the idea of converting paper-grade pulp into dissolving-grade pulp by removing the hemicelluloses present has gained much attention due to the flexibility of the process, capital investment and operational advantages [20-25]. Paper-grade pulp can be a suitable basis of manufacturing dissolving pulp providing that selective and efficient

extraction processes for hemicelluloses can be found. A number of publications are available in the literature regarding the use of several technologies, such as Cold Caustic Extraction (CCE), Hot Caustic Extraction (HCE), Ionic Liquid (IL), and enzymatic treatment [25-30].

### **1.3 $\Gamma$ -valerolactone related biorefining processes**

Using a solvent (and its mixture) is another potential technology to separate hemicelluloses from cellulose. One of these solvents is the biomass-derived  $\gamma$ -valerolactone (GVL). GVL can also be a platform bio-derived chemical that can be used as an organic intermediate in the synthesis of other chemicals, even as a liquid fuel or food additive [31].

GVL exhibits the most important characteristics of an ideal organic solvent to fractionate cellulosic materials, with the possibility for use in the production of both energy and carbon-based products [32]. It is renewable, and it can be derived from biomass-derived carbohydrates [33-36]. It has a low melting point and a high boiling point, thus the GVL-based organosolv pulping operation can be carried out at relatively low pressure. Furthermore, GVL has low toxicity, high solubility in water, and does not form even a trace amount of peroxide over time [36, 37]. Using GVL as the solvent increases the rate of hemicellulose (like xylose) degradation and in addition, water or hemicellulose degradation chemicals (like furfural) usually have higher volatility than GVL and can thus be obtained as a top product in a distillation operation. Therefore, this results in a less energy-demanding process for the separation of these products from GVL solvent, and lower costs in the recycling of GVL.

## **1.4 Objectives of the Study**

The general objectives of this thesis are:

- 1, To develop feasible and economical biorefinery processes for the separation of hemicelluloses from the cellulose/ hemicelluloses matrix (paper grade bleached pulp).
- 2, To recover hemicelluloses as value-added chemicals from extraction liquor of the separation process.
- 3, To recover the components of the solvent mixtures after extraction, including the ionic liquid, GVL, and water.

## **1.5 Research statement and hypotheses**

Paper grade hardwood bleached kraft pulp is a mature product in the market, the main components are cellulose and hemicelluloses, lignin is thoroughly eliminated in the production process. Using this paper grade pulp to produce dissolving pulp or other high purity cellulose products is superior due to much lower environmental impact and less investment related to treating the effluents.

Hemicelluloses, compared to cellulose, have a much lower molecular weight and degree of polymerization (200 for hemicellulose compared to 800-1200 for cellulose). They only have the amorphous area, while cellulose has both amorphous and crystalline areas. As a result, hemicelluloses are more accessible to chemical treatment than cellulose, such as acid hydrolysis, or cellulose/hemicelluloses solvents like ionic liquids. So the aforementioned chemical treatments are able to dissolve hemicelluloses from the cellulose/hemicelluloses matrix, and leave the cellulose as untouched solid, as long as

the treatment can be tailored to a preferable level.

## **1.6 Delimitations of the Study**

This study is limited to the selective separation of hemicelluloses from commercial bleached paper grade pulp, i.e. the hemicelluloses and cellulose matrix, and the discussion on the recovery of solvents. The usage exploration of purified cellulose (such as that used as dissolving pulp to produce viscose fibre or to produce crystal nanocellulose) was not included in this research. Using the separated hemicelluloses as material to produce furfural or  $\gamma$ -valerolactone and other value-added chemicals was not included either.

## **1.7 Novelty of Work**

A novel method of introducing GVL into the selective separation of hemicelluloses from hardwood bleached kraft pulp to produce high purity cellulose products, such as dissolving pulp.

First-time proposal/validation of EmimAc/water/GVL ternary system as high-efficiency extraction solvents to selectively dissolve hemicelluloses from cellulose/hemicelluloses matrix.

An overall process concept of utilizing both hemicelluloses and cellulose from the commercial paper grade pulp to integrate forest biorefinery into dissolving pulp mills.

## **1.8 Thesis Outline**

This thesis was written in the form of articles and it consists of seven chapters. Each chapter is a stand-alone document with references.

Chapter 1 provides the background knowledge of this project and the objective of the research. Chapter 2 presents a literature review to summarize the theoretical approach and methods for separation of cellulose and hemicelluloses from various cellulosic sources, as well as an introduction of GVL and ionic liquid used in this research.

Chapters 3 to 6 (papers to be submitted) comprised of introduction; materials and methods; results and discussion; and conclusions sections.

Chapter 3 focuses on the separation of hemicelluloses and cellulose using GVL/water/acid.

Chapter 4 explores the ability of ionic liquid and water mixtures in hemicelluloses removal from CHM and the role of water in tuning the solubility of the mixture.

Chapter 5 explores the extraction of hemicelluloses from cellulose/hemicelluloses matrix using OES solutions as well as the GVL/water/ionic liquid ternary mixtures.

Chapter 6 discusses a proposed concept for recovering ionic liquid and GVL by centrifugation and evaporation.

Chapter 7 gives the conclusions drawn from this research and the recommendations for future work on this topic.

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**CHAPTER 2**  
**LITERATURE REVIEW**

## **2.1 Current status of Canadian biorefineries**

Biorefining is a process that is similar to petroleum refining. This process refines multiple products from various biomasses as feedstock and makes full use of all the components in the feedstock, which is similar to a petroleum refinery that is currently in use. A biorefinery is a facility that integrates the various biomass conversion processes or unit operations and related equipment to produce various bioproducts including fuels, power, materials and chemicals from biomass. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic bio-based industry, producing an entire spectrum of bioproducts or bio-based products.

The pulp and paper industry is an ideal place to implement this integrated forest biorefining (IFBR) concept [1]. This industry is also one of the pillars of the Canadian economy in terms of jobs, investments and exports. With the addition of biorefining units, existing pulp and paper mills can be upgraded to IFBRs with great economic potential for the production of biofuels, chemicals, and biomaterials, while maintaining production of traditional products like pulp, paper, and other wood products. It has been suggested that forest biorefinery may increase the competitiveness of the Canadian pulp and paper industry globally. Therefore, a better balance between demand and supply; and new product development, can improve the economic situation of this sector.

## 2.2 The conventional dissolving pulp process

Dissolving pulp has a very low content of hemicelluloses, and trace amounts of lignin and other extracted compounds. These impurities are extracted from the cellulose matrix by hydrolysis, pulping, and bleaching processes. Dissolving pulp is mainly produced by acid sulphite (AS) and pre-hydrolysis kraft (PHK) processes. Both processes are paper grade pulping with an emphasis on hemicelluloses removal, but major differences exist between the two methods.

The main difference between AS and PHK processes is that the removal of lignin and hemicelluloses occurs at different stages. In the AS pulping process, the lignin and hemicelluloses are removed from the wood chips during the same pulping process. In the PHK process, they are removed in two separate steps: hemicelluloses in the prehydrolysis step and lignin mainly in the kraft pulping step [2]. Another significant difference between the AS and PHK processes is the acidity/alkalinity of the cooking liquor, which results in differences in the chemical changes of the carbohydrate chains and the subsequent pulp properties. In the AS process, the glycosidic linkages in carbohydrate chains are randomly cleaved under acidic conditions, while in the PHK process, stepwise peeling is the dominant mechanism [3, 4]. Therefore, AS pulp exhibits a higher viscosity, a higher low-molecular-weight fraction content, and a broader molecular weight distribution compared to the PHK pulp. However, the PHK pulp has a higher  $\alpha$ -cellulose content and lower reactivity [5, 6].

The AS process was once considered the most common dissolving pulp process. Benefits of this technique include high removal rates of lignin and hemicelluloses in the

cooking process [7]. However, the PHK process has gained much research highlight. This is because of the difficulty of chemical recovery in the AS process, and stricter environmental regulations [8].

PHK is performed in a combined process of both acidic (liquid or water/steam prehydrolysis) and alkaline (kraft cooking) conditions. Hemicelluloses are extracted and removed from the wood chips during the prehydrolysis stage, the kraft cooking stage, and multi-stage bleaching process to reach the desired purity of dissolving pulp [9].

Acidic prehydrolysis, prior to alkaline cooking to selectively degrade hemicelluloses, is necessary because alkaline pulping processes are not capable of selectively removing long-chain hemicelluloses. Prehydrolysis can be conducted using autohydrolysis (water/steam prehydrolysis process) and liquid hydrolysis with the addition of acid (liquid prehydrolysis and concentrated acid hydrolysis) at the laboratory scale. However, prehydrolysis at the industrial scale is performed only by hot water or steam due to economic considerations [10-12]. In a liquid hydrolysis operation, pH adjustments can easily be made, and the process features the flexibility of acid usage, lower temperature, and shorter time requirements.

Besides the commercial production processes producing dissolving pulp from biomass, the idea of converting paper-grade pulp into dissolving-grade pulp by removing the hemicelluloses present has gained a lot of attention due to the fact that commercial bleached paper grade pulps only contain cellulose and hemicelluloses. With proper added processes to eliminate the hemicelluloses, commercial bleached paper grade pulps

are a successful candidate which can be used as a material to produce dissolving pulp. A number of research studies have proven the feasibility of these technologies.

### **2.3 Hemicelluloses selective separation chemistry**

There are three major differences between hemicelluloses and cellulose. First, hemicelluloses are a group of polymers that consist of different monosaccharides including glucose, xylose, mannose etc., whereas cellulose is made of only glucose. Second, natural hemicelluloses are branched short chains with a degree of polymerization (DP) of 150-200, whereas cellulose is a long-chain polymer with a DP up to thousands. Finally, the difference in the crystalline structure, hemicelluloses are amorphous, whereas cellulose is made of both crystalline and amorphous areas. The above factors result in differences in their chemical accessibility; hemicelluloses are much more vulnerable than cellulose during chemical treatments.

## **2.4 Typical techniques for purification of cellulose products**

Several separation techniques such as Cold Caustic Extraction (CCE), Nitren extraction, Ionic Liquid (IL), and enzymatic treatment have been reported for the selective removal of hemicelluloses from paper grade bleached kraft pulp to upgrade it to dissolving pulp [13-16].

### **2.4.1 Cold caustic extraction (CCE)**

Among the methods mentioned above, CCE, typically with NaOH concentrations of 8% - 10% and temperatures below 40°C, has shown satisfying effectiveness in hemicelluloses removal.

Schild et al. reported their study on the application of CCE as post-treatment after kraft pulping and soda-AQ pulping (SAQ), as well as the pulp properties with dissolving pulp from PHK and PH-SAQ processes (prehydrolysis SAQ) [2]. Results showed all the pulp from the processes mentioned above meet the requirements of specifications for the lyocell and viscose process with a cellulose content at 91-94%. The pulp from paper pulp modified by the CCE process exhibited a significant yield advantage; about 95% of the original cellulose was retained for the final product. The yields of K-CCE (Kraft pulping + CCE) and SAQ-CCE (SAQ pulping + CCE) processes were about 50% while the PHK and PH-SAQ processes were both around 37%. The CCE and SAQ-CCE processes showed greater resource efficiency.

However, in a typical CCE stage, with its alkaline concentration of 8%, the treatment includes a gradual transition of cellulose crystal lattice from cellulose I to cellulose II.

Cellulose II is characterized as an increased number of inter-planar hydrogen bonds compared to cellulose I. The interfibrillar spaces of cellulose II would collapse during drying, results in an intensely decreased surface area and pore volume, consequently decreasing the reactivity of pulp, lower filter values and higher particle contents in the spinning dope [2]. Also, removing residual alkali from the highly swollen pulp after a typical CCE process requires excessively high capital investment and a large chemical consumption [17].

#### **2.4.2 Hot caustic extraction (HCE)**

Studies have shown that CCE can successfully extract xylan to achieve xylan content as low as less than 5%. However, the removal of glucomannan is limited to about 50% (versus 90% for xylan). Therefore, it is anticipated that CCE performed under conventional conditions is not efficient for softwood pulp purification for dissolving grades. As a result, HCE was developed as a modification of CCE.

Arnoul-Jarriault and his colleagues [18] reported an HCE process by treating a softwood kraft pulp with a caustic soda solution at 35-110°C. Results showed that 70% of the hemicellulose could be removed and this procedure combined swelling and some chemical degradation of the hemicellulose. The removal of glucomannan was increased by 1.5% by increasing the temperature from 35°C to 110°C as shown in Table 2.1. The hemicellulose content was also reduced from 6.3% to 4.1% which demonstrated that temperatures higher than 90°C have a positive effect on hemicellulose removal. However, a decrease of the cellulose degree of polymerization occurred from 1155 to 800 indicating that alkaline hydrolysis took place under these conditions.

Table 2. 1 Results of the HCE test at 35-110°C for the fully bleached pulp [18]

Temperature /°C	NaOH solution concentration/w/w%	Cellulose content/%	Glucomanan content/%	Xylan content/%	Hemicellulose content/%	Cellulose degree of polymerization
110	11	95.9	3.2	0.9	4.1	800
85	11	94.6	4.1	1.3	5.4	1045
35	11	93.7	4.7	1.6	6.3	1155

While in this process most of the cellulose was converted to cellulose II, an alternative approach was investigated to avoid the complete formation of cellulose II. An acid stage at high temperature (up to 150°C) was introduced prior to the hot caustic extraction at 110°C (A-HCE). An efficient hemicellulose removal of more than 60% was achieved, which was slightly below the CCE performance. Based on the <sup>13</sup>C solid-state NMR spectroscopy, no cellulose II was formed during this process, which would benefit the pulp reactivity.

### 2.4.3 Enzymatic treatments

Other approaches to separate residual hemicelluloses from paper grade pulps have also been suggested. Among which, enzymatic treatments have been proven to be beneficial for the reduction of the hemicellulose content. Although the direct removal of hemicelluloses during the enzymatic treatment is limited, their removal in the subsequent alkaline extraction stage is enhanced significantly [19, 20].

Kopcke et al. [19] have demonstrated the feasibility of using birch and eucalypt kraft pulp as the raw material to produce high purity cellulose. The combination pretreatments

of a xylanase treatment followed by alkali extraction and finally an endoglucanase treatment was found to be effective in terms of reactivity, viscosity and hemicellulose content. The monocomponent endoglucanase gives an improvement in cellulose reactivity, impeding the hornification effect associated with the alkali treatment and the final reactivity of products. This reached the reactivity value of commercial dissolving pulp (65-70%). An alkali extraction after xylanase treatment was reported to have greatly enhanced the reduction of xylan content to 2.5% for eucalypt and 3.8% for birch pulp. This research is supported by Ibarra et al. [20]. Paper grade pulps from non-wood biomass including flax, hemp, sisal, abaca, and jute were selected as materials. A sequence of treatments consisting of an initial xylanase treatment followed by cold alkaline extraction and a final endoglucanase treatment was investigated as a process for upgrading non-wood paper-grade pulps to dissolving-grade pulps for viscose production. From the results, sisal soda/AQ pulp showed a hemicellulose content and a cellulose reactivity value comparable to that of commercial eucalyptus dissolving pulps. Uniform and narrow molecular weight distribution was obtained, displaying a very similar pattern to that of pre-hydrolysis kraft dissolving pulp, with a structure predominately consisting of cellulose I. The results also indicated that when subjected to different hemicellulose resource and compositions, the combination of enzymatic and chemical treatments should also be modified.

#### **2.4.4 Nitren extraction**

Nitren is a strong alkaline solution consisting of tris(2-aminoethyl) amine (abbreviated as tren =N[CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>) and nickel(II) hydroxide with a molar ratio of 1:1. It can

dissolve xylan and cellulose by coordinative binding of the OH groups in the C2 and C3 position of the anhydrosugars [21, 22].

Janzon et al. [23] introduced the combination of nitren and alkali extraction to separate the xylans from bleached hardwood kraft paper pulp such as birch and eucalyptus, and demonstrated that they are applicable sources for the isolation of pure and polymeric xylan. The high delignification of fully bleached pulp reduces the hindrance of lignin xylan bonds and consequently facilitates the extraction of xylans. Furthermore, the minor portion of mannan ( $\leq 0.5\%$ ) in the initial pulp is an additional advantage regarding the purity and isolation procedures of the xylans. It was determined that at an L/P (liquid to pulp) ratio of 20:1, the nitren extraction of the birch and eucalyptus pulp allowed 98% of the xylans presented were isolated in the initial pulp. Generally, nitren dissolves the xylans with a high selectivity when the nitren concentration does not exceed 5%, and thus the cellulose portion constitutes no more than 2% of the extracts.

Janzon et al. [24] also confirmed their discoveries of hardwood pulps extracted by 5% nitren yielded a cellulose content of 93.6-95.9%. He also investigated the performance of nitren extraction on softwood pulp, which resulted in a slightly lower cellulose content of 91.4%. This is due to the fact that nitren is highly selective for xylan but not as much for mannan. Additionally, the carbonyl contents were diminished by up to 50% and the carboxyl groups up to 65%, which could be attributed almost exclusively to the extraction of hemicelluloses. On the other hand, no significant increases in the number of oxidized groups could be further detected in the cellulose portion of the pulps. Furthermore, nitren extracted pulp retained the cellulose I structure. However, for NaOH

extraction of comparative purity levels, there was a significant portion that was converted to cellulose II.

The nitren system (a tris (2-aminoethyl) amine nickel complex) has been reported to have a high selectivity for xylan which makes it very suitable for use on hardwood pulp. However, when applied to softwood pulp, the performance is rather discounted. A drawback is that nickel can easily contaminate the extracted pulp, which can be quite difficult to deal with [25].

## **2.5 $\Gamma$ -valerolactone (GVL), ionic liquids, and their applications**

Since the present technologies for upgrading paper grade pulp to dissolving grade pulp have their drawbacks, as mentioned in the previous chapters, there is a need for novel, environmentally friendly, and economically attractive separation processes that allow for a comprehensive exploration of the utilization of hemicelluloses and efficient recovery besides the production of high purity cellulose.

As a research spotlight for years, GVL is considered to be a promising and sustainable solvent derived from lignocellulosic biomass for biomass fractionation and separation [28-31]. The main intermediates produced when starting from cellulose are glucose, HMF (Hydroxymethylfurfural), LA (levulinic acid), and formic acid, all of which are miscible with water, which facilitates their biodegradability. There are no dangerous, halogenated or phosphorous compounds involved in GVL synthesis [32].

Ionic liquids (ILs) are liquid-phase salts in which the ions are poorly coordinated and cannot form a stable crystal lattice. ILs emerged as effective cellulose solvents in the early 2000s and became a research highlight since then because of their good cellulose dissolution capacity, high thermal and chemical stability, and nonflammable nature [33]. The most promising ILs for cellulose dissolving purposes are the ILs with methylimidazolium and methylpyridinium cores as cations, and chloride, acetate, and formate as anions [34]. The IL used in this research is EmimAc (1-Ethyl-3-methylimidazolium acetate).

In this chapter, I will focus on the introduction of the unique properties, the mechanisms of these chemicals, and examples of using these chemicals in biorefining.

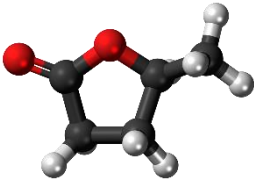
## 2.5.1 $\Gamma$ -valerolactone (GVL)

### 2.5.1.1 Properties and synthesis of GVL

GVL is a natural organic compound occurring in fruit and it is frequently used as a perfume and food additive [35]. Meanwhile, it exhibits the most important characteristics of an ideal sustainable liquid, which could be used for the production of both energy and carbon-based products [28, 29]. As listed in Table 2.2, GVL is a colourless liquid with a similar density to water. It has a low melting point and a high boiling point, and it can be mixed with water at any ratio.

Table 2. 2 Properties of GVL [29]

Chemical formula	$C_5H_8O_2$
Molar mass	100.116
Appearance	colourless liquid
Density	1.0465 g/mL
Melting point	$-31^\circ C$
Boiling point	207 to $208^\circ C$
Flashpoint	$96^\circ C$
Solubility in water	$\geq 100$ mg/mL



Horvath [29] and his colleagues compared the properties of GVL to several popular solvents including methanol and ethanol. Methanol has attractive properties for fuel-cell applications and can be converted to ethylene or propylene, but its high miscibility with water, combined with the acute toxicity, could lead to serious environmental threats. In

addition, it is not readily available from renewable resources [36]. On the contrary, ethanol is a sustainable liquid that can be produced from renewable resources, but the usual fermentation method results in low production concentration limits in water, requiring further separation processes, thus consuming a large amount of energy. The production of 95% ethanol is straightforward, but the removal of the rest of the water requires an energy demanding separation using azeotropic distillation or molecular sieves. Its sustainability was recently challenged when pointed out by Pimentel [37] that about 29% more energy is used to produce a gallon of ethanol than there is energy in that gallon of ethanol.

GVL could be considered a sustainable liquid since it has several very attractive physical properties (as listed in Table 2.2), occurs naturally, and has been widely used by the food industry. In addition, it can be converted to 2-methyl-tetrahydrofuran (2-Me-THF), which has already been considered as a renewable component of an alternative fuel [29].

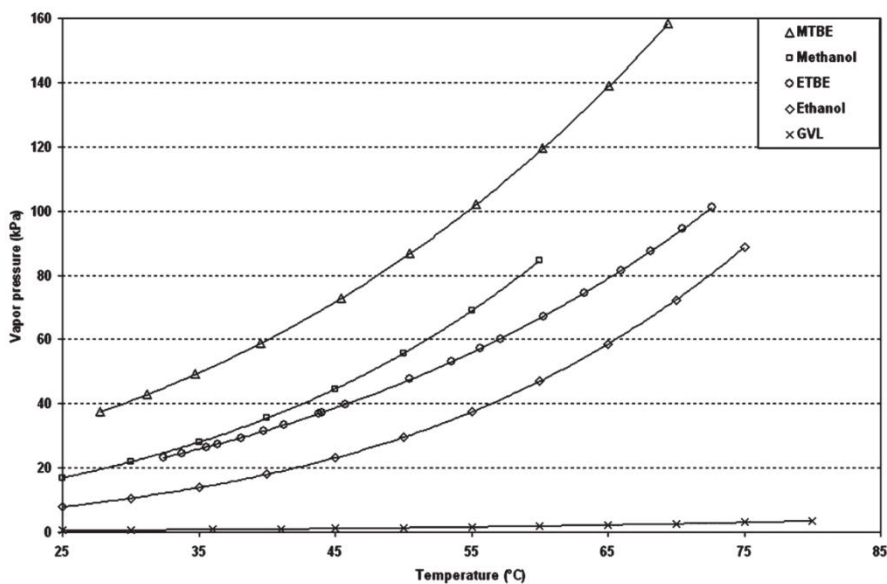


Fig. 2. 1 Temperature-dependent vapour pressure of methanol, ethanol, MTBE, ETBE, and GVL [29].

The temperature dependence of the vapour pressure of GVL, a fundamental characteristic was also established because it is an important parameter for controlling VOC emission. While the vapour pressure of GVL is 0.65 kPa at 25°C, it only increases to 3.5 kPa at 80°C (Fig. 2.1). In comparison to other solvents including methanol and ethanol, GVL shows a significantly lower vapour pressure. At the same time, GVL is very stable in the ambient environment and in mixtures of 5% GVL and 95% <sup>18</sup>O-enriched water. The solution was stored at room temperature for 60 days, and at 60°C for 28 days, where no incorporation of <sup>18</sup>O-isotope was observed by GC-MS.

GVL and abs. ethanol as a fuel additive was compared [38] by preparing a mixture of 10 v/v% GVL or EtOH and 90 v/v% 95 octane gasoline. Most of the data for GVL is comparable with ethanol, its lower vapour pressure indeed leads to improved performance. GVL can also be used as an illuminating liquid in glass lamps or for lighting charcoal. The ignition time with different mixtures of GVL (95 or 90 vol %) and ethanol (5 or 10 vol %) was conveniently reduced to just a few seconds.

The applications of GVL are summarized in Fig. 2.2 [29,39].

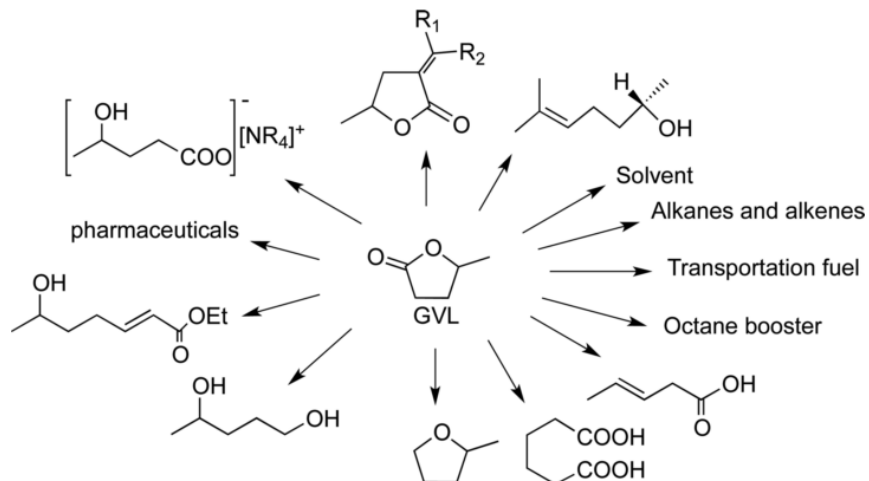


Fig. 2. 2 Selected applications of GVL.

### 2.5.1.2 GVL assisted acid-catalyzed reactions

Organic solvents can be beneficial in the biorefining process of converting biomass to sugars and other chemicals [40-42]. GVL is one such solvent, being produced from biomass itself, and displays significant improvements in lignocellulose conversion compared to conversions in an aqueous medium, such as improved reaction rates and higher selectivity [43, 44].

Mellmer et al. [45] demonstrated the effects of GVL on acid-catalyzed biomass conversion reactions. The Brønsted acids catalyzed dehydration of xylose to furfural serves as a probe reaction in his study. The turnover frequencies for xylose degradation using homogeneous acid catalysts is 30–55 times more than those when in H<sub>2</sub>O medium. Replacing SA with Propylsulfonic acid (PSA), a weaker acid than SA, resulted in a 10-time increase in turnover frequency. The use of GVL as a solvent decreased the activation energy barrier for xylose dehydration from 145 kJ/mol to 115 kJ/mol, thus

improving the reaction rate. At the same time, the activation energy barrier for furfural degradation increased from 85 kJ/mol to 105 kJ/mol, which means a higher furfural selectivity from xylose. Increases in reactivity by using GVL as a solvent were also demonstrated in hydrolysis reactions, such as the acid-catalyzed hydrolysis of cellobiose to glucose. A reactivity increase of 30 times was achieved by using GVL as the solvent compared to the reaction in H<sub>2</sub>O. It is thought that the higher reactivity of a Brønsted acid catalyst in GVL (or other aprotic solvents) is caused partially by the decreased solvation of the acidic proton by GVL molecules, opposite to what is in H<sub>2</sub>O. Thus, the proton catalyst is more active in GVL than in H<sub>2</sub>O. This lower stability in GVL leads to a higher reactivity. The solvent changes the stabilization of both the proton (H<sup>+</sup>) and the conjugate base (B<sup>-</sup>), as well as the protonated transition state (RH<sup>+</sup>) (Fig. 2.3).

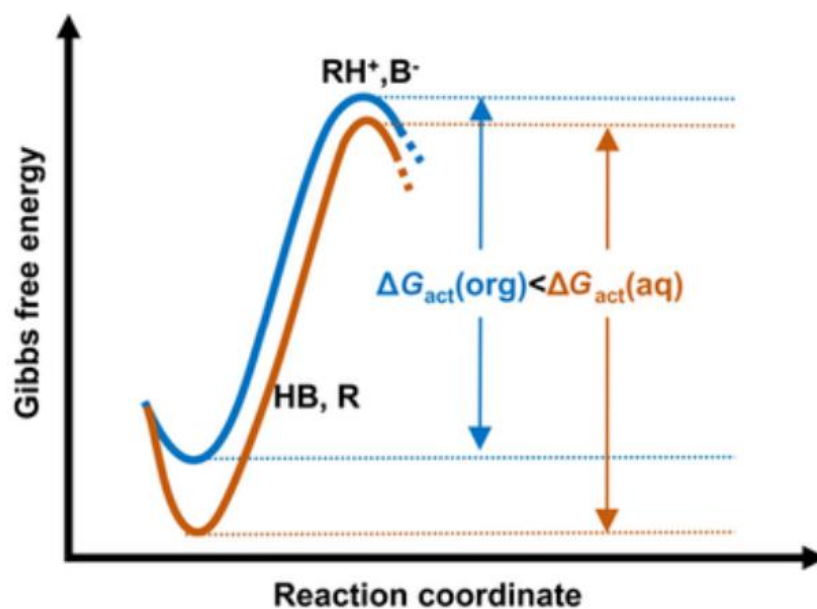


Fig. 2. 3 Gibbs free energy surface in H<sub>2</sub>O and polar aprotic organic solvents of the conversion of reactant R into product P catalyzed by a Brønsted acid [45,46].

### 2.5.1.3 GVL used in organic electrolyte solutions (OES)

Ionic liquids (ILs) are salts with low melting points, usually lower than 100°C. Their solvent properties can be tailored by carefully choosing the cations and the anions of the ionic liquids [47]. The imidazolium salts are identified as good cellulose solvents, as the hydrogen-bond formation is favoured by the acidic nature of the hydrogen atoms of imidazolium salts and depend largely on the nature of the anion [48]. Up to 25 wt% of high Mw cellulose (DP up to 1000) could be dissolved in 1-butyl-3-methylimidazolium chloride, [C4C1im]Cl or BmimCl, assisted by 3–5-second microwave heating pulses, leading to a clear viscous solution [49].

Organic electrolyte solutions (OES) are mixtures of ionic liquid with an organic, polar co-solvent. Adding an organic polar co-solvent into ionic liquid can enhance the cellulose dissolution abilities, reduce the viscosity, and enhance the thermal stability of the solvent mixtures [50]. Rinaldi [51] demonstrated that a complete dissolution of 10 wt% Avicel cellulose was achieved at very low mole fractions of the IL, such as  $\chi_{IL} = 0.08$  ([C4C1im]Cl–DMSO), 0.10 ([C4C1im]Cl–DMF) or 0.18 ([C4C1im]Cl–DMI). Pinkert [34] reported that complete dissolution of 10 wt% cellulose was achieved far more rapidly in the OES than in the corresponding pure IL. A flow diagram to aid in choosing the appropriate cation, anion and co-solvent combination for cellulose dissolution is shown in Fig 2.4.

## Designing Organic Electrolyte Solutions for cellulose solubility...

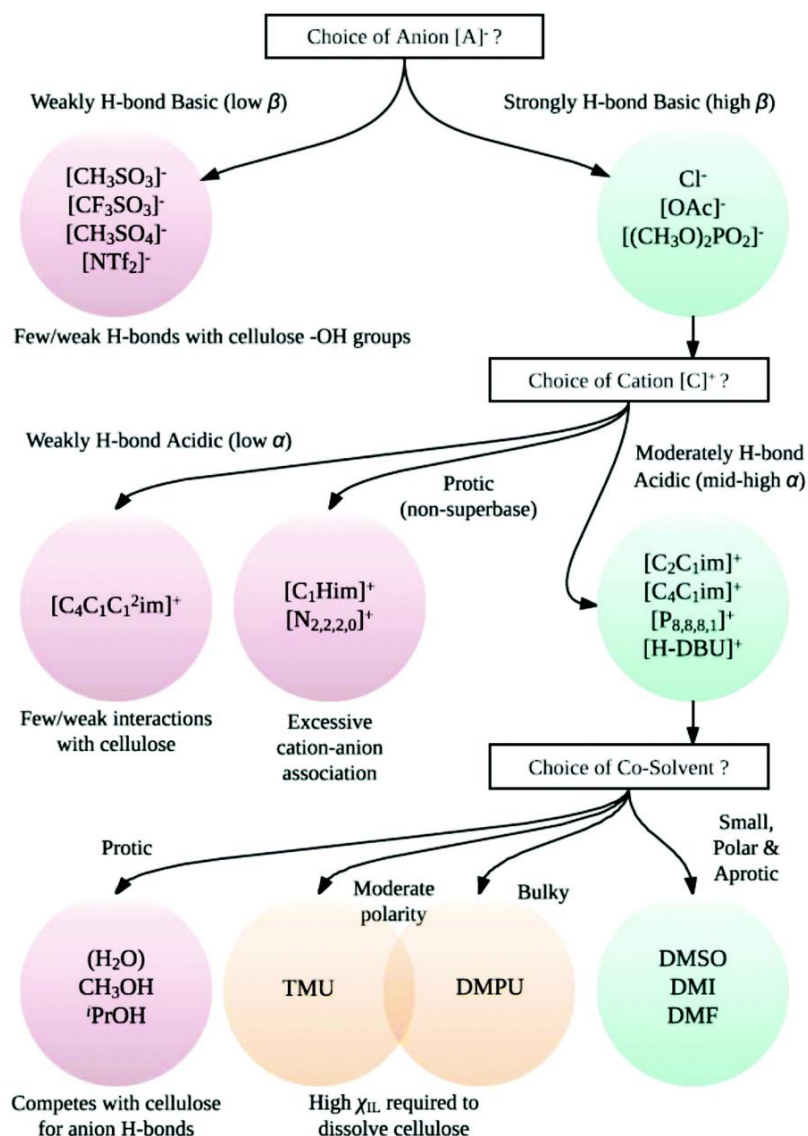


Fig. 2. 4 A flow diagram to aid in choosing the appropriate cation, anion and co-solvent combination for cellulose dissolution [50].

GVL is present in the last group of co-solvents: small, polar, and aprotic candidates, which is the most favourable group designed to dissolve cellulose.

### 2.5.1.4 Examples of GVL assisted biomass valorization

Increasing rates and selectivity are essential for maximizing product yield and improving conversion efficiency. By doing so, renewable resources can become economically competitive with petroleum products. GVL has been shown to have significant effects on reaction rates and product selectivity in biomass conversion processes, which could play a key role in future biomass conversion processes.

Petrus' work (WO2006134126 A1) [52], proposed the use of a  $\gamma$ -lactone in a solvent for the organosolv pulping process. The process involves the heating of solid lignocellulosic feedstock to a temperature in the range of 50 to 210°C in a solvent to obtain a cellulose-rich fraction containing at least 50 wt% of the cellulose present in the feedstock. The liquid fraction will comprise at least 10 wt% of lactones with molecular formula in Fig. 2.5 wherein R1 to R6, each represents independently, a hydrogen atom, or an organic group. In  $\gamma$ -valerolactone, R1 to R5 are hydrogen atoms whereas R6 is a methyl group.

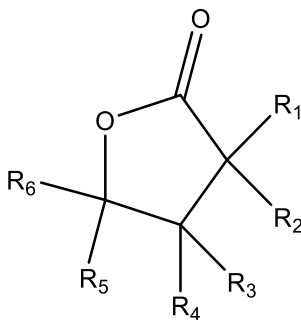


Fig. 2. 5 General molecular formula for the lactone in WO2006134126 A1[52]

Shuai et al. [46] reviewed the effects of organic solvents on biomass conversion processes, in terms of reaction rates, selectivities and overall yields. In this review, solvent effects were evaluated by their abilities in: (1) affecting the solubilities of biomass fractions (e.g., lignin, hemicellulose, and cellulose) and biomass-derived

molecules (sugars, furans, etc.), and (2) affecting chemical reaction thermodynamics, which is referred to as the free energy of the catalyst, reactants, transition state, and products.

Luterbacher et al. [53] reported a laboratory-scale production of soluble carbohydrate from corn stover, hardwood, and softwood at high yields (70-90%) in a solvent mixture GVL (80-90%), water (20-10%), and dilute acid (0.05 weight percent H<sub>2</sub>SO<sub>4</sub>). GVL promoted thermocatalytic saccharification through complete solubilization of the biomass, including the lignin fraction. Additionally, GVL prevents reprecipitation of lignin by-products on the surface of cellulose, which is a known phenomenon in water that decreases accessibility to the reactive cellulose surface. The carbohydrates produced in the process can be recovered and concentrated (up to 127 grams per litre) by extraction from GVL into an aqueous phase. This strategy is very suitable for catalytic upgrading to furans or fermentative upgrading to ethanol at high titers and near theoretical yield.

Shuai et al. [54] reported that GVL can be used to facilitate the mild pretreatment of lignocellulosic biomass prior to its conversion to soluble sugars. Up to 80% of original lignin could be removed by a 120°C pretreatment with a mixture of 80% GVL, 20% water, and an acid loading of 75 mM H<sub>2</sub>SO<sub>4</sub>. About 96–99% of the original cellulose was retained in the pretreated substrates. Negligible degradation of sugars could be detected as a mild temperature and low acid concentrations were applied. Glucan (99% of the original content) and 96% of the original xylan could be recovered after pretreatment. Then the pretreated substrate was quantitatively converted to sugars (99%

and 100% total glucose and xylose yield) with an enzyme loading of 15 FPU g<sup>-1</sup> glucan. These digestibilities were 20 times higher than when pure water was used during pretreatment. Over 99.5% of GVL could be recovered by liquid-CO<sub>2</sub> extraction of the pretreated slurries while removing less than 1% of the sugars. A final glucose and xylose yield of up to 90% and 97%, respectively, were obtained, and a sugar stream with sugar concentrations of up to 182 g L<sup>-1</sup> was generated.

Luterbacher et al. [55] demonstrates an experimental approach for upgrading lignin that has been isolated from corn stover via biomass fractionation using GVL as a solvent. Corn stover was first treated in a high-solids batch reactor at 393 K using a solvent mixture of 80 wt% GVL and 20 wt% water for 30 min. Lignin was then precipitated in water. The isolated lignin showed a similar structure to native lignin, due to the low acidity and the low extraction temperatures when GVL was used as a solvent. Lignin-derived monomers with corresponding carbon yields of 48% were obtained, which is comparable to yields of native lignin, and it is much higher than yields obtained by other processes. These results suggest that GVL-based biomass fractionation could facilitate the integrated conversion of all three biomass fractions.

### **2.5.2 Ionic liquids (ILs)**

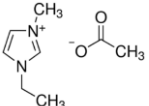
The most common examples of cellulose dissolving ILs include salts of organic cations, such as alkyl imidazolium and alkyl pyridinium, and anions, such as halides, and acetates. Room-temperature ionic liquids are the ILs with a melting temperature below 100°C. ILs are also called task-specific, because the properties of ILs can be tailored for certain purposes by varying the combinations of the cations and the anions [56].

### 2.5.2.1 Properties and synthesis of ILs

As mentioned, the properties of ILs can be tailored according to need, some of them have the ability to dissolve cellulose. From the report published by Swatloski et al. [49] in 2002, ILs consisting of 1-butyl-3-methyl imidazolium cation and  $\text{Cl}^-$  anion was an effective cellulose solvent with a relatively high viscosity. While the ILs with the same cation, but anions such as acetate, formate, and phosphate possess lower viscosities [57]. Most ILs exhibit high thermal stability, and the decomposition decreases as the hydrophilicity of the anions increase [58].

EmimAc (1-Ethyl-3-methylimidazolium acetate) is a commonly used IL in cellulose dissolution. Main properties are listed in Table 2.3.

Table 2. 3 Properties of EmimAc

Empirical Formula	$\text{C}_8\text{H}_{14}\text{N}_2\text{O}_2$	
Molecular Weight	170.21	
Density	1.101 g/cm <sup>3</sup> (20°C)	
Flash Point	327.2°F (164°C)	
Viscosity	~800 mPa·s (25°C)	

The imidazolium ionic liquids are generally synthesized in two steps: the formation of the desired cations and then the exchange of the anions. The scheme is shown in Figure 2.6 [34].

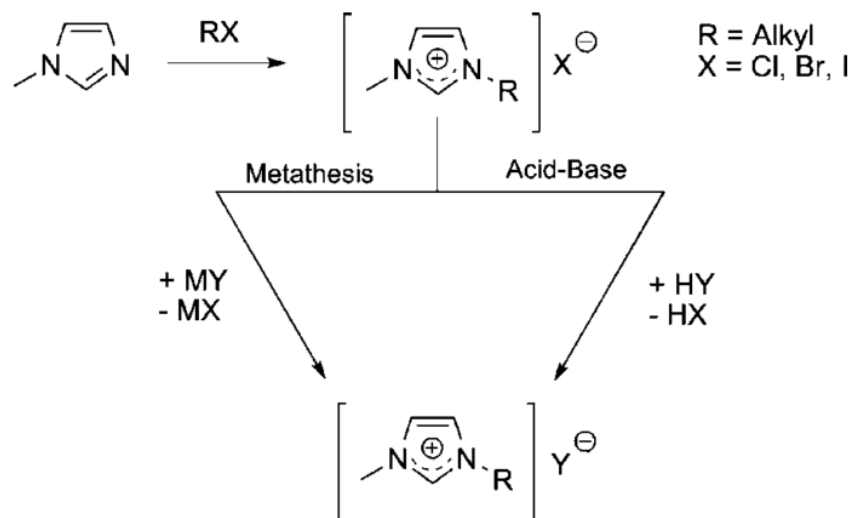


Fig. 2. 6 Typical synthesis paths for the preparation of ionic liquids [34].

### 2.5.2.2 Mechanism of cellulose dissolving in ILs

Both of the anions and cations from ILs are involved in the dissolution process as depicted in Fig. 2.7 [59]. The oxygen atoms of the hydroxyl groups from cellulose act as electron donors and form H-bonds with the cations from ILs; the hydrogen atoms of the hydroxyl groups from cellulose act as electron acceptors and form H-bonds with the anions from ILs. These interactions occur primarily between the C6 and C3 hydroxyl groups of adjacent cellulose molecules [60], resulting in the separation of the H-bonds between the adjacent cellulose molecules and the dissolution of the cellulose matrix in the ionic liquid [34,59].

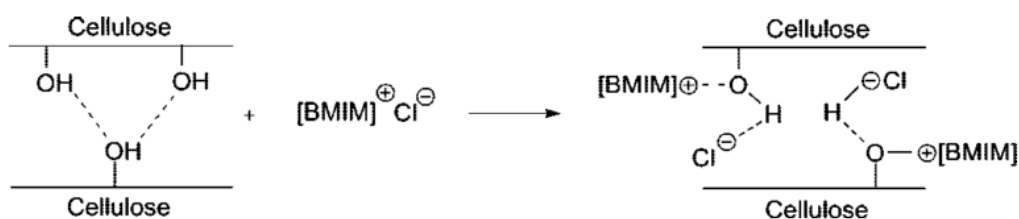


Fig. 2. 7 Proposed mechanism of cellulose dissolved in BmimCl [59]

### 2.5.2.3 Examples of ILs used in biorefining

ILs are used alone and in organic electrolyte solutions (OES) [61] in pretreatment of birchwood [62], chemical modification of cellulose [33, 63], and separation of hemicelluloses [16] in biorefining processes.

EmimAc was selected as the solvent for pretreatment of birchwood meals before autohydrolysis by Hauru et al. [62]. Untreated birchwood was not completely dissolved in EmimAc but with 15% insoluble even when wood meal particles were very small (< 0.125 mm). While the wood meal was totally dissolved after autohydrolysis and in the precipitate, the cellulose to lignin ratio increased from 2.7 to 5.7. The crystalline structure of this cellulose-rich fraction was converted to cellulose II. The other fraction was a high-purity lignin fraction. However, this proposed process was not sufficient to compete with a conventional PHK process.

Four ILs ([C4mim]<sup>+</sup>Cl<sup>-</sup>, [C2mim]<sup>+</sup>Cl<sup>-</sup>, [C2mim]<sup>+</sup>Cl<sup>-</sup>, and [C4dmim]<sup>+</sup>Cl<sup>-</sup>) were investigated as solvents for the acylation and carbanilation of cellulose by Barthel and Heinze [63]. The ILs can dissolve cellulose with a DP of up to 1200 without significant degradations of the polymer. It was demonstrated that cellulose acetates with DS (degree of substitution) of 2.5 to 3.0 can be obtained by varying the molar ratio and the reaction time. By reacting with chloride lauroyl chloride, cellulose laurates with DS from 0.34 to 1.54 can be obtained. All reactions are carried out under mild conditions and short reaction periods. The ILs applied can be easily recycled and reused.

Mixtures of EmimAc and cosolvents were used to fractionate paper pulps as reported by Froschauer et al. [16]. Kamlet–Taft parameters were introduced in this research to

monitor the mixture properties. The concept of the net basicity  $\beta-\alpha$  was adopted. EmimAc with 15–20 wt % of water can dissolve CCE xylan, while cotton linters remained insoluble, possessing KT parameters of  $0.26 < \beta-\alpha < 0.45$ , with  $0.81 < \beta < 0.96$ . These EmimAc/water mixtures were able to selectively extract (for 3 h) hemicelluloses from a paper-grade kraft pulp at 60°C, allowing the fractionation of a paper pulp into a high-purity cellulose and a regenerated hemicellulose fraction.

## **2.6 Overview of research**

In this study we applied three different systems, involving the use of GVL or IL, or both of them, to selectively remove hemicelluloses from commercial hardwood bleached kraft pulp, which is also called the cellulose/hemicelluloses matrix (CHM) in this study, either by acid hydrolysis or by selective dissolution. The first system was acid hydrolysis-based separation where CHM was treated by GVL/water mixture with a small amount of sulfuric acid. The second and third processes were CHM be treated by IL and water mixtures, and GVL and IL mixtures, or mixtures of the three components. These processes were based on the selective dissolution of hemicelluloses from the CHM.

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## **CHAPTER 3**

### **CELLULOSE/HEMICELLULOSES SEPARATION USING $\gamma$ - VALEROLACTONE (GVL)/WATER BINARY MIXTURES**

### **3.1 Introduction**

The rapid depletion of petroleum-based feedstock and serious environmental problems caused by its extensive consumption in various industries calls for urgent seeking of possible substitutes [1,2]. Cellulosic biomass is a highly functionalized composite representing more than 90% of all plant biomass ( $170 \times 10^9$  t/a) [3,4], providing a potential opportunity for carbon-neutral products while avoiding competition with food production (the advantage against starch-based feedstock). Therefore, cellulosic biomass has been identified as the most feasible substitute for fossil feedstock [5,6]. Generally, cellulosic biomass is converted to a paper-grade pulp, with a global annual production of around 170 million tons in 2013 [7]. However, the competitiveness of the pulp and paper industry is decreasing with the decline of paper medium and the rise of the electronic medium [8]. There is an urgent need to explore the potential usage of traditional pulp products.

Hardwood bleached kraft pulp (HBKP), as one of the main paper-grade pulp products in North America, was invented over 60 years ago, and is now a very mature product with an annual production of about 76.5 million metric tons globally [9], accounting for a large portion of today's commercial cellulosic materials. HBKP is particularly attractive for use as a biorefinery feedstock. With the removal of lignin, bleached kraft pulp can be treated as pure carbohydrates matrix consisting of cellulose and hemicelluloses. It is a promising material for various kinds of value-added applications, such as upgrading to dissolving grade pulp or producing soluble carbohydrates [10-12].

In recent years, the idea of purifying paper-grade cellulose (the cellulose content is about 80% in HBKP) by removing the hemicelluloses present, to produce high-purity cellulose for further applications, has gained much attention due to the flexibility of the process, capital investment, and operational advantages [11-13]. Many processes have been reported on the purification of cellulose, such as alkaline extraction [14], nitren extraction [15], and ionic liquor (IL) extraction [16, 17]. The use of xylanases alone or in combination with alkaline extraction, have also been reported [18]. Among the listed methods, cold caustic extraction (CCE), typically with NaOH concentrations of 8% – 10%, has shown effectiveness in hemicelluloses removal [14,19,20]. However, in a typical CCE stage, with an alkaline concentration of 8%, the treatment includes a gradual transition of cellulose crystal lattice from cellulose I to cellulose II, consequently decreasing the reactivity if the purpose is to produce dissolving pulp [21]. In addition, removing residual alkali from the highly swollen pulp after a typical CCE process requires excessively high capital investment and large chemical consumption [22]. The enzymatic treatment proved beneficial for the reduction of the hemicellulose content. Although the direct removal of hemicelluloses during the enzymatic treatment is limited, their removal in the subsequent alkaline extraction stage enhanced significantly. It has been reported that treating eucalyptus kraft pulp with xylanase, endoglucanase, and alkaline solution, results in residual xylan of as low as 2.4 wt% [23]. The nitren system (a tris (2-aminoethyl) amine nickel complex) has been reported to decrease the xylan content of birch kraft pulp down to 3.5 wt%, with considerably better selectivity, but the drawback is that nickel can easily contaminate the extracted pulp [15,17]. Typically,

ionic liquids (ILs) with an imidazolium derived cationic moiety show good dissolution properties towards cellulose. The dissolution capacity of ILs depends strongly on the water content [24,25], which brings increased selectivity to the IL/water system. ILs are considered good solvents for cellulose because of their low vapour pressure and high thermal stability [26], and are more environmentally friendly than their volatile, toxic counterparts. Ionic liquids are also more expensive and thus not readily available [27]. Consequently, there is a need for novel, environmentally friendly, and economically attractive processes that allow highly efficient cellulose purification.

Using an organic solvent (and its mixture) is another potential technology to separate hemicelluloses from cellulose. One of these solvents is the biomass-derived  $\gamma$ -valerolactone (GVL), which can be used as an organic intermediate in the synthesis of other chemicals, even as a liquid fuel, or food additive [28]. Being derived from biomass, both pentose and hexose, and its green nature, GVL has been recognized as a promising platform chemical and an ideal solvent for various applications [29-31]. The main intermediates produced when starting from cellulose are glucose, HMF, LA, and formic acid, all of which are miscible with water, which facilitates their biodegradability. There are no dangerous, halogenated or phosphorous compounds involved in GVL synthesis [30].

Recently, the use of GVL as a green solvent in the fractionation of lignocellulosic biomass has shown to be beneficial [30-32].

Luterbacher et al. [32] reported a study on the nonenzymatic sugar production from

biomass using biomass-derived GVL. The report introduced a laboratory-scale production of carbohydrates from corn stover, hardwood, and softwood at high yields of 70 to 90% in a solvent mixture of GVL, water, and dilute acid (0.05 w% H<sub>2</sub>SO<sub>4</sub>). The carbohydrates could be recovered and concentrated up to 127 g/L; GVL could be extracted from the aqueous phase by NaCl salting out or liquid CO<sub>2</sub> extraction.

Fang et al. [33] reported the use of  $\gamma$ -valerolactone (GVL)/H<sub>2</sub>O as a solvent and reaction medium for the fractionation of wood. Wood sawdust was treated at 170°C for 2 hours without the addition of an acid in the GVL/water co-solvent (water wt% varies from 0 to 100). In all, 79.6% of the hemicellulose was selectively extracted into the organic liquor, with a very low cellulose loss of 1-3%. With the addition of 0.05 M sulfuric acid in the GVL/water system, the separation of hemicellulose improved due to the acid-catalyzed polysaccharide hydrolysis, which removed almost all the hemicelluloses and even part of the cellulose. The cellulose purity of the resulting pulp reached up to 90.5%.

The recovery of GVL is operationally simple and efficient, as it does not form an azeotrope with water [29,30]; the latter can be removed readily by distillation, which results in a less energy-demanding process for the recycling of GVL. It was also reported that the dehydration of sugars to furanic compounds results in much higher yields when GVL is used as a solvent together with a small amount of water, compared to the properties of ionic liquids. Besides favourable yields, the treatment conditions are milder, as reported by previous research [34,35]. One important attribute is that GVL

has good affinity to lignin, and the largest solubility to lignin among the three main components of biomass (cellulose, hemicelluloses, and lignin) [36,37]. The relatively easy removal of lignin provides porosity and promotes the accessibility of the cellulosic part of whole biomass, improving the separation efficiency of hemicelluloses from biomass.

Using bleached kraft pulp (such as HBKP) as the raw material in the GVL/water mixture for the manufacturing of high purity cellulose would provide a “cleaner and greener” essence. On one hand, the pre-elimination of lignin would lower the energy consumption with a much simpler process, as no lignin recovery or lignin-rich effluent treatment is required. On the other hand, the subsequent treatments and usages of lignin and carbohydrates are different. For instance, only carbohydrates will be present in the cooking liquor when HBKP is used as the raw material, allowing for the one-pot method application of converting dissolved carbohydrates to GVL or other chemicals, requiring no separation.

Based on the aforementioned contributions by numerous researchers, we suggest that, with proper cooking conditions, such as GVL/water ratio, benign acidity, and mild cooking temperature and duration (comparing to the organosolv pulping methods), hemicelluloses could be separated from cellulose, thus HBKP could be converted to high purity cellulose for further use, either as dissolving pulp or as a precursor to producing microfibrillated cellulose or nanocrystalline cellulose.

We report here that by using GVL/water binary mixture, it is possible to produce high

purity cellulose and hydrolyzed hemicelluloses in a one-step process from the purification of commercial cellulosic material. The resultant solid residues (purified cellulose) were analyzed using ion chromatography (IC), gel penetration chromatography (GPC), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FT-IR).

## **3.2 Materials and methods**

### **3.2.1 Materials**

Bleached hardwood kraft pulp (HBKP) was generously provided by a pulp mill located in Eastern Canada. The pulp consisted of a blend of wood species: 58.0% maple, 13.0% birch, 8.0% poplar, and 21.0% other. Original CSF was 500 mL. The identified chemical compositions of the HBKP is 81.2% glucan, 18.1% xylan, and 0.7% mannan. The pulp board was disintegrated in deionized water and air-dried to around 85% dryness and sealed in plastic bags, then stored at room temperature.

GVL was purchased from Sigma Aldrich with  $\geq 98$  wt% purity. Pure water was obtained from a Millipore Synergy® UV purification system (water resistivity of 18.2 M $\Omega$  cm). Sulfuric acid was purchased from Sigma Aldrich. All chemicals were used as received, without any further purification.

### **3.2.2 Methods**

#### **3.2.2.1 GVL/water purification**

To identify the optimum conditions for hemicelluloses removal, small scale purification trials were conducted in 125 mL vials heated in a silicon oil bath reactor. For each trial, 2.0 g of oven-dried HBKP was used, with a 40 g -2 g liquid-to-solid ratio. To facilitate the penetration of the cooking liquor into the cellular structure of HBKP, the 2.0 g OD (oven dry) HBKP was soaked and disintegrated in deionized water for 30 min at room temperature. Water was removed by filtration using an 800-mesh stainless steel sieve,

the sample was torn into small pieces (5x5 mm) and mixed with cooking liquor. For trials using 98% GVL as the cooking liquor, samples were transferred to 100 mL of GVL after dewatering and were soaked for another 30 mins. Extra GVL was removed by filtration before mixing with cooking liquor. The GVL content in the fractionation liquor ranged from 0–98 wt%. The oil bath was preheated to objective temperatures before placing the vials containing pulps and cooking liquors. The reaction mixture was held at the set cooking temperature for 5 min as preheating, and then kept at the cooking temperature for a specific cooking time as required. After cooking, the vials were cooled to 55-60°C by natural convection using ambient air. Then, the pulp and the spent liquor were separated by filtration with an 800-mesh stainless steel net equipped in a clip-funnel set. The solid was then washed with 100 mL of hot GVL (85°C) and room temperature deionized water sequentially. After filtration and washing, the pulp was dried at 50°C in an oven overnight. The pulp yield was determined gravimetrically using an oven at an operating temperature of 105°C. The spent liquor and washing water were collected for subsequent analyses.

#### **3.2.2.2 Analytical characterizations of purified cellulose**

The carbohydrate content in the purified solids was analyzed in accordance with the 2-step hydrolysis method described in the NREL/TP-510-42618 standard. The pulp was first hydrolyzed in 72% H<sub>2</sub>SO<sub>4</sub>, with an acid-to-material ratio of 20 mL g<sup>-1</sup>, at 30± 1°C, for 60 minutes. The hydrolyzed suspension was then subjected to the second hydrolysis in 4% H<sub>2</sub>SO<sub>4</sub>, by adding deionized water to dilute 72% H<sub>2</sub>SO<sub>4</sub> to 4%, at 121± 1°C, for

60 minutes. The carbohydrates composition of the pulp samples was determined using an Ion Chromatography (IC) unit equipped with CarboPac™ PA1 column (Dionex-300, Dionex Cooperation, Canada) and a pulsed amperometric detector (PAD). The cellulose and hemicelluloses contents in the HBKP and cooked samples were estimated with the Janson formula based on the amounts of neutral monosaccharides. Selected samples were analyzed for viscosity in accordance with the TAPPI standard method (T230 om-99).

The sugar content of extraction liquor was analyzed using the same IC system described above. All operations were the same as the analysis of purified, the only difference was that liquid samples were hydrolyzed in 4% H<sub>2</sub>SO<sub>4</sub> only.

### **3.2.2.3 Intrinsic viscosity**

The intrinsic viscosity of all samples was measured according to the TAPPI T230 om-99 standard method using copper-ethylene-diamine (CED) solution as the solvent. All measurements were carried out in duplicate.

### **3.2.2.4 Molecular weight distribution**

The determination of molecular weight distribution (MWD) of samples was conducted on a gel permeation liquid chromatography (GPC device, Waters 600E), equipped with a differential refractometer detector (Waters 410) and a Waters Styragel HR 5E column. Prior to the determination, the pulp sample was dissolved in an 8% DMAc/LiCl solution. The mobile phase of 0.5% DMAc/LiCl was pumped into the system at a flow rate of 0.3 mL/min. The column temperature was 50°C, and the injection volume was 10 µL.

### 3.2.2.5 X-ray diffraction (XRD) spectrum analysis

The XRD scattering analysis of pulp was carried out on a Bruker D8 XRD system using Cu–K as a source ( $\lambda = 0.154$  nm) in the  $2\theta$  range ( $5^\circ - 40^\circ$ ) and a scanning speed of  $1.2^\circ/\text{min}$ .

The cellulose crystallinity index (CrI) was calculated based on Eq. (1) [12, 38-40]:

$$CrI, \% = \frac{I_c}{I_a + I_c} \times 100\% \quad (1)$$

where the  $I_c$  and  $I_a$  are the integral scattering intensities of crystalline and amorphous regions, respectively, based on the peak convolution method.

### **3.3 Results and Discussion**

GVL is not capable to selectively dissolve hemicelluloses from cellulose/hemicelluloses matrix even at elevated temperatures. However, if chemical reactions such as acid hydrolysis are applied in GVL treatment, due to the differences of these two in physical and chemical properties, it is plausible to separate hemicelluloses from the matrix at much milder conditions than traditional acid hydrolysis. On the one hand, there is an apparent difference in the chemical accessibility between cellulose and hemicelluloses, which is due to differences in the degree of polymerization (DP), chain branches, and crystallinity. Cellulose usually has a DP up to thousands; its molecule is a linear chain without branches, crystallinity is more than 50%; while hemicelluloses are branched and much shorter, usually with a DP lower than 200, and there is no crystalline area in hemicelluloses. On the other hand, GVL as a reaction medium is able to increase the acid hydrolysis rate compared to reactions in water, by decreasing the apparent activation energy [34], which favours much milder reaction conditions. The overall concept of this research is depicted in Fig. 3.1 as below.

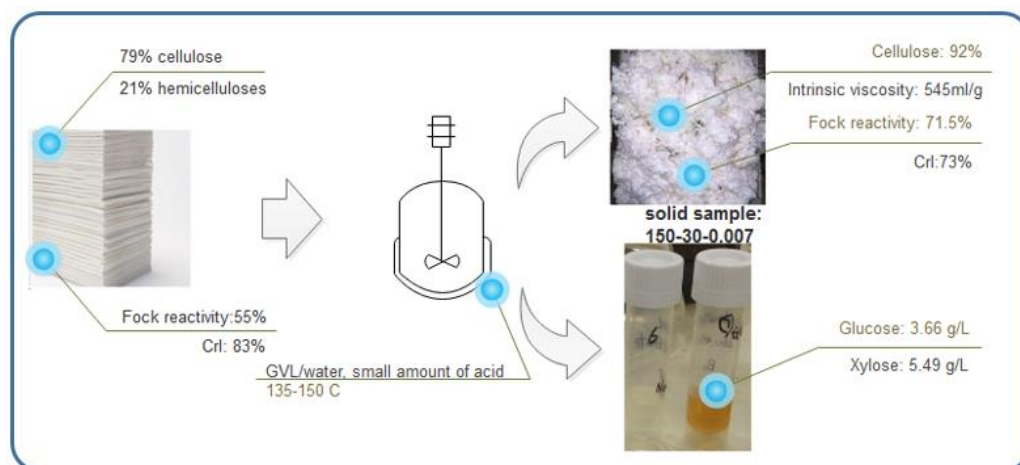


Fig. 3. 1 Schematic and mass balance of separation of cellulose and hemicelluloses in an acid-catalyzed GVL/water system (98% GVL, 150°C, 30 min, sulphuric acid 0.007 N).

### 3.3.1 Effects of purification conditions

The optimization of the purification conditions was carried out. For the first set of trials, the cooking time was set at 150°C, with a GVL ratio of 98%, while the acid addition and purification time varied from 0 to 0.01 N and 30 to 60 min, respectively. The solid residue was collected and washed, then analyzed for glucan and xylan. The “Selectivity” defined as the ratio of hemicelluloses removal to cellulose loss was used to evaluate the performance of the system.

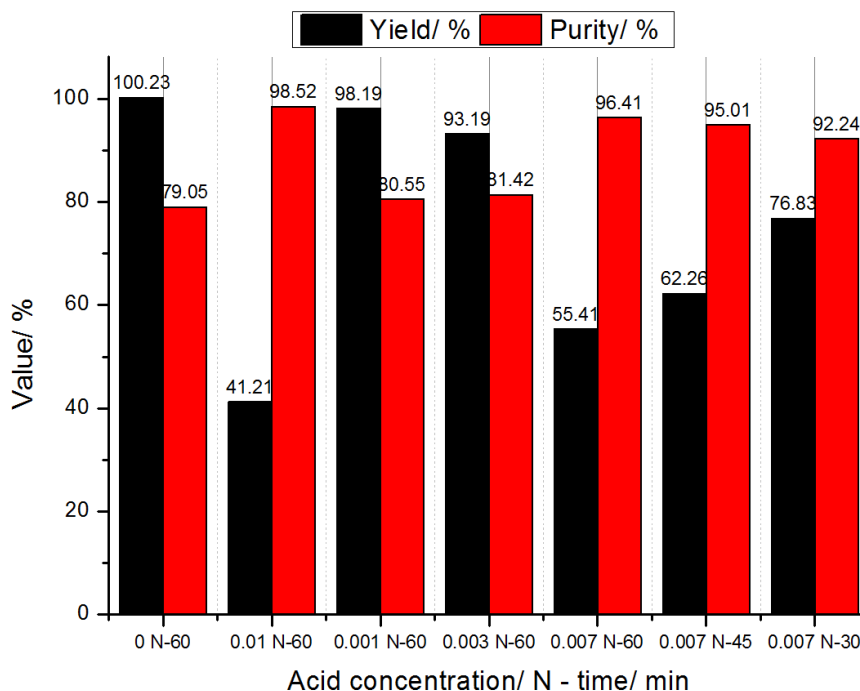


Fig. 3. 2 Effects of acidity and time on the purification results (98 % GVL, 150°C)

By comparing the result (Fig. 3.2) of 0N-60 (without the addition of sulfuric acid and cooking time is 60 min) to the ones in the presence of different concentrations of sulphuric acid (0.001 to 0.01 N), there is a strong indication that acid concentration in this purification process is critical. The yield of 0N-60 was 100%, which means no hemicelluloses removal during the 60 min of purification time. Whereas with 0.001N of SA in the liquor (0.001N-60) resulted in about 2% yield loss. At a 0.01 N acid concentration, the yield was 41%, with purity of 98.52% (0.01N-60). Based on the results of trials with different acid concentrations (0N-60, 0.001N-60, 0.003N-60, 0.007N-60, and 0.01N-60), it was clear that an acid concentration between 0.003 N to 0.007 N would be more reasonable. The 0.007 N acid concentration was chosen to study

the effect of cooking time on the performance of the purification process.

When the cooking time was reduced from 60 min to 45 min and 30 min, the yield increased from 55.4% to 62.3% and 76.8%, but the purity decreased from 96.4% to 95.0% and 92.2%. The changes in yields were more obvious than the changes in purities, indicating that during the first 30 min of purification, there were less cellulose loss than in the second 30 min of purification. This was also supported by the selectivity data (Fig. 3.3, 150°C). At the 30 min point of the fractioning process (150 °C), a large quantity of xylan (67.1%) degraded and dissolved from the cellulose/hemicellulose matrix while only 12.8% of the glucan dissolved (Fig. 3.2, 0.007N-30), with a selectivity of 5.3 (Fig. 3.3, 30 min). As the fractioning process continued, more glucan dissolved with descending dissolution of xylan, demonstrated by the fact that from 30 min to 45 min, about an equal percentage of glucan and xylan (both were about 15%) dissolved into the liquid phase, showing a selectivity of 3.0. At the end of the fractionation process (from 45 min to 60 min), as the “easier” part of hemicelluloses and amorphous area of cellulose had already been dissolved, the reaction rate decreased, supported by the removal of glucan and xylan, both were only about 7% compared to 15% in the same period of 15 mins. Therefore, at 150°C, the fractionation liquor is able to hydrolyze both hemicellulose and cellulose continuously while processing goes on, but at a decrease selectivity.

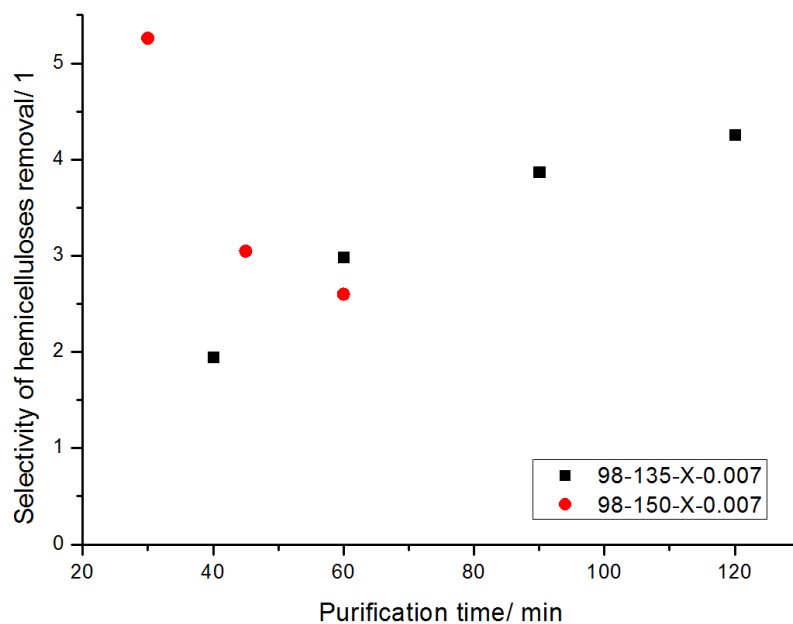


Fig. 3. 3 Selectivity of hemicelluloses removal showed different trends at 135°C (black) and 150°C (red) as purification time increases

The selectivity of hemicelluloses removal at 135°C increased as purification time increased, which means more hemicelluloses were dissolved into the liquid phase, though as purification continued, the increase of selectivity was smaller, but still more hemicelluloses than cellulose dissolved. Therefore, at 135°C, the fractionation condition is not “harsh” enough to hydrolyze both hemicellulose and cellulose. The lower purification temperature together with low sulfuric acid usage formed a milder hydrolysis condition, which favours the selective removal of hemicelluloses, with most of the cellulose remaining.

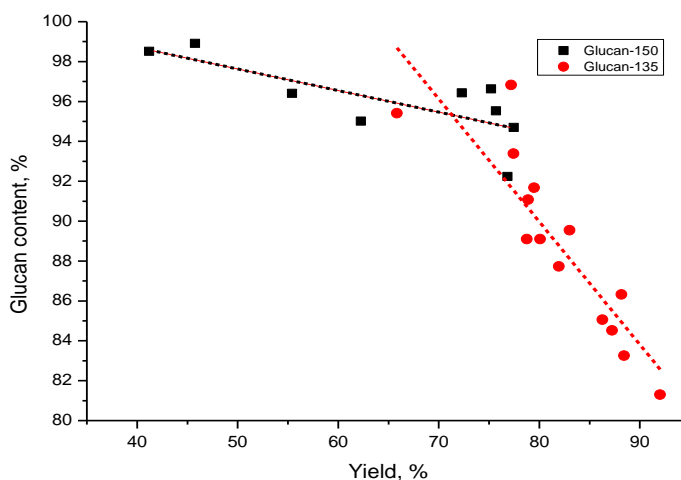


Fig. 3. 4 The relationship of glucan contents of the purified cellulose and the cooking temperature

Results from various trials with the same sulfuric acid concentration but different cooking temperatures, and cooking time (from 20 mins to 120 mins) are depicted in Fig. 3.4. The two purification temperatures led to two different straight-line relationships, with the two intercepting at a yield of about 72% and glucan content of 95%. At 150°C, it was easier to get a high purity of the resultant cellulose in the solid residue, but as the process continued, mainly cellulose was dissolved into the liquid phase since the yield decreased from 80% to 40% and the cellulose content only increased by from 94.5% to 98.5%. However, at 135°C, as the yield decreased from 95% to 75%, the cellulose content increased from 81% to 95%. Therefore, concluding that a lower processing temperature favours a higher hemicelluloses removal selectivity.

### 3.3.2 Purified cellulose characterization

Although the treatment conditions using GVL/water mixtures in this work were relatively mild [41,42], the surface structure of cell walls was extensively destroyed, long fibres were shortened, more fragments and wrinkles appeared, and cracks were visible in the image of the treated samples, as illustrated by SEM (Fig. 3.5, a).

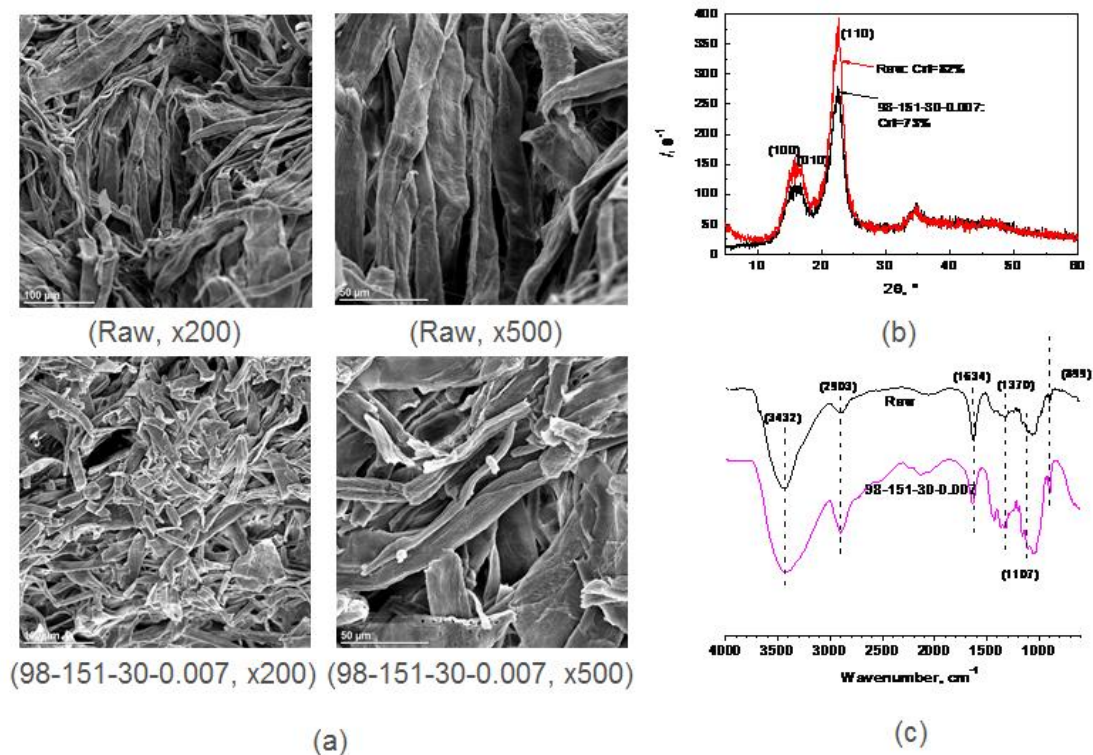


Fig. 3. 5 (a): Solid surface morphology of original HBKP and the purified cellulose sample (98-151-30-0.007); (b): XRD spectrum of the original HBKP and purified samples; (c): FT-IR spectrum of the original HBKP and purified cellulose.

The crystalline index (CrI) of the purified cellulose samples was calculated for a quantitative comparison (Fig. 3.5, b). The CrIs of the resulting solid sample (98-151-30-

0.007) was 73%, while the CrI of the original HBKP was 82%, a decrease was observed. This is attributed to the swelling of the cellulose and the destruction of the cellulose crystalline structure. Together with the morphology examinations of the purified cellulose samples, the XRD spectra and CrI analysis suggested strongly, that the fibre structure and some of the crystalline areas of the cellulose were also destroyed during the purification process.

FT-IR spectroscopy was used to investigate potential changes of components and structures during the GVL/water cooking process (Fig. 3.5, c), and the peaks were assigned by comparing with data reported in the literature [43,44]. The peaks at around  $2903\text{ cm}^{-1}$  and  $1370\text{ cm}^{-1}$ , were assigned to C-H stretching relevant to amorphous and crystalline regions of cellulose, respectively. Notice the signals at  $1727\text{ cm}^{-1}$  of the solid samples treated by GVL/water mixture, which was attributed to the stretching of C=O groups of hemicelluloses, were much weaker than that of the original HBKP, indicating that only small amounts of hemicelluloses were retained in the solid samples. This observation was consistent with the purity results in Fig. 3.2.

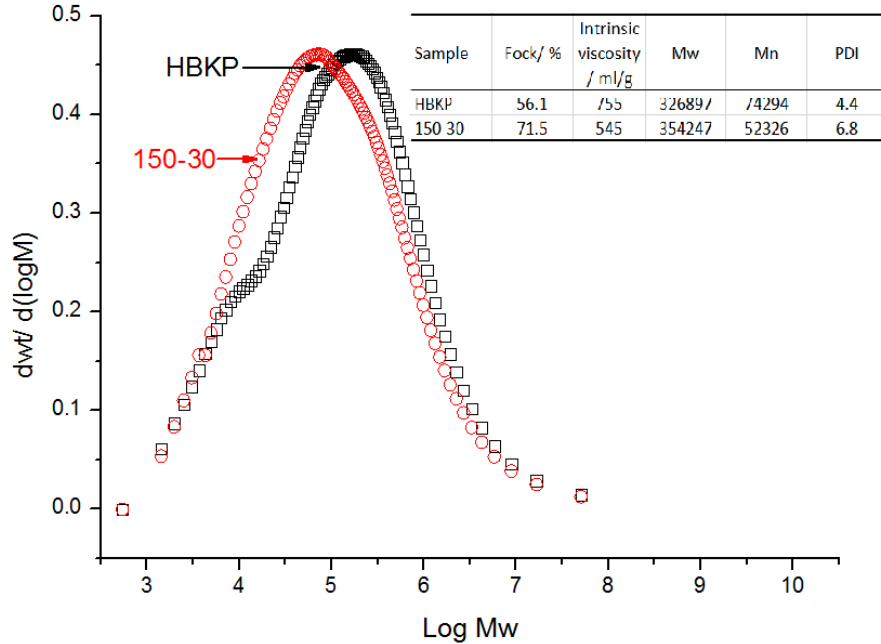


Fig. 3. 6 Molecular weight distribution (MWD) of original HBKP and cellulose sample obtained from GVL/water fractionation at 150°C, 30 min, 0.007 N sulphuric acid

As shown in Fig. 3.6, the MWD of the cellulose sample obtained from GVL/water fractionation was distinct from the original hardwood bleached kraft pulp. For the HBKP pulp, there was an apparent shoulder which represents the low Mw hemicelluloses, which was also observed by other researchers. Roselli et al. [17] investigated the MWD of eucalyptus kraft pulp before using it as the material to produce dissolving pulp. The original eucalyptus kraft pulp showed a similar bi-peak profile, which was significantly different from the dissolving pulp product that was made from his ionic liquid involved extraction method. While for the GVL/water treated cellulose sample, a clear single peak with a lower molecular weight was observed (sample marked as 150-30), indicating that the low Mw hemicelluloses were eliminated from the CHM. This was in

agreement with other researchers' observations. Li et al. [45] examined the MWDs of dissolving pulp treated by various dosages of cellulase, each of the MWD profile was a nice single peak curve. The hemicelluloses were effectively removed after the GVL/water fractionation process, while the acid hydrolysis is responsible for the decreased Mw of cellulose. As a result, the intrinsic viscosity of the treated sample was decreased from 755 to 545 mL/g. The treated HBKP gained an obvious reactivity improvement to 72%, which is a much higher value than ordinary PHK dissolving pulps [46]. These results were in agreement with data reported in the literature. Duan et al. [12] reported that when HBKP was upgraded to dissolving pulp by a modified process consisting of a mechanical refining, a low-alkali (5.5% NaOH) cold caustic extraction, and an endoglucanase treatment, a decrease in intrinsic viscosity from 628 mL/g to 522 mL/g and a decrease in Mw were observed.

### **3.3.3 Dissolved hemicelluloses and cellulose in liquor**

The sugar analysis of the extraction liquor was performed to determine the amount of glucan and xylan in the liquor, which could possibly be converted to GVL. The total sugars in the liquor accounted for a yield of 18.3 wt% based on the original HBKP, with 59.9% of xylose and 40% of glucose (Table 3.1). The C6 and C5 sugars were both good to produce GVL using a suitable catalyst and hydrogen sources, as reported by Alonso et al. [30]. Deng et al. [47] reported a route to produce GVL from cellulose and starch without using an external hydrogen source, the key was to tune the base and ligand in Ru-based catalytic systems. Gonzalez Maldonado [48] reported a key step for producing

GVL from the C5 sugars in hemicelluloses, that is the production of levulinic acid (LA) from furfural alcohol (FAL). The evidence of multiple pathways for the formation of LA from FAL was presented using NMR and LC-MS techniques, demonstrating the certainty of producing GVL from C5 sugars.

Table 3. 1 Mass balance of 150-30 trial

Sample	Cellulose fraction (Solid)				Dissolved cellulose and hemicellulose		
	yield/wt %	xylan/wt %	cellulose/w t%	$\eta$ /mL/ g	yield/wt %	xylose/wt %	glucose/w t%
HBKP	100	20.9	79.1	755			
98-150-30-0.007	76.8	7.8	92.2	545	18.3	59.9	40

### 3.3.4 Industrial application

The GVL/water acid-catalyzed system to selectively separate cellulose/hemicelluloses is proposed for application in an industrial process, as shown in Fig. 3.7. Bleached kraft pulp in its dried pulpboard is first disintegrated to pulp fibres in a hydraulic repulper by using GVL as the liquid phase. Next, a small amount of sulphuric acid can be added on-line to the pulp slurry. Hemicellulose is selectively hydrolyzed in the digester. The extracted kraft pulp is then separated from the liquid phase in a filter, the solid fibres were then washed and are ready to be used as dissolving pulp. The liquid from the filter is sent to a catalytical reactor and the conversion of glucose and xylose to GVL is finished [47,49] and it is a compensation to the GVL used in the whole process.

The proposed process is simple and straightforward and has several advantages including:

- 1) Lower equipment investment compared to traditional dissolving pulp process
- 2) No effluent to cause environmental issues
- 3) No cost in treating effluent
- 4) Separated sugars can be used to produce GVL

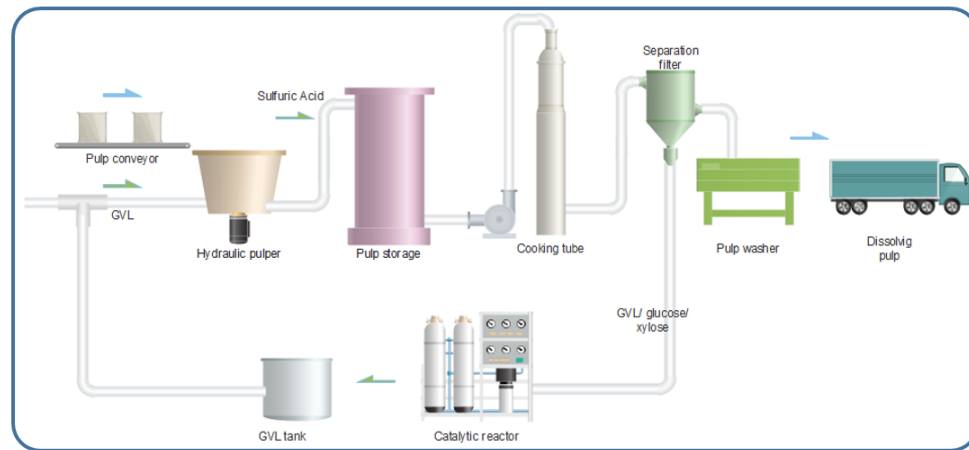


Fig. 3. 7 The proposed process of dissolving pulp production from HBKP by using GVL/dilute acid treatment

### **3.4 Conclusions**

This paper has demonstrated a method for the fractionation of commercial cellulosic material (HBKP) using GVL/water binary mixture to produce purified cellulose. The produced solid residual was characterized by a high cellulose content (96- 98%) and a CrI of about 72%, under optimized conditions. The acid concentration was found to be critical among the cooking conditions, and only very dilute acid was needed in the purifying process, about 0.007 N sulfuric acid in this work. The cooking temperature was also found to be a very important parameter which dictates the dissolution rate of the carbohydrates, thus affecting the yield to a large extent. With the recovery of GVL and utilization of hydrolyzed hemicelluloses (there are many successful examples in literature), this method of producing high purity cellulose (dissolving pulp) demonstrated as a good fit with the Integrated Forest Biorefinery concept.

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## **CHAPTER 4**

# **STUDY OF EMIMAC/WATER BINARY MIXTURES ON SELECTIVE DISSOLUTION OF HEMICELLULOSES FROM A CELLULOSE/HEMICELLULOSES MATRIX**

## 4.1 Introduction

The processing and dissolution of cellulosic materials using ionic liquids (ILs) have been highlighted in research since 2002. This is due to the progress in discovering the low melting point temperature of (lower than 100°C) ionic liquids, or the so-called room temperature ionic liquids (RTILs). Among the RTILs, the dialkyl imidazolium-based ILs receive a lot of attention, especially AmimCl, BmimCl and EmimAc [1]. The first reported IL that could dissolve cellulose, molten N-alkyl pyridinium chloride, was discovered in 1934 by Graenacher [2]. However, it could only dissolve about 5wt% of natural cellulose at 110-115°C with continuous stirring for hours. These RTILs have lower melting points and viscosities, and they are much more powerful for dissolving and processing cellulosic materials. As reported by Zhang and his colleagues [3], by using AmimCl as cellulosic fibre solvent, a 30 wt% cellulose with a degree of polymerization (DP) of 650 was prepared within 30 min. By using methods such as molecular dynamics (MD), simulations and quantum chemistry calculations, the mechanisms of cellulose dissolution in ionic liquids could be attributed to: (1) the intramolecular hydrogen bonds of cellulose are removed because of strong H-bonding interactions between cellulose molecules and the IL [4], or/and (2) anions of the IL can strongly interact with hydroxyl protons of cellulose [5], and (3) the coupling of cations to side chains and linker oxygen is stronger in the peeled-off state [6].

Apart from being used alone, ILs are also used with one or more solvents to achieve a specific target such as separating hemicelluloses from cellulose in plant fibres. The most

commonly used cosolvents are water, ethanol, and dimethyl sulfoxide (DMSO), which cover both polar protic (water and ethanol) and polar aprotic (DMSO) solvents.

The presence of water in ionic liquids significantly impacts the solubility of cellulose. This is because of the competitive hydrogen-bonding of water molecules to the cellulose microfibrils which decreases the interactions between ionic liquid molecules and cellulose microfibrils [7]. Water was reported to have the ability to link units of sugar, cause aggregation, and decrease carbohydrates accessibility and reactivity [8]. When water was added to BmimCl at concentrations greater than ca. 1 wt % (approximately 0.5 mole fraction H<sub>2</sub>O) [7], the solvation ability was significantly impaired, and cellulose was no longer soluble. Water is usually used as an anti-solvent to ionic liquids, which makes it possible to meticulously control the solubility of the solvent mixtures, or to use it as a precipitation agent for cellulose recovery.

Selectively dissolving hemicelluloses from the cellulose-hemicelluloses matrix (CHM) is of special interest to increase the purity of cellulose (or on the other hand, hemicelluloses). This method is necessary to add its value as a sustainable material. Selectively dissolving hemicelluloses from the semi-crystalline matrix requires a suitable swelling ability and subtle solvent power to dissolve hemicelluloses without the solvation of much cellulose.

The objective of this chapter is to investigate whether separating hemicelluloses from CHM is possible by using suitable IL/ water mixtures. This chapter further describes how the impact of the proportion of water/ EmimAc on selectively extraction

hemicellulose from CHM, especially HBKP. The swelling and dissolution mechanisms of solvent mixture systems, mass transfer parameters such as viscosity and conductivity, as well as the solvent performances in the selective dissolution of hemicelluloses from CHM were studied.

## 4.2 Materials and methods

### 4.2.1 Materials

Ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimAc) (95%, Sigma Aldrich), were used as received without any further purification. Mixed hardwood bleached kraft pulp which was used as CHM in this research, was obtained from a pulp mill located in eastern Canada. The CHM was air-dried under  $50.0 \pm 2.0\%$  RH and  $23.0 \pm 1.0^\circ\text{C}$ , for 24 hours, and was fluffed in a coffee bean grinder prior to use for better solvent accessibility. The dyes used in determining K-T parameters were purchased from Sigma Aldrich.

Table 4. 1 A summary of material and chemicals used in this research

	Purity	Provider	Note
1-ethyl-3-methylimidazolium acetate (EmimAc)	95%	Sigma Aldrich	
Hardwood bleached kraft pulp (CHM) (79.2% glucan, 20.1		Pulp mill	Made from mixed hardwood: maple 60%, birch 20%,

xylan, 0.7% mannan)		poplar 20%
Reichardt's dye (RD)	90%	Sigma Aldrich
N, N-diethyl-4-nitroaniline (DENA)	98%	Sigma Aldrich
4-nitroaniline (4NA)	98%	Sigma Aldrich

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## **4.2.2 Methods**

### **4.2.2.1 Fiber swelling**

Thanks to the series of work by Cuissinat & Navard [14-17], the swelling and dissolution of CHM fibres were categorized into 5 different modes described below:

Mode 1: fast dissolution by disintegration into fragments

Mode 2: large swelling by ballooning, and dissolution

Mode 3: large swelling by ballooning, and no dissolution

Mode 4: homogeneous swelling, and no dissolution

Mode 5: no swelling, and no dissolution

The CHM fiber morphology was observed using an optical microscope (Leica DM4000 M) equipped with a digital camera (Leica DFC480).

### **4.2.2.2 Viscosity and conductivity**

The viscosity of the solvent mixtures was determined using a Brookfield digital viscometer (HT-115) equipped with a programmable temperature controller (HT-115A).

The accuracy of the viscometer is  $\pm 1\%$ . The conductivity of the solvent mixtures was determined by using a Symphony™ handheld meter (VWR, Radnor, PA, USA). The measurements were taken at room temperature with an MP5 Pt conductivity electrode, calibrated using a KCl standard solution at various concentrations. The accuracy of the Symphony handheld meter is  $\pm 0.5\%$ . All measurements were performed under a nitrogen atmosphere, an average value of three measurements was reported.

#### **4.2.2.3 The selective solution of hemicelluloses from CHM**

To explore the effects of water when it was used as a co-solvent for the selective dissolution of hemicelluloses, cellulose/hemicellulose-containing bleached kraft hardwood pulp fibres were fluffed and treated by co-solvent and ionic liquid mixtures. Different molar ratios of deionized water (e.g. 1, 2, and 4 moles of water to 1 mole of EmimAc, were marked as WE1, WE2, and WE4 respectively) were added to 4 g of EmimAc. A 5 wt% HBKP (based on EmimAc) was dispersed into the solvent mixtures before they were transferred to a 20 mL glass vial. Solubility tests were conducted in an oil bath which was set to specific temperatures. When the test was finished, the sample was filtered using a 2-layer 400 mesh stainless steel film. The samples were washed with the same amount of solvent mixtures with the same ingredients and temperature. The extraction conditions were set to 120 minutes at temperatures of 25°C, 60°C, and 90°C.

#### **4.2.2.4 Characterization of extracted CHM**

##### **Carbohydrate analysis**

The carbohydrate content in the purified solids was analyzed in accordance with the 2-

step hydrolysis method described in the NREL/TP-510-42618 standard [9]. The pulp was first hydrolyzed in 72% SA (sulfuric acid), with an acid-to-material ratio of 20 mL/g, at  $30 \pm 1^\circ\text{C}$ , for 60 minutes. The hydrolyzed suspension was then subjected to the second hydrolysis in 4% SA, by adding deionized water to dilute 72% SA to 4%, at  $121 \pm 1^\circ\text{C}$ , for 60 minutes. The carbohydrates composition of the pulp samples were determined using an Ion Chromatography (IC) unit equipped with a CarboPac<sup>TM</sup> PA1 column (Dionex-300, Dionex Cooperation, Canada) and a pulsed amperometric detector (PAD). The cellulose and hemicelluloses contents in the HBKP and cooked samples were estimated with the Janson formula, based on the amounts of neutral monosaccharides, as described in Li's research [10].

### **Intrinsic viscosity**

The intrinsic viscosity of all samples was measured according to the TAPPI T230 om-99 standard method using a copper-ethylene-diamine (CED) solution as the solvent. All measurements were carried out in duplicate.

### **Crystallinity**

The XRD scattering analysis of the pulp was carried out on a Bruker D8 XRD system using Cu-K as a source ( $\lambda = 0.154 \text{ nm}$ ) in the  $2\theta$  range ( $5^\circ - 40^\circ$ ) and a scanning speed of  $1.2^\circ/\text{min}$ . The samples (CHM and extracted CHMs) that were powdered but not further processed, were placed inside metallic sample holder rings which are 1 mm thick and sealed on both sides with Mylar foil. The calculation of crystal size and crystallinity was carried out as previously presented in the literature [11]. The cellulose crystallinity index

(CrI) was calculated based on Eq. (1) [12]:

$$CrI, \% = \frac{I_c}{I_a + I_c} 100\% \quad (1)$$

where the  $I_c$  and  $I_a$  are the integral scattering intensities of crystalline and amorphous regions, respectively, based on the peak convolution method. The crystallite size in the 002 lattice plane ( $D_{002}$ ) was calculated based on Scherrer Eq. (2) [13]:

$$D_{002}, nm = \frac{K\lambda}{\beta_{002} \cos \theta_{002}} \quad (2)$$

where  $D_{002}$  is the width size of crystallinity;  $K$  is the constant that depends on the crystal shape ( $K = 0.94$  for cellulose);  $\lambda$  is the wavelength of the X-ray source ( $\lambda = 0.154$  nm);  $\beta_{002}$  is the peak width at half the maximum (PWHM) of the 002 reflections in radians, and  $\theta_{002}$  is the Bragg angle at the maximum angle of refraction (002).

### 4.3 Results and Discussion

EmimAc can be used to dissolve cellulosic fibres as introduced in the previous section. In order to use it to separate cellulose and hemicelluloses from a matrix, its cellulose dissolution ability has to be modified. In addition, the mobility of the ions from EmimAc should be improved, to improve the swelling of the whole matrix, thus a more thorough extraction of hemicelluloses could be realized. Water was added at various ratios to improve the viscosity of solvent mixtures, and to generate a milder solvent mixture for selective dissolution of hemicelluloses; the schematic is shown in Fig. 4.1.

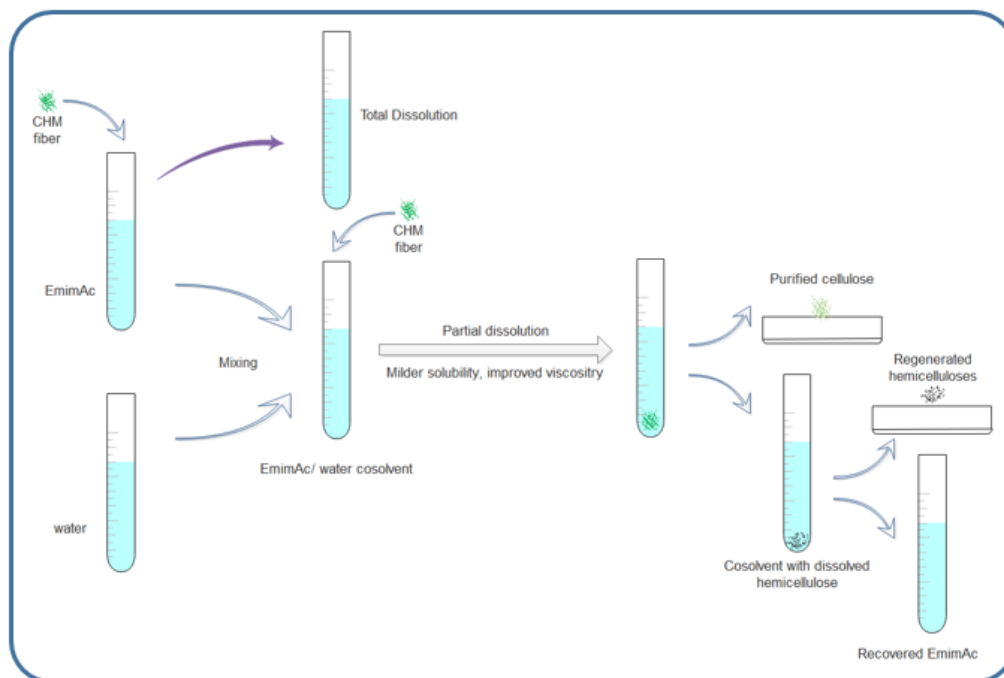


Fig. 4. 1 The schematic of water-tuned EmimAc as a solvent to selectively dissolve hemicelluloses from cellulose/hemicellulose matrix

#### 4.3.1 Water-EmimAc mixtures on fibre swelling

Cellulosic fibres are insoluble in water because of the strong intra- and inter-molecular hydrogen bonding in the cellulose/hemicelluloses matrix. Many studies focus on improving swelling and dissolution of cellulose. Fibre swelling occurs when swelling agent (solvent) travels through a system of pores and the fibre lumen in plant cell wall, which leads to a small degree of hydrogen bonds breakage in the cellulose matrix.

Cellulose is difficult to dissolve because of a tight array of inter- and intra- hydrogen bonds. For this reason, cellulose needs to be “activated” or “accessible” for dissolving by swelling cellulose matrix first. There are 5 different modes when fibre is placed in

solvents, from fast dissolution (mode 1) to no swelling or no dissolution at all (mode 5) as described in Cuissinat's series of papers [14-17].

Herein, the swelling behaviours of fibres in the solvent mixtures were studied prior to performing a hemicelluloses extraction process. Cellulosic fibres were soaked in solvent mixtures of water and EmimAc of different ratios until they were swollen (Fig. 4.2).

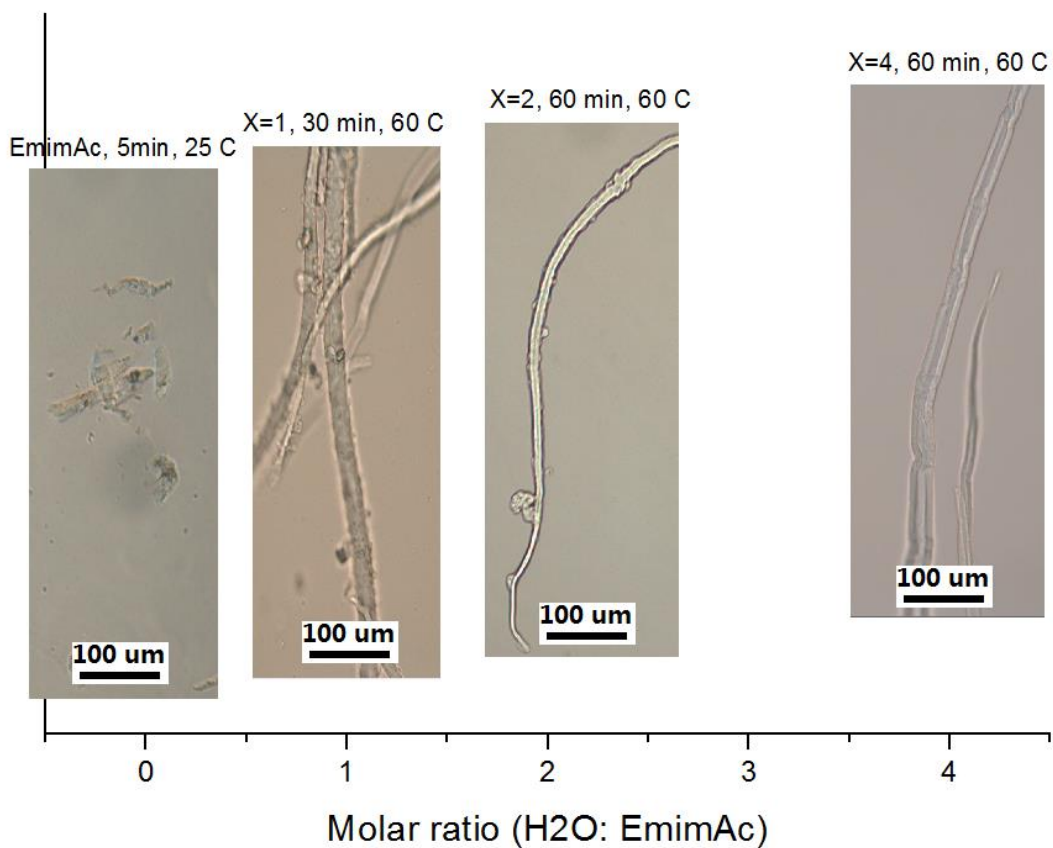


Fig. 4. 2 Dissolution and swelling of fibres in IL/water mixtures (optical microscopy in transmitted light)

The HBKP fibres were soaked in IL/water mixtures with increasing water to IL molar

ratio to investigate the effect of water in the mixtures. As shown in Fig. 4.2, pure EmimAc could dissolve a large part of the HBKP fibres in 5 minutes at ambient temperature, leaving fractions of fibres in the solution. No bubbles indicative of fibre swelling were observed as the dissolution process was thorough and fast. With prolonged dissolution time (more than 30 min), the fibres were totally dissolved in EmimAc, which resulted in a homogeneous cellulose solution. When one mole of EmimAc was mixed with one mole of water, the mixture could not dissolve the main trunk of the fibre, only the fragments attached to the surface of the fibre were swollen and dissolved after 30 mins at 60°C. When the molar ratio of water to EmimAc increased to 2, the whole fibre was swollen at 60°C after 1 hour, and some bubbles could be observed along the fibre. When the water ratio increased to 4, within the experiment period and temperature, the fibre in the mixture was well swollen with increased width (up to 10%), but no dissolution (bubbles or fragments) could be seen, which is defined as mode 3 by Cuissinat[14]. The results demonstrated that pure EmimAc has good solubility of cellulose fibres even at room temperature, which is much lower than previously reported EmimAc can dissolve cellulose fibres, MCC [18] or Eucalyptus pulp [19], at a temperature range of 85-110°C. Water was a strong anti-solvent which decreases the dissolution of cellulose in the ionic liquid at 1:1 molar ratio. This was supported by Swatloski et al. [7], as in his observation, even 1wt% of water (that is about 0.1 mole of water added to 1 mole of BmimCl, X=0.1) could sufficiently prevent biopolymer dissolution in BmimCl.

From the above observation, it is concluded that the solubility of the mixture may be tuned to just dissolve hemicelluloses in the matrix, leading to the production of purified cellulose. Based on observation, the WE2, and WE4 were used as the starting point, because in these conditions cellulose is not dissolved. Other parameters such as the mass transfer properties of the cosolvents were considered in the optimization of extracting conditions.

#### **4.3.2 Effects of water on mass transfer properties of mixtures**

An disadvantage of ionic liquids is their relatively high viscosities, which causes processing difficulties during the dissolution process. Decreasing Ionic liquid viscosities will facilitate their use for various applications [20].

In this study the viscosity of the solvent mixtures were investigated. The viscosities of solvents with soaked/dissolved cellulose in them were not explored because the viscosity is likely to be influenced by the amount of polymer and the molecular weight of the polymers dissolved in the agents, as well as the undissolved solid materials. As seen in Fig. 4.3, water has very low viscosity, while EmimAc is quite viscous with an original viscosity of 33 mPa·s at room temperature. With the addition of water into ionic liquid, the viscosity of the mixture decreased. When the molar ratio of water to EmimAc was 1:1, the viscosity of the mixture decreased from 33 mPa·s to 15 mPa·s, a 55% drop. At higher ratios of 2:1 and 4:1, it continued to decrease to 10 mPa·s and 5 mPa·s respectively. The viscosity decline improves the mobility of the ions, facilitating their penetration into pores and lumens of the fibres during the dissolution process.

Furthermore, water molecules may interact with the cations and anions of EmimAc, which would, in turn, decrease the dissolution ability of the system.

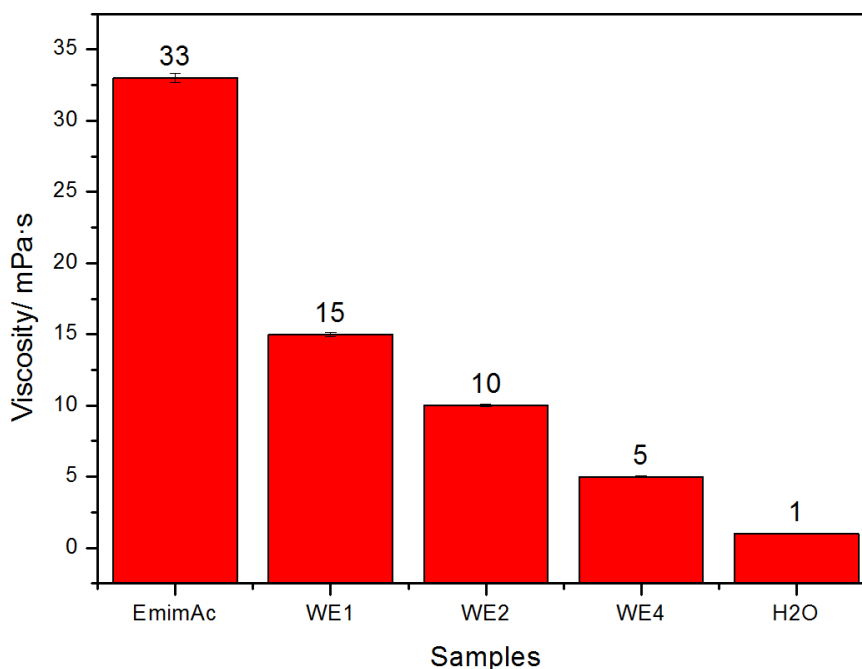
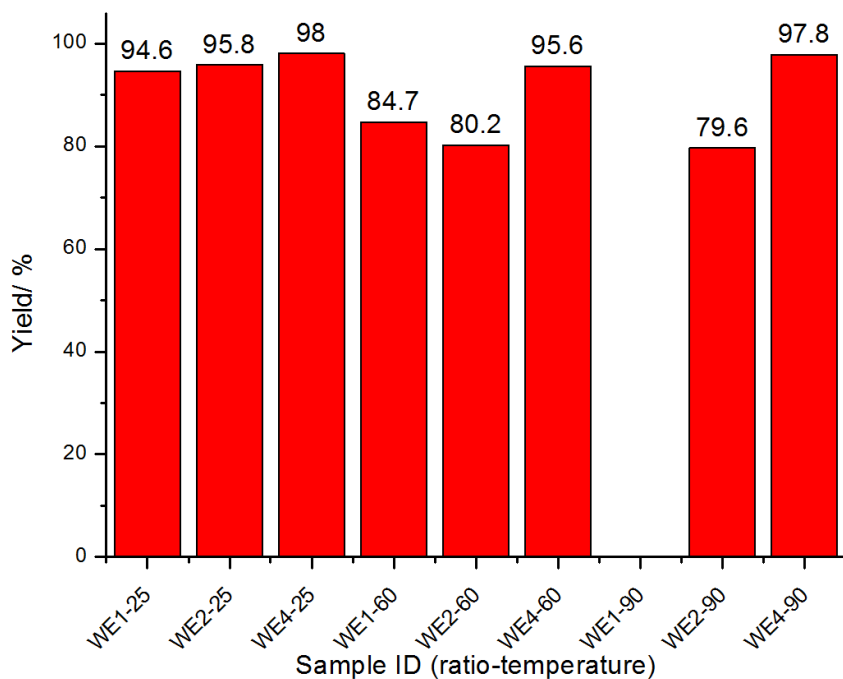


Fig. 4. 3 Solvents viscosity of binary mixture solvents with various water molar ratios at room temperature

#### 4.3.3 Role of water in the selective dissolution of hemicelluloses

The WE mixtures were pre-screened based on their performance in fibre swelling and mass transfer parameters; then they were used as a medium to extract hemicelluloses from the CHM selectively. The yields of the solid phase extracted by WE mixtures were highly influenced by the molar ratio of the cosolvents and the extraction temperature, as revealed in Fig. 4.4 (a). At 90°C, the yields of all treatments were lower than at the other two temperatures (25°C and 60°C), especially the WE1 trial (1-90), where no solid

residue was obtained. Some transparent gel was present, but the others were dissolved. All the WE4 trials (4-25, 4-60, 4-90 in Fig.4.4 a) showed very high yields above 95%, indicating a water molar ratio of 4 is too high for our purpose. Similar yield results were obtained from all trials at 25°C (1-25, 2-25, and 4-25). Thus, 25°C is not high enough to be used to separate hemicelluloses from cellulose using the solvent mixtures in this study. WE1 at 60°C (1-60), WE2 at 60°C (2-60) and 90°C (2-90) showed reasonable yields, indicating that a large proportion of hemicellulose was removed, which was supported by the sugar composition analysis results in Fig. 4.4 (b). The cellulose purities of the three trials (1-60, 2-60, and 2-90) were 89.7 %, 92.2%, and 93.1% respectively. While at the same time, only 6.6-6.9% of cellulose was dissolved. The high selectivity of hemicelluloses dissolution was attributed to the optimum dissolution ability of the solvent mixtures.



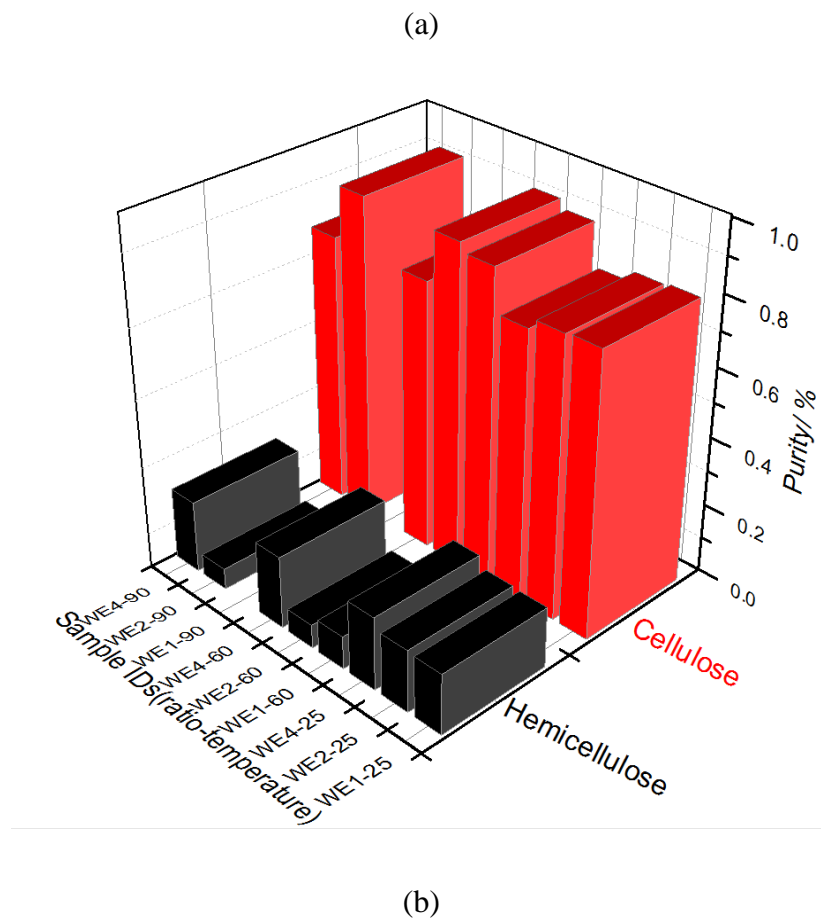


Fig. 4. 4 (a) yield of the solid phase extracted by water/EmimAc mixtures; (b) cellulose (red) and hemicelluloses (black) contents in the extracted matrix

The mass balance of WE2 mixture extraction at 60°C is shown in Fig 4.5. The CHM fibres were separated to a cellulose-rich solid fraction and a hemicellulose-rich liquor fraction. A mass balance of 94.9% was reached for these two fractions. Specifically, the yield of the cellulose-rich fraction was 78.0%, containing 92.2% of cellulose and 7.8% hemicelluloses; the yield of the hemicellulose-rich fraction was 16.9%, with 73.4% hemicelluloses and 26.6% cellulose in it. About 96.5% (76.4g in the two fractions out of

79.2 g in CHM) of the cellulose content and 88.9% of the hemicelluloses content (18.5 g out of 20.8 g) in the CHM were identified in the mass balance.

These results indicated that further degradation products, such as furfural, were small with ionic liquid under the conditions tested. In contrast, in an acid-catalyzed separation process, the recovery of components, especially that of the hemicelluloses, was usually lower than 80% [21], due to the formation of dehydration products, such as furfural, under these conditions.

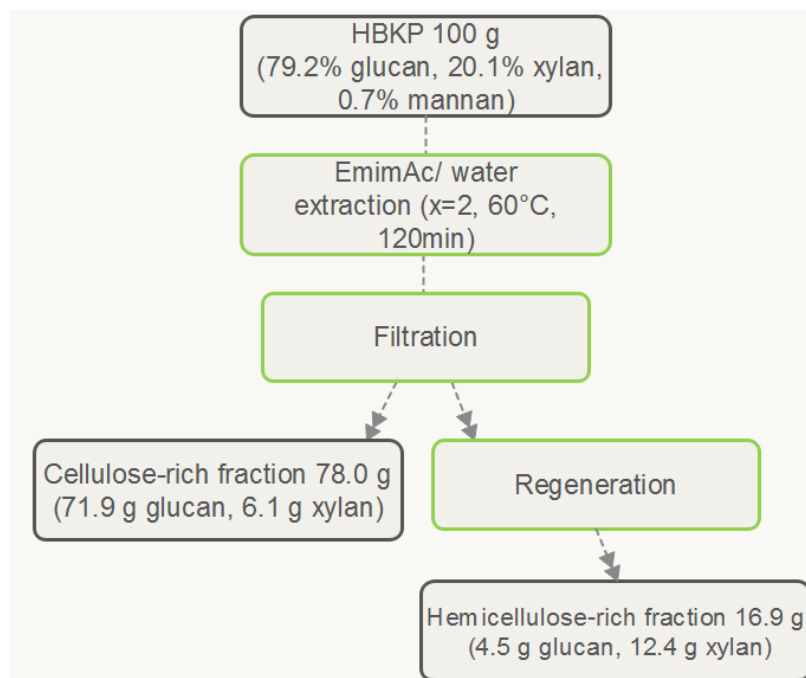


Fig. 4. 5 Mass balance of cellulose and hemicellulose in the EmimAc/water extraction process (x=2, 60°C, 120 min)

#### 4.3.4 Crystallinity index (CrI) of a cellulose-rich solid fraction

Cellulose exists in several forms in plant cell walls, including amorphous (non-

crystalline) cellulose and crystalline cellulose (cellulose I). Cellulose I is thought to be in a parallel arrangement. [22,23] When it is dissolved and recrystallized, it adopts a new crystalline structure with the cellulose chains in an anti-parallel arrangement, and this new crystal structure cellulose is called cellulose II [24,25]. The anti-parallel arrangement is more thermodynamically favourable than parallel arrangement, and extensive inter-molecule hydrogen bonding makes cellulose II a very compact structure. As a result, cellulose II exhibits a reduced reactivity when it is used as dissolving pulp [26].

In this part, the crystalline structure of the purified cellulose was analyzed using X-ray Diffraction method (XRD), and the results were shown in Fig. 4.6. The crystalline index of the untreated CHM is 76%, the samples treated at 25°C had very similar CrIs for cellulose I like the original CHM, and the diffraction patterns were nearly identical, indicating negligible changes in the crystal structure of these samples. The sample treated by WE1 at 60°C showed a much lower CrI for cellulose I (63.6%) than the others, and a CrI for cellulose II was calculated as 11.7%, indicating that part of the cellulose I was transformed to cellulose II due to the strong swelling effect of the solvent mixture for the crystal regions and the dissolution of the amorphous regions. The WE2-90 treated CHM exhibited high cellulose I CrI, which is reasonable since the dissolution of amorphous regions could result in a higher CrI. The result of WE2-60 was interesting, as it had a CrI very different from WE1-60, likely caused by the weaker dissolution ability of the mixture that can only dissolve the amorphous region while leaving the crystal

region untouched. The crystal structure analysis revealed that a water molar ratio beyond 2 is favourable to maintain the original crystal structure of the CHM, considering the yields and cellulose purities of the treated CHM, WE2 (at 60°C and 90°C) is suitable.

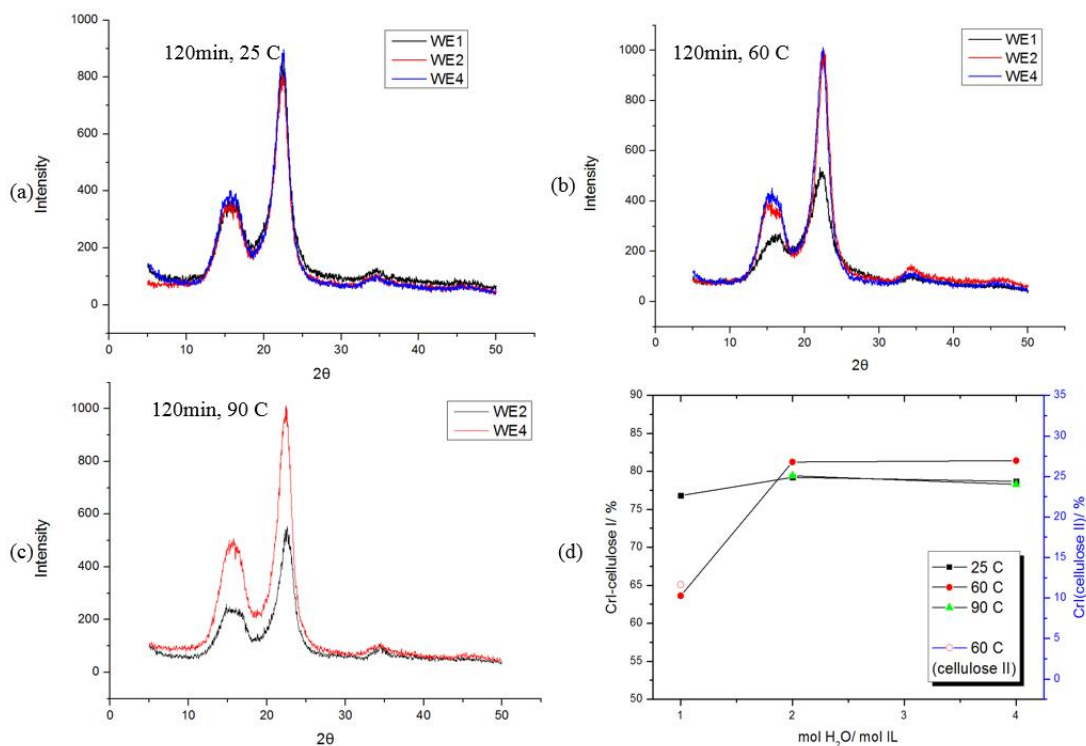


Fig. 4. 6 XRD (a, b, c) and crystalline index (d) of CHM extracted by water/EmimAc mixtures: solid symbols represent the CrI for cellulose I (left Y-axis), hollow symbols represent the CrI for cellulose II (right Y-axis).

#### 4.4 Conclusions

EmimAc and water mixtures extraction demonstrated to be a viable technology for selective removal of hemicelluloses from CHM to produce purified cellulose, with high yield and efficiency. Different operation parameters, such as water molar ratios and

extraction temperature were evaluated in this study. Cellulose purity increased with extraction temperature and ionic liquid content in the mixture. In contrary, purified cellulose yield and cellulose I content decreased with higher temperature and ionic liquid content. At those operating conditions, a more efficient extraction with high yield (78 wt%) and purity (92.2 wt%) of cellulose was obtained when a molar ratio of water to EmimAc of 2 (WE2) was used at 60°C, with a CrI of cellulose I over 80%.

The results presented in this study are the basis to develop more efficient and green separation processes to upgrade paper grade pulp to high-purity cellulose. This research demonstrates the effectiveness of water and EmimAc mixtures and its advantage to recover most of the hemicelluloses that were separated.

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## **CHAPTER 5**

### **SELECTIVE DISSOLUTION OF HEMICELLULOSES FROM CELLULOSE/HEMICELLULOSES MATRIX USING IONIC LIQUID/GVL AND IONIC LIQUID/GVL/WATER MIXTURES**

## 5.1 Introduction

Cellulosic fibres, the most abundant natural resource in the world, have been used in many areas of our life due to their advantages; they are renewable and green, biodegradable, environment-friendly, and have good mechanical strength. The mechanical strength of cellulosic fibres comes from the abundant hydrogen bond in and between the cellulose molecular chains. These hydrogen bonds are the main barrier that keeps cellulose fibres from dissolving in ordinary solvents such as water or ethanol. Therefore, research efforts have focused on the development of efficient and green solvents to facilitate dissolution and processing cellulosic fibres.

The current industrial process mostly used to dissolve and process cellulose is the viscose process, unfavourable because of environmental issues [1]. Ever since Swatloski et al. [2] reported that ionic liquids could dissolve cellulose efficiently in 2002, a lot of different ionic liquids have been tested for this task [3]. A number of them showing good potential, especially the imidazolium ionic liquids [4], have been extensively researched. Ionic liquids are usually highly viscous [2,3], with the addition of high molecular weight (MW) cellulose, will make the solution even more viscous. Therefore, the amount of cellulose dissolved in this ionic liquid would be limited, not to mention the troubles that would surface in the following transferring and processing operations.

To decrease the viscosity of the ionic liquid, operating at elevated temperatures is a promising method as it has been demonstrated by Nazet et al. [5] that the dynamic viscosities of investigated ionic liquids such as EmimAc, EmimFAP, and BmimBETI

would decrease from hundreds of mPa·s at 273K to 30-50 mPa·s at 523K. However, some ionic liquids are not as stable at higher temperatures, which would cause a problem in the application and recycle process [6]. Another option to decrease the viscosity of ionic liquids is to add cosolvents into them without sacrificing the desired ability of cellulose dissolution. From the view of environmental impact and operation cost, this method is even more attractive. For the specific purpose of removing hemicelluloses from a cellulose/hemicelluloses matrix (CHM), a cosolvent such as water that will affect the dissolving ability, is desirable, because of the tunable dissolution ability of the binary system, as demonstrated in chapter 4. Another group of organic, polar cosolvents, can be added into ionic liquids, forming the organic electrolyte solutions (OES). These OES have several advantages compared with simple ionic liquids, including rapid or instantaneous cellulose dissolution (at proper mixing ratios), reduced viscosity, and tunable physicochemical properties [7-10].

This paper reports a novel method of separating hemicelluloses from cellulose/hemicelluloses matrix for upgrading paper grade pulp to high purity cellulose, together with a hemicellulose-rich fraction was reported. The solvent system is a new OES system, which consists of an ionic liquid that can dissolve cellulose and a polar, organic solvent. In this case, EmimAc was chosen as the IL, because it is a good cellulose solvent [11,12].  $\gamma$ -valerolactone (GVL) is also an aprotic, strongly polar (with a  $\mu = 4.71$  D) organic solvent with a high boiling point (at 208°C) and good thermal stability [13]. GVL is a green organic solvent, which can be found in fruits and is used

as flavour additives in the food industry. More preferably, GVL can be synthesized from both glucose and xylose [14], which opens the possibility of transferring the separated hemicelluloses into GVL and making this method a closed loop. The mixtures of GVL and EmimAc show an upper critical solution temperature (HCST) type phase transition property, which facilitates the recycling of IL and GVL after use with thermo-responsive phase separation. When the fractionation was finished at the set temperature, the solvent mixtures were cooled to room temperature, the IL and GVL molecules were separated from each other by forming two liquid phases.

The physical properties of the OES solutions were studied, and cellulosic fibres were soaked and swelled in the mixtures to determine a suitable ratio of the two components for the purpose of selectively dissolving hemicelluloses from the CHM. The performance of the OES solutions was investigated in CHM fractionation; the resultant cellulose-rich fraction was characterized. Based on the outcomes of this study, a facile and green concept involving the use of a novel OES system was developed, which provides a practical process of upgrading paper grade pulp to high purity cellulose and a possible closed-loop process that the consumed GVL could be replenished by the GVL converted from the separated hemicelluloses in the previous step. The application of an IL/GVL/water ternary system (IGW) was also investigated for the same purpose of purifying CHM to high purity cellulose.

## **5.2 Materials and methods**

### **5.2.1 Materials**

Bleached hardwood kraft pulp (HBKP) was used as the cellulose/hemicelluloses matrix (CHM) in this paper, and it was generously provided by a pulp mill located in Eastern Canada. The pulp was produced from a blend of wood species: 58.0% maple, 13.0% birch, 8.0% poplar, and 21.0% other. The analytical compositions of HBKP by Ion Chromatography is 79.2% glucan, 20.1% xylan, and 0.7% mannan. The pulp board was first treated using a fluffer contactor (developed by Pulp and Paper Research institute of Canada, 1975) to break its compact board structure and make it more accessible in the consequential fractionation process.

GVL was supplied by Sigma Aldrich with  $\geq 98$  wt% purity. Pure water was obtained from a Millipore Synergy® UV purification system (water resistivity of 18.2 M $\Omega$  cm). 1-ethyl-3-methylimidazolium acetate (EmimAc), purchased from Sigma Aldrich with a purity of 95%, was used as received without further purification.

### **5.2.2 Methods**

#### **5.2.2.1 Viscosity and conductivity**

The viscosity of the solvent mixtures was determined using a Brookfield digital viscometer equipped with a programmable temperature controller. The conductivity of the solvent mixtures was determined using a symphony H10C with an MP5 Pt conductivity electrode. The conductivity of the solvent mixtures with different molar

fractions was measured at room temperature using an H10C Symphony™ handheld meter (VWR, Radnor, PA, USA), calibrated using KCl standard solutions at various concentrations. The accuracy of the Symphony handheld meter is  $\pm 0.5\%$ . The average value from three measurements was reported.

### **5.2.2.2 Swelling and observation**

CHM was treated with a fluffer contactor, and the fibres were soaked in OES and GVL/IL/Water ternary systems. The CHM fibre morphology was observed using an optical microscope (Leica DM4000 M) equipped with a digital camera (Leica DFC480).

### **5.2.2.3 CHM fractionation using OES and IGW ternary system**

Bleached kraft hardwood pulp fibres were used as CHM in this paper. The fibres were first treated by a fluffer contactor and conditioned to constant moisture. Then, the fibres were treated by OES solutions and GIW solutions with a series of ratios. Different molar ratios of GVL (e.g. 1, 4, 8, and 12 moles of GVL to 1 mole of EmimAc, were marked as GE1, GE4, GE8, and GE12 respectively) were added to 4 g of EmimAc. A 5 wt% HBKP (based on EmimAc) was dispersed into the solvent mixtures before they were transferred to a 20 mL (or 100 mL as needed) glass vial. Solubility tests were conducted in an oil bath set to specific temperatures. Once the test was finished, the sample was filtered using a 2-layer 400 mesh stainless steel film. The samples were washed with the same amount of solvent mixtures with the same ingredient and same temperature. The extraction conditions were set at temperatures of 25°C, 60°C, and 90°C, with an extraction time of 120 mins.

For experiments with IGW solutions, all operation parameters were the same except for the ingredient of the solution that is used. The ratios of IL, GVL, and water varied from 1:1:1 to 1:4:4.

#### **5.2.2.4 Fock reactivity test**

Cellulose-rich samples were air-dried from a wet state to equilibrium in a 50% RH, 23°C atmosphere. The cellulose xanthation was performed in a water bath at 19°C; all operations of Fock reactivity followed the instruction in the modified method reported by Tian et al. [15].

#### **5.2.2.5 Intrinsic viscosity**

The intrinsic viscosity of all purified cellulose samples was measured according to the TAPPI standard T230 om-99 using 50% copperethylenediamine (CED) solution as the solvent. All measurements were carried out two times and the average value was reported.

#### **5.2.2.6 Sugar Analysis**

The sugar contents in the HBKP and the treated solids were determined by using an ion chromatography unit equipped with CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD). The samples were first hydrolyzed in 72% SA, with an acid-to-material ratio of 20 mL g<sup>-1</sup>, at 30± 1°C, for 60 minutes. The hydrolyzed suspension was then subjected to second hydrolysis in 4% SA, by adding deionized water to dilute 72% SA to 4%, at 121± 1°C in an autoclave, for

60 minutes. Above operations are following the 2-step hydrolysis method described in the NREL/TP-510-42618 standard [16]. The samples were diluted prior to analysis to about 20 ppm, which was a concentration close to the standard sugar samples. Then, 5 mL of the above-prepared samples were filtered and added to plastic vials, and the analyses were carried out by using the ion chromatography.

## 5.3 Results and Discussion

### 5.3.1 Physicochemical properties of OES

The idea of OES is to gain a synergistic effect from the two components: non-cellulose dissolving organic solvent and cellulose-dissolving ionic liquid. The mixture of the two will obtain better cellulose solubility than pure ionic liquid, with less ionic liquid being used. Although selectively dissolving hemicellulose from CHM is different from dissolving cellulose, better cellulose dissolving ability means less ionic liquid used from an economic view and more freedom in manipulating the solubility from a technical view. To examine the effects of GVL addition on the physicochemical properties of the mixture, viscosity and conductivity were measured at different mixing ratios of the two components.

As shown in Fig. 5.1, the viscosity of pure EmimAc at 60°C is 33.0 mPa·s, and viscosity of GVL is 0.5 mPa·s. The viscosity of 1 mole of GVL/1 mole of the EmimAc mixture is 11.0 mPa·s. As more GVL was added to EmimAc (8 moles of GVL), the viscosity of the OES solutions continued to decrease, such that the viscosity was very close to pure GVL. From the view of the volume of the mixture, since their densities were close to each other (GVL is 1.05 g/mL, and EmimAc is 1.1 g/mL at 25°C), about 5 units of GVL was added into 1 unit of EmimAc. The conductivity is another parameter that indicates the improvement in mass transfer properties that are often used in solvent characterization [17]. The conductivity of pure EmimAc at 60°C was 6.55 mS/cm. With a mole of GVL added into EmimAc, the conductivity of the OES increased by about 55% to 10.12

mS/cm, this is in agreement with the observations of Cheng et al. on the addition of DMSO as a component in OES [17]. However, with more GVL being added into EmimAc, the conductivity decreased to 6.20 mS/cm at 4 moles of GVL addition and further to 4.30 mS/cm when 8 moles of GVL was added. The decrease of conductivity indicated that the dissolving ability of the OES for hemicelluloses would decrease when there is more GVL in the OES system. At the same time, the viscosity of the system decreased continuously, the trend of solubility became difficult to predict at this point. The dissolving capability of OES was improved when a small amount of GVL was added, such as the GE1 mixture, as both of the two properties, viscosity and conductivity were favourable.

By changing the proportion of GVL in the OES solutions, the solubility could be tuned to separate hemicelluloses from the CHM (Fig. 5.1). The CHM fibres were treated with optimized OES solutions, then the solid was filtrated and washed to produce purified cellulose. The dissolved hemicelluloses in the OES can be precipitated out by adding more GVL.

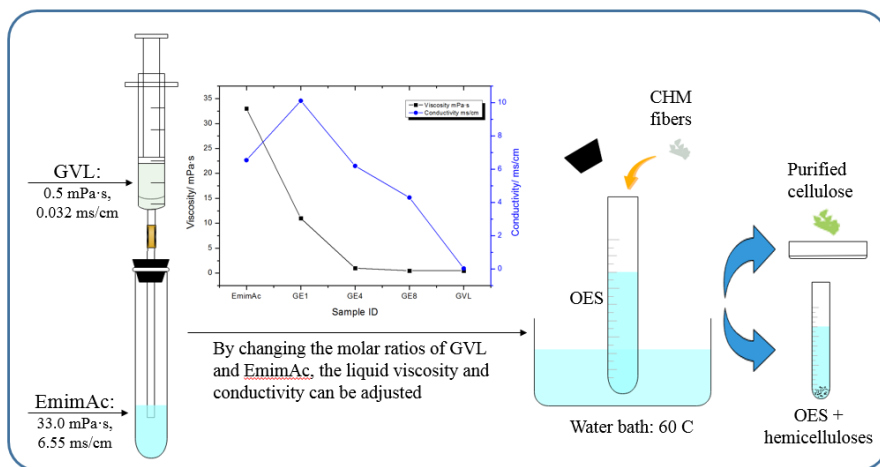


Fig. 5. 1 Schematic of OES fractionation of CHM

### 5.3.2 Swelling of CHM fibres

Cellulosic fibres are insoluble in water and common organic solvents like ethanol, acetone, and DMSO, because of strong intra- and inter-molecular hydrogen bonds in the cellulose fibre wall structure. These hydrogen bonds must be cleaved in a swelling or dissolving process before using the fibres for an industrial purpose.

The swelling behaviours of fibres in the solvent mixtures were studied prior to performing a hemicelluloses extraction process in order to select optimal solvent mixtures for selective dissolution of hemicelluloses from lignin-free cellulose/hemicelluloses matrix. As shown in Fig. 5.2, the solvent mixtures of GVL/EmimAc had strong swelling abilities and solubility of fibres. For GE1 mixture (X=1), the fibres could be dissolved in 5 minutes at room temperature, the dissolution process was thorough and fast, which could be fitted into a Mode 1 dissolution as defined by Cuissinat [18-21]. The fibres in GE4 were extensively swelled by forming

large balloons along the fibres in 6 mins at 60°C. The fibre tissue in the balloons was dissolved as seen in the picture, which is a Mode 2. While the fibres in GE8 were swelled, but no apparent dissolution could be observed, which is a Mode 3. The GE12 mixtures only swelled the whole fibre to a slightly bigger width, no balloons could be seen after 120 min of treatment at 60°C (Mode 4). The observation of swelling and dissolution of fibres in the mixtures confirmed that the OES solutions can have stronger dissolution ability than EmimAc. As in our observation, EmimAc only dissolved fibres into fragments whereas at the same temperature and time, the GE1 solution dissolved the fibres completely. Other researchers reported that EmimAc can only dissolve cellulose fibres, MCC [22] or Eucalyptus pulp [23], at a higher temperature range of 85-110°C. As the GVL content in the mixture continued to increase ( $X > 1$ ), the swelling and dissolution abilities started to decrease. The series of results from GVL/EmimAc mixtures exhibited the typical behaviour of an aprotic organic solvent that can enhance the solubility of an ionic liquid when it is added at a wide proportion. With an appropriate amount of organic solvent added to the ionic liquid, in this case, is 1-4 moles of GVL to 1 mole of EmimAc, the mobility of the ionic liquid improved. As the concentration of aprotic solvent exceeds a specific amount, the mobility of ions from IL continue to increase, but the organic solvent molecules tend to compete with ionic liquid ions for the sites of hydrogen bonding, reducing the solubility of the mixture.

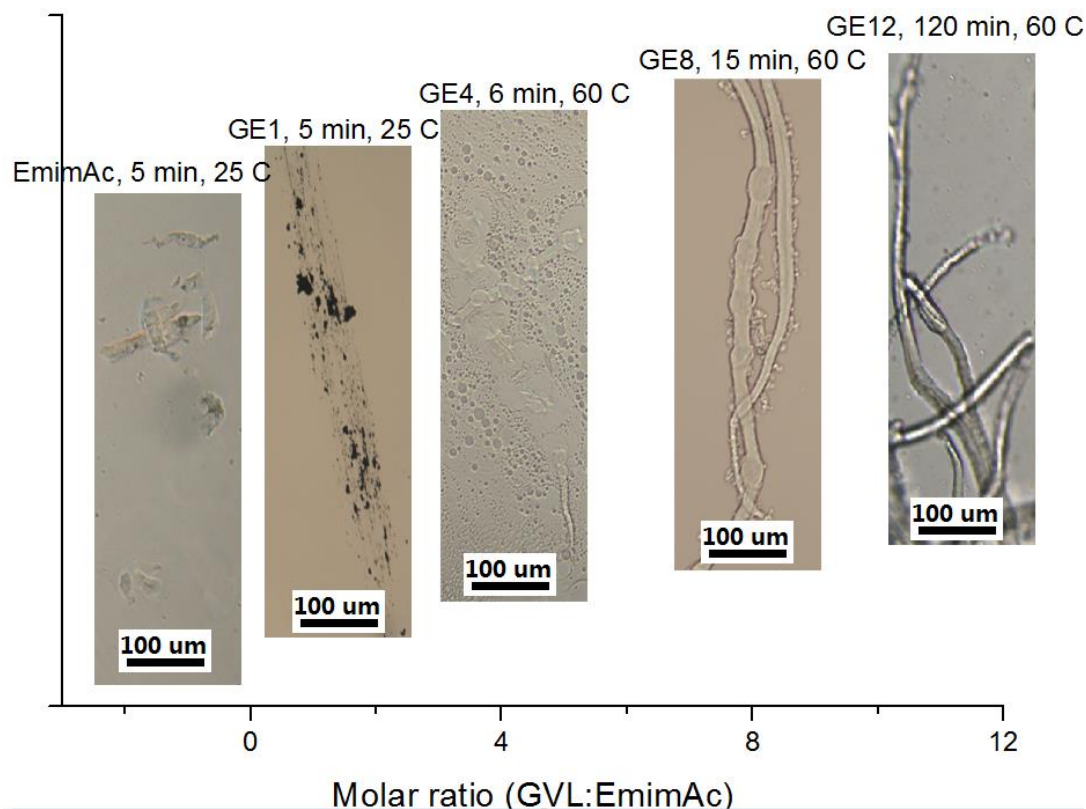


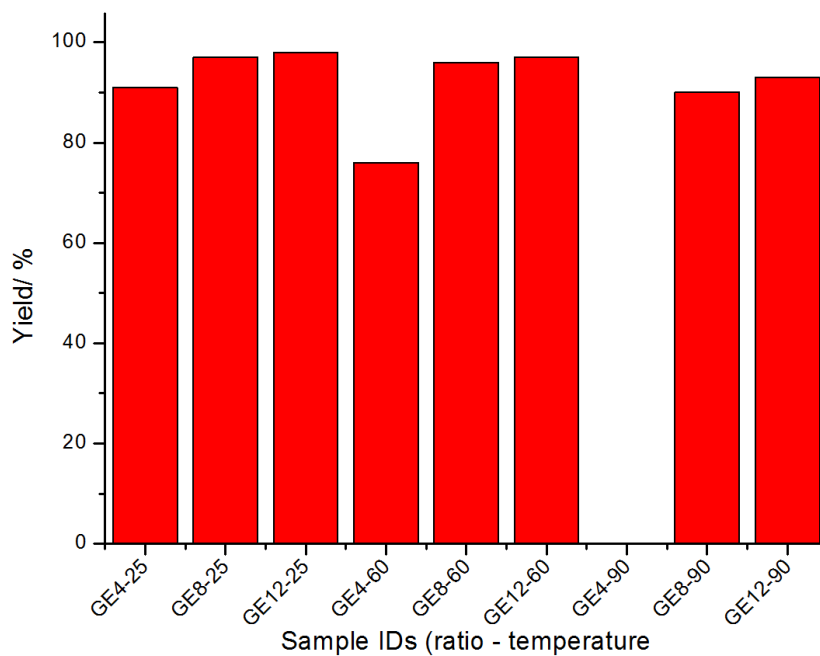
Fig. 5. 2 Swelling of CHM fibres in OES

Based on the swelling and dissolution situation of fibres in the OES mixtures (Fig. 5.2), the conclusion is that the dissolution capability of the OES solutions varies from very strong to weak depending on the cosolvent and its molar fraction in the mixtures. Therefore, it is possible that with a suitable molar fraction of GVL in EmimAc, the suitability of the OES for hemicelluloses removal could be tuned so that purified cellulose can be produced as a product. Furthermore, the GE4 and GE8 are better OES systems for selective removal of hemicelluloses from CHM.

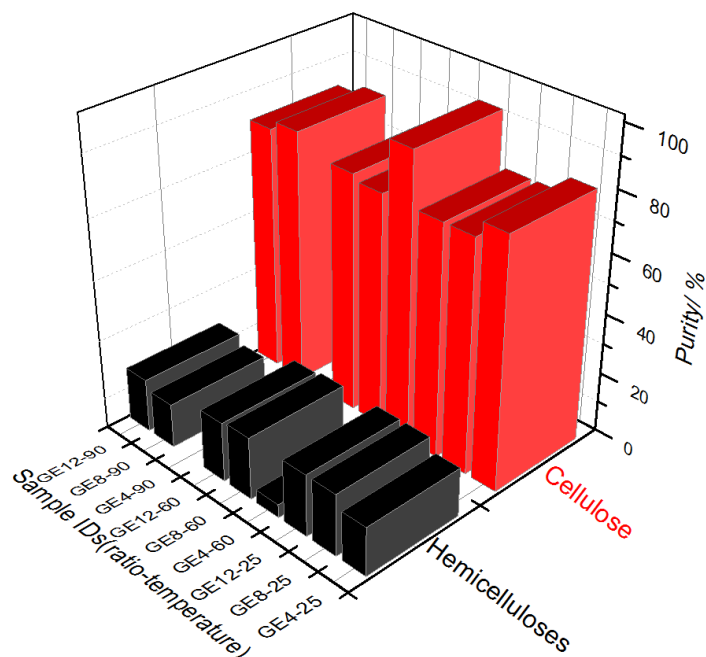
### 5.3.3 Purified cellulose analysis

The GE1 solution was too strong to be used in the selective extraction of hemicelluloses from the swelling results as it would dissolve the CHM with both cellulose and hemicellulose. The results from GE4, GE8, and GE12 OES systems are shown in Fig. 5.3. GE8 and GE12 are not effective in removing hemicelluloses at room temperature, while at higher temperatures, they were much more effective (Fig.5.3 a and b). The GE8 and GE12 solutions were not able to dissolve hemicellulose as effectively under experimental conditions, especially lower temperatures, and this resulted in a method of regeneration of the dissolved hemicellulose from the extraction liquor, which is done by adding more GVL into GE4 to boost its GVL content to the level of GE8 or even GE12. The solid phase of GE4 at 90°C could not be collected because the transparent gel-like solid phase, induced by the large dissolution of CHM, was too soft to collect. All the trials had a yield higher than 90% except GE4-60 and perhaps, GE4-90. Within experiment ratios used, At 25°C, none of the GE systems were effective in removing hemicelluloses from CHM. This is evident by the more than 90% solid remainders after extraction (Fig. 5.3 a and b), as in CHM hemicelluloses constitute 21% weight. At 90°C, neither GE8 or GE12 was effective, because the solid yield remained above 80%. The solid yield for GE4 at 90°C could not be determined, as the solid under this condition formed gel, which unable to separate. At 60°C, only GE4 was able to effectively extract hemicellulose, and achieve a solid yield of 76%. It was concluded that a molar ratio beyond 8 is not applicable in this task, the temperature was also important as at 25°C the yield was 91% when it was increased to 60°C and 90°C, a 76% and even lower yield could be reached. When GVL is added into EmimAc, it works as a cosolvent to facilitate

the dissolution ability (see swelling performance of GE1). However, when the molar ratio exceeds a certain point, in this case, 4 to 1, it behaves as an anti-solvent since the dissolution ability was decreased significantly. This behaviour of GVL is in accordance with other polar aprotic organic solvents, DMSO, for example [8, 17].



(a)



(b)

Fig. 5. 3 (a) yield of the solid phase extracted by GVL/EmimAc mixtures; (b) cellulose (red) and hemicelluloses (black) contents in the extracted solids

### 5.3.4 Purified cellulose characteristics

The crystalline structure was first examined to see if the residual cellulose still maintains its cellulose I structure. Then samples with high cellulose content were chosen for more tests, including Fock reactivity tests, molecular weight distribution, and intrinsic viscosity, to evaluate their quality as dissolving pulp.

The X-ray Diffraction method (XRD) results are shown in Fig. 5.4. The crystalline index of the untreated CHM is 76% for cellulose I, the samples treated at 25°C had very similar CrIs for cellulose I compared to the original CHM, and the diffraction patterns

were nearly identical, indicating negligible changes in the crystal structure of these samples. The GVL/EmimAc mixtures exhibited a very strong swelling ability, and most of the crystal structures of the treated CHM were changed, according to the XRD results. For those samples obtained at 25°C, its CrI for cellulose I was 75% and a CrI for cellulose II was 7.3%. For the GE8 and GE12 samples, their CrI for cellulose I was 78%. The treatments at 60°C showed what a strong swelling agent could do to CHM: GE4 showed highest CrI for cellulose I (62.5%) as well as the highest CrI for cellulose II (36%) among all 3 mixtures. While the other two mixtures, GE8 and GE12, showed lower CrI for cellulose I (60.4% and 60.7%) and lower CrI for cellulose II (24.5% and 22%). The treatments at 90°C were an enhanced version of the treatments at 60°C, with a more obvious trend described.

Considering the yields and cellulose purities of the treated CHMs, a GE molar ratio 8 or more will lead to a very limited dissolution ability of the mixture. However, the swelling abilities of the mixtures are not affected. Thus, the GE mixtures are able to disturb the parallel arrangement of the cellulose chains as the aprotic GVL molecules would not impair the ability of EmimAc ion pairs, but the dilution effect of many GVL molecules surrounding an EmimAc ion pair weakens its dissolution ability.

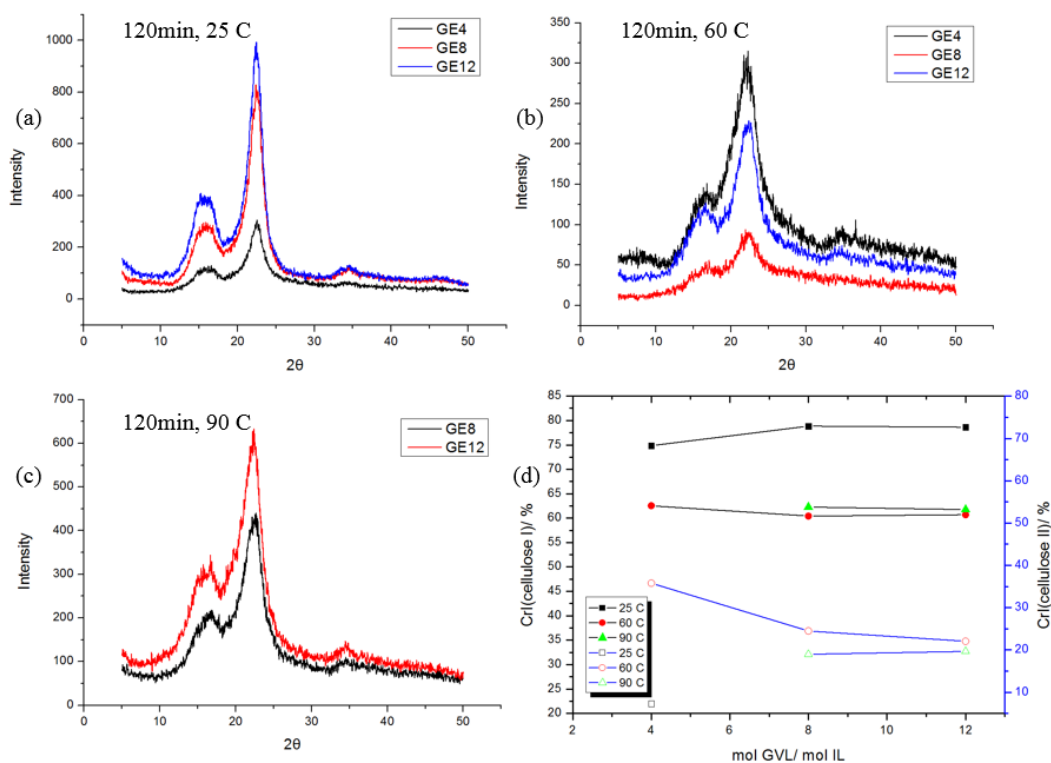


Fig. 5. 4 XRD (a, b, and c) and crystalline index (d) of purified cellulose extracted by GVL/EmimAc mixtures: solid symbols represent the CrI for cellulose I, hollow symbols represent the CrI for cellulose II.

### 5.3.5 Fractionation using IL/GVL/water mixtures

The possibility of using IL/GVL/water ternary system to remove hemicelluloses from the CHM selectively was also explored, and results showed that this IL/GVL/water ternary system was a good substitute for OES. The yields of the solids of the ternary system extraction are listed in Fig. 5.5. The yield of 111 (molar ratio of IL: GVL: water is 1:1:1) was 0 because the pulp fibres dissolved completely into the solution. For the yield of the 114 trial, no fraction of CHM dissolved in the solution. Therefore, for the

rest of the trials, the ratio of water was restricted to 2 or less, and the molar ratio of GVL was restricted to 4 (from previous OES extractions) or less. The 121 trial and the 131 trial showed promising results; with yields at 76.7 wt% and 81.7 wt% respectively, and cellulose purity of 94.8 wt% and 90.6 wt%, and very low hemicellulose contents (5.2 wt% and 9.5 wt%). The cellulose content of all other trials were all above 87.3%.. These results showed that the dissolution capacity of the ternary system decreased as more water and GVL was present in the system, and the addition of 1 water was more powerful than 1 GVL in decreasing the dissolution capacity. The 121 sample has a Fock reactivity of 57.5 %, an intrinsic viscosity of 698 mL/g, and a PDI of 4.1. These properties are close to those properties of PHK dissolving pulps reported by Duan et al [24]. In his work, it is reported that the two hardwood dissolving pulps (C and D) have reactivities between 55% to 68%, intrinsic viscosities close to 600 mL/g, and PDIs between 3.8 and 4.5. The ternary system was able to selectively remove hemicelluloses from CHM and produce dissolving pulp from paper grade pulp.

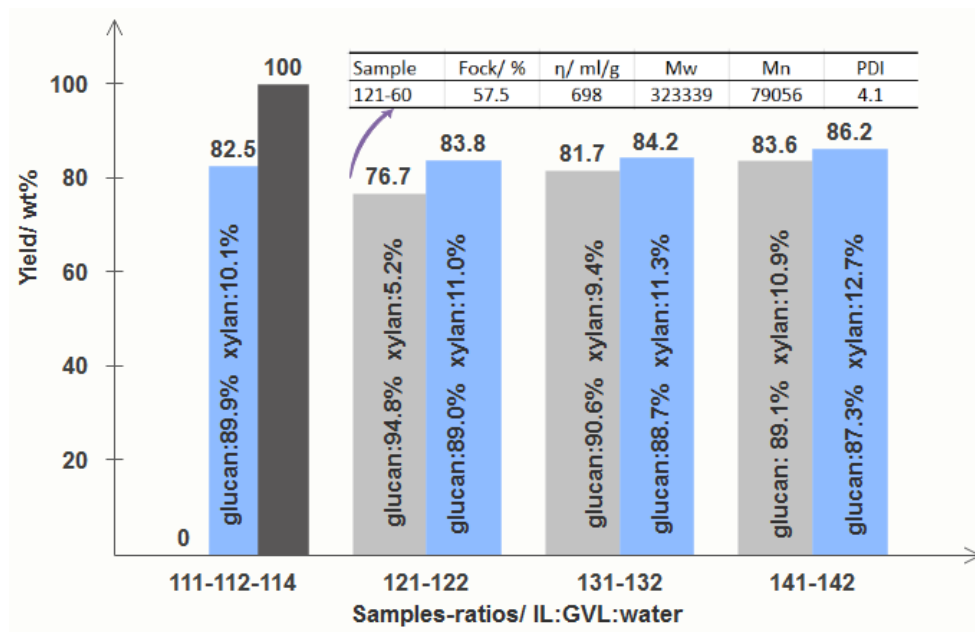


Fig. 5. 5 Yields and properties of IL/GVL/water ternary system extracted CHM (121 refers to the cellulose-rich fraction extracted by ternary solution with a molar ratio of IL:GVL:water=1:2:1)

### 5.3.6 Properties of purified celluloses from all three methods

The Fock reactivity, molecular weight, and intrinsic viscosity of the original CHM fibres, CHM fibres treated under selected conditions with GVL/water, EmimAc/water, EmimAc/GVL, as well as EmimAc/GVL/water are listed below in Table 5.1, for better comparison.

The Fock reactivity of the untreated HBKP was about 56%, and there was no significant difference between the IL/water, and the IL/GVL (OES) treated solids. They had similar reactivities as the original HBKP. However, the GVL/water treated solid had an improved reactivity, which could be attributed to the high processing temperature, and

more importantly, the acidic fractionation condition that introduced acid hydrolysis to the cellulose and hemicellulose chains. This result is in agreement with the intrinsic viscosities of the purified cellulose-rich samples: the GVL/water treated solid had a lower intrinsic viscosity than the other samples, indicating a lower DP of the cellulose molecules in this sample. While all the samples had a similar weight average molecular weights (Mw), the GVL/water treated possessed a wider molecule weight distribution. Duan et al. [24] compared the dissolving pulp made from AS and PHK processes. The dissolving pulp samples made from acidic processes had wider MWD (7.6 to 8.5) than PHK pulps (3.8 to 4.5). It was the same for hardwood and softwood species (one AS pulp was from spruce/maple, the other was from Eucalyptus).

Table 5. 1 Reactivity, intrinsic viscosity, and Mw of cellulose-rich fraction

Sample	Fock/%	Intrinsic viscosity/mL/g	Mw	Mn	PDI	Method
CHM	56.1±0.4	755	326897	74294	4.4	raw material
150-30	71.5±0.9	545	354247	52326	6.8	GVL+water
WE2-90	54.7±0.7	767	363625	84564	4.3	IL+water
GE4-60	56.8±0.2	723	343469	75654	4.5	IL+GVL
121-60	57.5±1.2	698	323339	79056	4.1	IL+GVL+water

Note: 150-30 refers to the GVL/water treated cellulose, WE2-90 was treated by water/IL (ratio 2:1, at 90°C), GE4-60 was treated by GVL/IL (ratio 4:1, at 60°C), 121-60 was treated by IL/GVL/water (ratio 1:2:1, 60°C)

### 5.3.7 Recovery of solvents/overall process

The IL/GVL (with or without water) hemicelluloses removal technology can be readily

implementable in an industrial process, as shown in Fig. 5.6. All the machinery and processing equipment are readily chosen from industry, no specially designed or manufactured devices are needed. Paper grade pulp is disintegrated using OES (IL/GVL) or IL/GVL/water ternary solutions in a hydraulic pulper; it will then be transferred to a cooking tower with temperature control to allow selective removal of hemicelluloses. After extraction, the slurry will go through a separation screw with a gradually smaller pitch between thread foils to separate solid from the extracting liquor. The solid fraction, which is cellulose-rich, will be washed and used as dissolving pulp. The extracting liquor containing dissolved hemicellulose and OES (or OES with water) will be cooled to room temperature, the liquor will be separated by high-speed centrifugation into the GVL layer on the top and EmimAc with hemicellulose (and water) dissolved in it. The GVL phase can be collected and recycled; the EmimAc phase will be sent to another high-speed centrifuge where large amounts of water will be added to precipitated/regenerate the dissolved hemicelluloses. In the second centrifuge, regenerated hemicellulose can be collected, and the leftover EmimAc and water mixture will be separated via a 2-step recovery process which involves a freeze crystallization and an evaporation operation. The separated solid and vapour that form water are collected in a water tank, ready to be used in the whole process again.

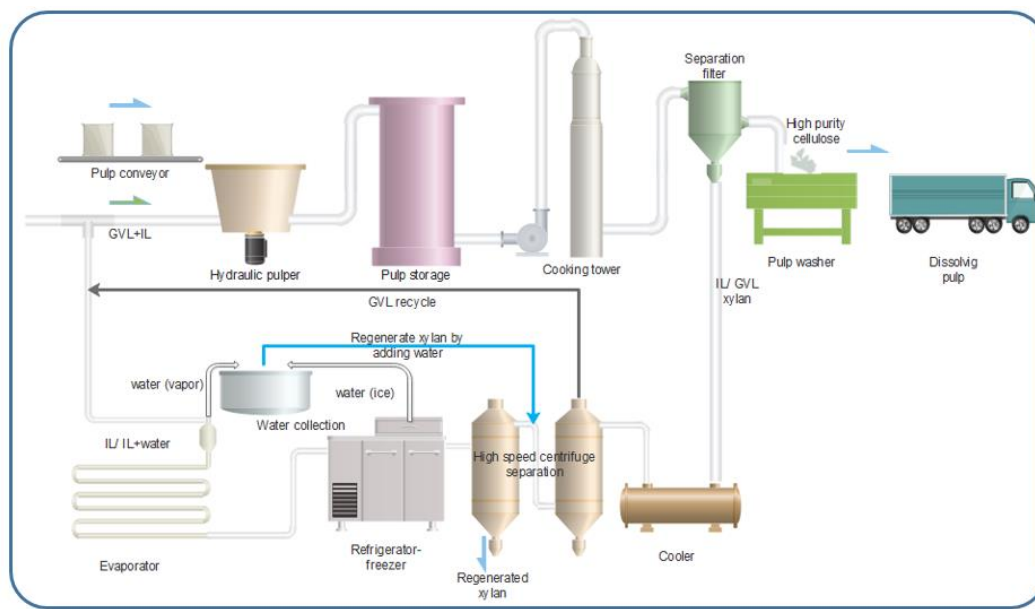


Fig. 5. 6 Industrial application of OES or IL/GVL/water hemicellulose extraction process

Another extracting liquor recovery strategy is to use the thermo-responsive phase separation property of OES. From fractionation results, GE4 and GE8 solutions are miscible as one phase at the extracting temperature (60°C), while GE8 (and OES with a higher GVL content such as GE12) is not strong enough to dissolve either cellulose or hemicellulose. Therefore, a GVL stream that is heated to an operation temperature can be added as a regeneration anti-solvent to the liquor to adjust GE4 to GE8 or OES with an even higher GVL content. Using this method, the dissolved hemicelluloses can be regenerated and recovered. After the collection of hemicelluloses, the resultant OES is cooled down to room temperature (lower than its UCST) to separate the two liquid phases by using a high-speed centrifuge. This is a strategy with less energy consumption

and simpler operation. However, the drawback is that if there is water in the system, evaporation is still needed to recover the ionic liquid.

## 5.4 Conclusions

1 The OES system containing EmimAc and GVL can selectively separate hemicellulose from a CHM with high efficacy. The cellulose-rich fraction could reach a high cellulose content close to 95% with a GVL/EmimAc mixture with a molar ratio of 4:1. A molar ratio of GVL larger than 8 is not able to dissolve hemicellulose, 60°C is a suitable temperature for GE4 as extraction liquor.

2 The cellulose-rich fraction purified by OES solutions had a lower CrI (82% to 62%) for cellulose I, which means there is a disturbance of the original crystalline cellulose I structure. The loose crystalline structure was compromised by the formation of some cellulose II structure (CrI 46% for cellulose II), leading to an overall reactivity similar to the original CHM.

3 The IL/GVL/water ternary system was able to separate hemicelluloses from the CHM as efficiently as the OES system, with water as a controlling constituent. The molar ratio of water should not exceed 2, as well as the ratio of GVL should not exceed 4.

4 The recovery and recycling of the extraction liquor are low-energy consuming and are ready to be applied in industry.



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## **CHAPTER 6**

# **RECOVERY OF GVL AND IONIC LIQUID FROM EXTRACTION LIQUOR OF SELECTIVE DISSOLUTION OF HEMICELLULOSES FROM CELLULOSE/HEMICELLULOSES MATRIX**

## 6.1 Introduction

The pressure of economic development and awareness of environmental issues has led to an increased demand for renewable resources, fuels, and products. Integrated forest biorefining is the most promising concept and technique to address the increasing need for renewable resources. According to the biorefining concept, one of the basic criteria is to make full use of all components of the feedstock. Therefore, the recycling and recovery of GVL, ionic liquid, and sugars from the extraction liquor are critical for producing value-added products and reducing operating costs. This chapter reviews the up-to-date technologies of recovering GVL and ionic liquid (EmimAc as in this project) from spent liquors, then proposes a combination of technologies for the recycling and recovery of all components from the extraction liquor generated by the selective dissolution of hemicelluloses from the cellulose/hemicelluloses matrix.

As in the case of this project, there are four different types of extraction liquors: the water-GVL mixtures (type I), the water-EmimAc mixtures (type II), the GVL-EmimAc mixtures (type III), and the mixtures of all three components (type IV). Different strategies are discussed and proposed for these extraction liquors. In type I liquors, the key is to recover GVL from the mixtures. Based on the end-use design of sugars dissolved in the mixtures that come from the dissolved hemicelluloses, sugars can be recovered together with water and are then transformed to ethanol via a fermentation process, or they can be transformed to GVL with or without being separated from the mixtures first [1-3]. For type II extraction liquors, the main task is to separate the ionic

liquid from the water phase, and distillation is the most straightforward method. Water can be evaporated from the ionic liquid easily because ionic liquids have remarkably low vapour pressures even at elevated temperatures; 3.5 kPa at 80°C [4]. Other methods include extraction, adsorption, membrane separation, crystallization, which will be discussed in detail later in this chapter. The type IV extraction liquors are mixtures of all three components; a combination of extraction and distillation or other processes are necessary to recover GVL and ionic liquid consequently. Excluding the strategies mentioned above, the reuse/recycle of the mixtures is a better choice in industrial applications. For the reuse/recycle purpose, the only treatment that is required is to remove the sugars and part of the water by simple aqueous extraction. A schematic of the reuse/recovery of the extraction liquors is presented below (Fig. 6.1):

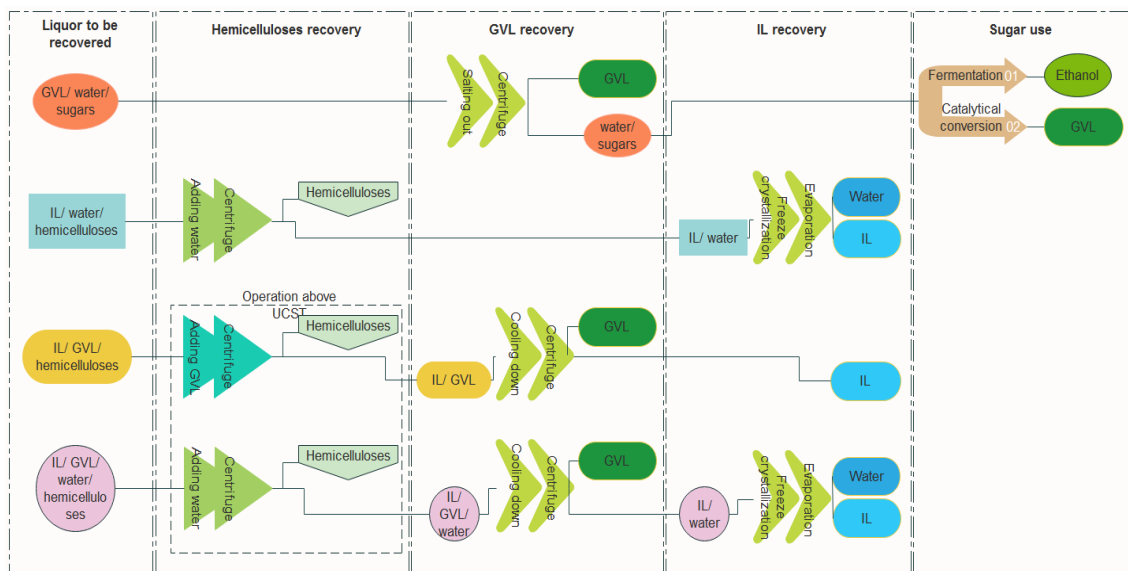


Fig. 6. 1 Schematic of recovery strategies for different extraction liquors

## 6.2 Recovery of hemicelluloses from extraction liquors

Purified cellulose maintained its solid phase. Thus, it is collected from the system by filtration. Hemicelluloses dissolved in the system are first precipitated by adding anti-solvents, such as water, and GVL, and are then collected by centrifuging. The rest of the extraction liquor is then recovered according to the proposed processes in Fig. 6.1.

In the GVL/water/sugars liquors (type I), no hemicelluloses could be precipitated from the liquor since the hemicelluloses were hydrolyzed into mono-sugars or oligosaccharides. GVL can be recovered by salting out. It is a better strategy to convert the sugars to ethanol or other value-added chemicals directly than to separate or recover the sugars from the aqueous solutions.

For the IL/water/hemicelluloses liquors (type II), hemicelluloses were precipitated by adding excessive amounts of water into the system. From chapter 4, when the mole ratio of water to EmimAc was larger than 8, hemicelluloses were not able to dissolve. To recover the hemicelluloses completely, 20 mL of water was added to 20 mL extraction liquor before collecting the precipitated hemicelluloses, and this operation was repeated 3 times. A yield of 16.9 wt % of hemicelluloses based on CHM could be recovered, which accounted for 88.9 wt% of the hemicellulose from CHM.

For the IL/GVL/hemicelluloses liquors (type III), hemicelluloses can be precipitated by adding plentiful GVL into the system. From chapter 5, when the mole ratio of GVL exceeds 8, hemicelluloses can hardly be dissolved. Thus, when the GE4 mixtures were converted GE12 by adding GVL, the hemicelluloses were precipitated. It was noticed that the IL/GVL mixtures exhibit a UCST (upper critical solution temperature)

behaviour, so the addition of the GVL and hemicelluloses collection should be carried out above UCST temperature (60°C is sufficient). Another strategy is to cool the GE4 mixture down to room temperature, the homogeneous liquid will be separated into two liquid phases, the GVL above and EmimAc below with hemicelluloses dissolved in it. Then, GVL could be recovered, and hemicelluloses could be precipitated by adding ethanol or water. Eventually the extraction liquor could be recovered using the operations just as type II liquors.

For the IL/GVL/water/hemicelluloses liquors (type IV), the recovery strategy for hemicelluloses is similar to IL/GVL/hemicellulose liquors (type III): water is used as anti-solvent to precipitate the hemicelluloses, and again, the operations should be above UCST temperatures.

### **6.3 Recovery of GVL from aqueous solutions**

GVL exhibits the most important characteristics of an ideal sustainable liquid and could be used as a green solvent. GVL as a solvent used for biomass processing also leads to significant improvements in product yields and a more simplified process for producing biomass-derived chemicals such as LA, furfural, and hydroxymethylfurfural. It is relatively easier to recover GVL from ILs as described in 6.1 and 6.2. Thus, the focus is on the recovery of GVL from aqueous solutions. GVL has a high boiling point (207°C), which is much higher than water (100°C) and has very low volatility, favouring the evaporation of water and leaving GVL as residue. It has a high solubility in water at room temperature, and a similar density to water. By adding salt, water density would be tuned by to favour a phase separation.

#### **Salting-out**

The salting-out method can be used for separating GVL from water. A typical salting-out process is described below:

A given amount of sodium chloride (NaCl) is added to the GVL/water mixture to create separate aqueous phases. The resulting liquid mixture is repeatedly shaken and sonicated in a sonication bath until there are no visible solids. This operation is to ensure that NaCl dissolves, and the dissolved sugars are mobilized into the water phase, so that pure GVL is obtained as the product. The mixture is then centrifuged at a high rotation speed for a few minutes in a centrifuge to create two separated liquid phases. The heavier aqueous phase (the density of saturated NaCl solution is about 1.33 g/m<sup>3</sup> while the density of

GVL is 1.05 g/m<sup>3</sup>) stays below GVL phase.

Luterbacher et al. [5] reported the use of a solvent mixture of biomass-derived GVL, water, and dilute acid (0.05 weight percent H<sub>2</sub>SO<sub>4</sub>) to produce soluble carbohydrates from biomass. The solvent mixtures contain 80% GVL and 20% water. Soluble carbohydrates were recovered in NaCl aqueous phase by the addition of NaCl at 12 wt%. This separation yielded a total soluble carbohydrate concentration up to 112 g/L, accounting for 75% to 91% of the total carbohydrates in the system. There were still small amounts of carbohydrates in the GVL phase, which needed to be further eliminated by membrane separation.

### **Supercritical CO<sub>2</sub> extraction**

With the addition of supercritical CO<sub>2</sub> into the GVL aqueous solutions, a CO<sub>2</sub>-expanded GVL phase is formed, which is no longer miscible with water.

Luterbacher et al. [5] also investigated the extraction performance of liquid CO<sub>2</sub> on the separation of GVL from the aqueous solutions. Their operation is described below:

10 g of the solution containing 80% GVL and 20% water was loaded into a 42 mL vessel. The vessel was made with a stainless steel tube, with corresponding stainless steel fittings, ball valves and needle valves. Once closed, the vessel was pressurized to 1100 psi using a high-pressure syringe pump connected to a CO<sub>2</sub> siphon tank. The reactor was allowed to equilibrate for 10 min, re-pressurized to 1100 psi and again equilibrated for 20 min. Each time a sample was taken from the bottom of the vessel. Following this step, the vessel was re-pressurized to 1100 psi and allowed to equilibrate

for 10 min before another sample was taken for analysis.

This separation yielded a total soluble carbohydrate concentration up to 127 g/L, when the separated GVL was recycled three times since the carbohydrates in GVL would be brought to the solution mixtures, any recycled sugars would contribute to increased concentrations after biomass conversion. More than 70% of the non-extracted carbohydrates that remain in the GVL phase could be recovered with a single re-extraction after 10 wt% water addition of extracted GVL. A single extraction resulted in 75% to 91% of the carbohydrates recovered. Adding a re-extraction would provide 92.5% to 97.3% of the carbohydrates to be recovered, based on a simple calculation. This was because the subsequent extractions with CO<sub>2</sub> lowered the GVL concentration in the water below 2 wt% while removing less than 4% of the carbohydrates.

Shuai's [6] reported a modified liquid CO<sub>2</sub> extraction method to recover GVL from pretreatment liquor which consisted of 80% GVL and 20% water. In his experiment, the modified technique involved pumping liquid CO<sub>2</sub> through the liquor continuously at high pressure and continuously recovering GVL in a connected low-pressure vessel. Over 99.5% of GVL could be recovered when the amount of CO<sub>2</sub> used was over 5 times larger than the amount of GVL, and almost all sugars, lignin and solid material were left in the aqueous phase.

### **Liquid-liquid extraction**

Liquid-liquid extraction is also effective in separation of GVL from aqueous solutions if suitable organic solvents are applied, as they can be effective phase modifiers to render

the GVL phase insoluble with water.

In another paper by Luterbacher et al. [7], he demonstrated that phenolic solvents—sec-butylphenol, nonylphenol, and lignin-derived propyl guaiacol—are effective at separating GVL from the aqueous phase using only small amounts of solvent (0.5 g per g of the original water, GVL, and sugar hydrolysate). The GVL concentrations in aqueous sugar solutions were less than 10% after two cycles of extraction, and only a trace amount of GVL could be detected after 4 cycles of extraction.

### **Distillation**

GVL exhibits a high boiling (207°C) and flash (96°C) points, and very low volatility. While the vapour pressure of GVL is 0.65 kPa at 25°C, it only increases to 3.5 kPa at 80°C, compared with 3.17 kPa and 47.4 kPa of water. GVL does not form an azeotrope with water; the latter can be readily removed by distillation. Thus, it is less energy-demanding to produce GVL than absolute ethanol or other organic solvents.

Horvath et al. [4] reported the recovery of GVL from aqueous solutions via distillation. A 50% GVL and 50% water mixture was made by mixing 250 mL GVL and 250 mL water. The distillation was performed in a 60 cm glass packed column. The glass flask was heated up to a boiling point (~100°C), and no azeotrope formation was observed. The collected product was 99.7% water in one phase, based on GC analysis.

### **6.4 Recovery of ionic liquid from aqueous solutions**

ILs are ideal solvents and strong reaction mediums because of their strong solvation

power and heat stability. Listed benefits of ILs also include the relatively easy reuse and recovery, which effectively reduces the amount of waste generated. Conventional processes such as distillation, membrane separation and liquid-liquid extraction are relevant. Distillation may be the first choice for the separation of volatile components owing to the negligible vapour pressure of ILs. For separating ILs and non-volatile products, extraction and membrane processes can be used. The operations to recover cellulose-dissolving ILs from aqueous solutions described in this chapter are classified as phase addition (for example, distillation, supercritical CO<sub>2</sub>, and crystallization) and barrier separation (membrane separation).

#### **6.4.1 Recovery by phase addition**

##### **Distillation**

Distillation is considered the simplest method for removal of the compounds having a low boiling point and high thermal stability from high-boiling point ILs (due to their different vapour pressures). The volatile components can be distilled by vacuum evaporation, column distillation, and molecular distillation. Even though energy consumption is high in the distillation process, it is usually applied as the final step in most of the published studies to recover and recycle ILs. For example, AmimCl was recovered by Huang et al. [8] from the aqueous solution of homogenous cellulose acetylation reaction media by molecular distillation. The volatile impurities were distilled as distillate, and the IL remained as a residue which was recycled and reused 5 times in the homogenous cellulose acetylation system without any change in the

structure.

### **Supercritical CO<sub>2</sub> extraction**

When substances are in their supercritical phase, the distinct liquid-gas interface disappears. A small change in pressure or temperature near the critical point could result in a large change in density, allowing for a supercritical fluid to be adjustable in its properties. Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) is one of the most popular supercritical fluids because it is non-toxic, non-flammable, inexpensive and it has a moderate critical temperature and pressure (31.1°C and 7.38 MPa) [9].

The scCO<sub>2</sub> was introduced by Blanchard et al. [10] for the quantitative extraction of naphthalene from [C4mim][PF6]. By using scCO<sub>2</sub> 94–96% of naphthalene was recovered at 13.8 MPa and 40°C. Additionally, a variety of other organic solutes (aromatic and aliphatic) were reported to be extracted from [C4mim][PF6] by using the scCO<sub>2</sub> with over 95% recovery.

#### **6.4.2 Recovery by barrier separation**

Excluding the separation of ILs and water by phase addition, membrane filtration has been considered a promising technology because of its low energy consumption and simple operation. The technologies in the membrane separation family include pressure-driven membrane techniques (such as microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO)), pervaporation [11], membrane distillation [12], and electrodialysis [13].

In Fernández's [14] study, the possibility to recover ionic liquids from their respective wastewater by nanofiltration was tested in two case studies. The experimental equipment was a commercial dead-end stirred cell and/or a cross-flow cell developed for this purpose. Hydrophilic ionic liquids (BmimCl and BmimAc) were used for the dissolution of cellulose and its further regeneration by water addition. Wastewaters containing a mixture of BmimCl and BmimAc were treated by nanofiltration, and the ionic liquids were recovered as an aqueous solution which is also almost free of undesired by-products. Wastewater containing hydrophobic ionic liquids derived from the conversion of 2-octane to 2-octanol was also tested, and the ionic liquids used can be recovered as a separate phase by concentrating them beyond the solubility limit. In this case, up to 69% of the ionic liquid originally present in the feed was separated.

The pervaporation (PV) process works as follows: the downstream membrane side is maintained under vacuum, while the membrane upstream side is in contact with the liquid feed and is kept at ambient pressure. Under the driving force of the chemical potential gradient, the volatile solute is preferentially partitioned into a dense, non-porous membrane. This method has been implemented to separate ILs from volatile mixtures. Schafer et al. [11] tested different hydrophilic and hydrophobic polymeric membranes (poly(octylmethyl-siloxane), polyether block amide and poly(vinyl alcohol)) to recover volatile solutes from [C4mim][PF6], resulting in recovery efficiency as high as 99.2% for all solutes tested.

Membrane distillation (MD) is a membrane technique for removing water vapour from

salts or other non-volatile substances. In the MD process, a hydrophobic and porous membrane is applied. This method is reported for use to successfully concentrate IL aqueous solutions from 5% to 50% by Lynam et al. [15]. However, membrane fouling would happen during the membrane distillation process due to the high viscosity and high polarity of hydrophilic ILs [16].

Electrodialysis (ED) has been applied in ILs recovery, with ion-exchange membranes as the separation medium and electric potential as its driving force. Wang et al. [17] employed electrodialysis to recover [C4mim][Cl] from water. The highest recovery ratio could reach 85.2%. While Trinh et al. [13] performed the recovery of [C4mim][Cl] with electrodialysis treatment from the aqueous mixture obtained after cellulose fractionation. Results indicated that the performance of electrodialysis decreased, owing to the deposition of foulants (mainly lignin depolymerization products) on the ion exchange membranes.

### **6.4.3 Crystallization**

Crystallization can be used for recycling ionic liquids (ILs) from a dilute aqueous solution of hydrophilic ILs. A typical application case is the cellulose spinning process, in which case a large amount of water is added to precipitate and eliminate dissolved hemicelluloses from ILs. The method involves the combination of freeze crystallization and evaporation of H<sub>2</sub>O from IL + H<sub>2</sub>O mixtures to recover the ILs.

Liu et al. [18] selected EmimAc + 12.5 wt% H<sub>2</sub>O and EmimDep + 4 wt% H<sub>2</sub>O as references to develop an IL recycling method, and demonstrated the advantages of this

method by a quantitative mass and energy analysis of the whole cellulose spinning and IL recycling process. The energy requirement for the freeze crystallization + evaporation method was compared to evaporation only for recycling of EmimAc and EmimDep. Based on the calculations, to produce 1 kg dry cellulose fibre, 45.4 MJ and 62.6 MJ are required for recycling EmimAc and EmimDep, respectively, by the freeze crystallization + evaporation recycling method. While using only evaporation, 66.9 MJ is required for EmimAc recycling and 99.9 MJ for EmimDep recycling per kg cellulose fibre produced. Therefore, to fabricate 1 kg of dry cellulose fibre using freeze crystallization + evaporation rather than evaporation, 21.5 MJ can be saved for EmimAc and 37.3 MJ for EmimDep recycling. Compared to a classical Lyocell fibre production method using N-methyl morpholine-N-oxide (NMMO) as a solvent, significantly less H<sub>2</sub>O is required in the cellulose spinning process with ILs, and in turn, less H<sub>2</sub>O has to be evaporated for the solvent recycling.

## 6.5 Conclusions

1 Hemicelluloses should first be recovered from the liquors by precipitation. For the recovery of GVL and IL from the liquor, many different methods can be applied, such as phase-added separation (salting out, distillation, and liquid-liquid extraction), and barrier separation (various membrane separation techniques). Method(s) should be carefully selected according to the properties of the targeted IL and the impurities (or ILs are considered as impurities in the mixture).

2 Membrane separation is low energy-demanding and highly selective, but it usually results in low IL recovery due to the high viscosity of IL mixtures, which is a barrier for industrial implementation.

3 Evaporation of H<sub>2</sub>O from IL+H<sub>2</sub>O mixtures has been investigated for recycling of the ILs, but this method is obviously energy consuming. This method is especially suitable to recover high concentration ILs solutions, and usually, ILs with high purity could be obtained.

4 Crystallization can be used to recover hydrophilic ILs from dilute aqueous solutions. This method is suitable to be used in the spinning process as large quantities of water are added to precipitate and eliminate hemicelluloses from ILs. This method requires much less energy than the direct distillation process.

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## **CHAPTER 7**

### **CONCLUSIONS AND RECOMMENDATIONS**

## 7.1 Conclusions

The focus of this research was to separate hemicelluloses from cellulose/hemicellulose matrix (CHM), recover the cellulose-rich fraction and the hemicellulose-rich fraction, as well as the extraction liquor, and to produce high purity cellulose and hemicelluloses with high efficacy. Several applicable separation technologies were investigated. In all cases, hemicelluloses could be separated from the CHM with high selectivity and a cellulose fraction close to 95 wt% (or even higher) could be obtained.

In the first approach, a very small amount of sulphuric acid was added to the GVL and water mixtures, which contained 2-50 wt% water. The CHM was fractionated at elevated temperatures (135°C and 150°C) for 0.5 of an hour to 1 hour. The fractionated cellulose-rich solids were characterized by a high cellulose content (96- 98%) and a CrI of about 72%, under optimized conditions (98% GVL, 135°C, 30 min, 0.007N SA). The acid dosage was found to be critical among the cooking conditions, and only very dilute acid (0.007 N) was needed in the purifying process. The cooking temperature was also found to be a very important parameter which dictates the dissolution rate of the carbohydrates and thus, affects the yield to a large extent.

In the second approach, an ionic liquid/water mixture was investigated as a potential method to remove hemicelluloses from CHM. The influence of water content and operation temperature on the process were studied, both of which showed a great effect on the hemicelluloses removal process and the crystalline structure of the cellulose-rich fraction. The results showed that this process could produce dissolving pulp (yield 78 wt%, purity 92 wt%) and hemicelluloses (yield 16.9 wt%, purity 73.4 wt%) from paper grade bleached pulp. The water content in the mixtures played an important role in

adjusting the solubility of the mixtures.

The third approach was to use the OES solutions made of EmimAc and GVL mixtures to separate hemicelluloses from the CHM. The ratios of GVL to EmimAc and operation temperature were identified as major operational parameters. The OES solutions showed a strong dissolution ability of CHM and the resultant cellulose-rich fraction had a much lower CrI than the CHM. A high cellulose content close to 95 wt% was found from extraction using a GVL/EmimAc mixture with a molar ratio of 4:1. A molar ratio of GVL larger than 8 is not able to dissolve hemicellulose. A suitable temperature for GE4 as an extraction liquor is 60°C. The IL/GVL/water ternary system was also investigated in this research; results demonstrated that it was able to separate hemicelluloses from the CHM as efficiently as the OES system, with water as a controllable constituent. A suitable composition is the molar ratio of EmimAc, water, and GVL is 1:2:4.

The last section of this research focused on the recovery strategies for components in the extraction liquors, including GVL, ionic liquid, and water. For the GVL/water liquor, a total yield of 18.3% of soluble sugars in water could be recovered for further applications; for the IL/water and OES systems, a high hemicellulose fraction of 73 wt% could be obtained with a yield of 16.9% based on the CHM, which was much higher than the hydrolysis process, as well as those reported by others. The recovery of GVL was completed readily by salting out or by the phase change caused by UCST property. The recovery of the ionic liquid was proposed via a combination of freeze crystallization and evaporation process as was determined to be the most promising energy-saving technology reported.

The acid hydrolysis pathway of separating hemicellulose from CHM produced very a

high purity product and improved reactivity as dissolving pulp, along with relatively low yields. However, the direct dissolution pathways, including IL/water, OES (IL/GVL), and ternary system (IL/GVL/water), all showed higher yields of hemicelluloses and a lower reactivity as dissolving pulp. However, the crystalline structure of the original cellulose I was largely conserved, especially for the IL/water treated cellulose.

## **7.2 Recommendation for Future Work**

1. The exploration of using concentrated soluble sugars from the GVL/water method to produce ethanol, xylitol, and other useful chemicals is well fitted into the integrated forest biorefining concept;
2. The catalytic conversion of soluble sugars in GVL and water mixtures to GVL is promising because GVL is a platform chemical;
3. Using the one-pot method to produce dissolving pulp and GVL from CHM is a process that is very suitable to pulp producers;
4. The valorization of regenerated hemicelluloses to produce value-added chemicals is an important part of upgrading paper pulp to dissolving pulp using non-hydrolysis processes;
5. Cheap and energy-saving technologies to recover ionic liquid from aqueous solutions is an important part of ionic liquid's industrial application.

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