

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Use of Ionic Liquids for the Treatment of Biomass Materials and Biofuel Production

El-Sayed R.E. Hassan and Fabrice Mutelet

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67026>

Abstract

Biomass, as fuel source, is renewable, environmental friendly and abundant in nature. It is of great interest to produce green energy and bio-products from lignocellulose. The replacement of conventional organic solvents by a new generation of solvents that are less toxic, less flammable and less polluting is a major challenge for the chemical industry. The aim of this work is to study the solubility of biomass-based materials in ionic liquids in order to overcome the lack of experimental data on phase equilibria of {carbohydrate-ILs} mixtures. Solubility data were successfully correlated using NRTL and UNIQUAC thermodynamic models. The fundamental natures of the interaction between carbohydrates and ILs were investigated using *ab initio* calculations. The pretreatment of miscanthus with ILs resulted in the regeneration of amorphous, porous cellulose almost free of lignin, which is suitable for enzymatic hydrolysis and fermentation processes. A successful ethanol production was obtained with an overall ethanol yield reached up to 150 g ethanol kg⁻¹ miscanthus.

Keywords: ionic liquids, biomass, biofuel, miscanthus, *ab initio* calculations

1. Introduction

Nowadays, governments and researchers are directing their attention toward the development of advanced biofuels. Lignocellulosic biomass is an alternative raw material for biofuel production [1, 2]. Lignocellulosic biomass materials are woody and straw residues from agriculture and forestry, nonfood crops, organic fraction of urban waste and algae-based feedstock. Lignocellulosic biomass consists mainly of lignin, hemicellulose and cellulose [3]. The direct production of sugars from biomass is expensive and inefficient if compared with starch-based feedstocks due to its complicated structure. Therefore, the first step of converting biomass into

biofuel is the pretreatment of biomass to break down the lignin-carbohydrate complex structure and to decrease the crystallinity of the extracted cellulose. The second step is the hydrolysis of extracted cellulose to fermentable sugars such as glucose and the final step is the fermentation of the sugars into liquid fuels [4, 5].

The pretreatment of biomass has been achieved using different technologies in order to extract cellulose. These technologies include ammonia fiber expansion, sodium chlorite and ethanol organosolv process [6]. These technologies showed acceptable results concerning the cellulose extraction. Nevertheless, the recovery of the lignin and hemicelluloses should be taken into consideration in order to optimize the production of bioethanol from biomass.

The replacement of conventional organic solvents by a new generation of solvents less toxic, less flammable and less polluting is a major challenge for the chemical industry. Ionic liquids have been widely promoted as interesting substitutes for traditional solvents. Ionic liquids are salts in the liquid state having melting point below 373 K [7]. They have unique physicochemical properties such as high thermal stability nonflammability, electroconductivity and negligible vapor pressure. Therefore, they are considered as more environmentally friendly than their volatile, toxic and organic counterparts. Ionic liquids, as green solvents, have been widely applied in important fields such as catalysis, separation and nanotechnology [8].

The solubility data of biomass materials in ILs are of great importance for chemical or bioprocesses. Indeed, a small number of studies have been published on the solubility of biomass materials in ionic liquids. Swatloski et al. found that 1-butyl-3-methylimidazolium chloride (BMIMCl) is able to dissolve up to 25 wt% of cellulose [9]. Sheldon et al. connected ILs with carbohydrates [10]. Carneiro et al. studied the solubility of monosaccharides in ILs and correlated these data using the NRTL and UNIQUAC thermodynamic models [11].

Currently, *ab initio* calculations play an important role in understanding the special nature of ILs and their interactions with dissolved components or interfaces [12]. Hydrogen bonding in ILs plays an important role in cation-anion and solvent-solute interactions. This phenomenon could be revealed by both experimental and theoretical investigations. In fact, the hydrogen bonding of ILs is considered to be a factor of great importance to design ILs as potential solvents for cellulose. Xu et al. [12] showed that both chloride anions and imidazolium cations of the IL interact with the cellulose via hydrogen bonds. The results emphasize that the chloride anions play a critically important role and the imidazolium cations present a remarkable contribution in the cellulose dissolution.

Miscanthus, as a biomass feedstock, is an interesting raw material for biofuel production, as it has a carbohydrate content up to 75% [6]. Indeed, there is a lack of data concerning the ionic liquid pretreatment, enzymatic hydrolysis and fermentation of miscanthus. Shill et al. reported the solubility of miscanthus and the extraction of cellulose using EMIMAOC ionic liquid [13]. Padmanabhan et al. found that acetate, chloride and phosphate imidazolium-based ionic liquids are able to dissolve miscanthus up to 5% [14].

Enzymatic hydrolysis process has many advantages such as the very mild conditions (pH = 4.8 and temperature 323 K) which give high yields. The maintenance costs are low compared to alkaline and acid hydrolysis due to no corrosion problems. Hydrolysis without preceding pretreatment yields typically lower than 20%, whereas it yields after pretreatment often exceed

90%. Yeast is currently the most popular method for converting cellulosic sugars into ethanol. The most common type of yeast used is *Saccharomyces cerevisiae*, also known as Brewer's yeast or Baker's yeast. *S. cerevisiae* has a relatively high tolerance to ethanol and inhibitor compounds. Furthermore, this yeast gives high ethanol yields from glucose [3].

This chapter presents an environmentally friendly method for extracting cellulose from biomass using imidazolium-based ionic liquids and also provides a new approach for utilizing biomass resources. This chapter is mainly divided into three parts: The aim of the first part is to overcome the lack of experimental data on phase equilibria of biomass carbohydrates in ionic liquids. The solubility of biomass materials in ionic liquids was measured within a temperature range from 283 to 383 K. Solubility data were correlated successfully with local composition thermodynamic models such as NRTL and UNIQUAC. The solubility of biomass materials in binary mixtures {ethanol + ionic liquids} is studied in order to evaluate the possible use of the antisolvent method for the extraction of carbohydrates from ionic liquids. The second part is devoted to investigate the interaction between carbohydrates, glucose and cellulose building unit and ionic liquids using ab initio quantum chemical methods. The third part aims to study the solubility of miscanthus, as a promising biomass feedstock, in ILs and cellulose extraction. The parameters affecting the extraction process are the ionic liquid structure, miscanthus size, miscanthus mass fraction, temperature and time. A Box-Benhen design expert was applied to evaluate the best conditions for the extraction process. Finally, the produced amorphous cellulose is subjected to hydrolysis and fermentation for biofuel production.

2. Study of the behavior of systems containing (carbohydrate-ILs)

The aim of this part is to overcome the lack of experimental data on phase equilibria of biomass carbohydrates in ionic liquids. The solubility of glucose, fructose, sucrose and lactose in five ionic liquids: 1-ethanol-3-methylimidazolium chloride, 1-butyl-1-methylpyrrolidinium chloride, 1,3-dimethyl-imidazolium methyl phosphonate, BMIMCl and EMIMSCN, was measured within a temperature range from 283 to 383 K (Table 1).

2.1. Solubility of carbohydrates in pure ionic liquids

Solid-liquid equilibria (SLE) of binary systems {IL + sugar} were carried out in a large range of temperatures 280–390 K and compositions up to 60% of sugar, (Figure 1). It is clearly obvious that the solubility of carbohydrates increases in the following order lactose < sucrose < glucose < fructose for ILs used in this study. The solubility increases at high temperature in the following order EMIMSCN < EtOHMIMCl ≤ BMIMCl < DMIMMPh. The Kamlet-Taft solvatochromic parameters are the most comprehensive and frequently used quantitative measure of solvent properties. Studies on the dissolution of cellulose in BMIMCl indicate that the anion of the IL acts as a hydrogen bond acceptor which interacts with the hydroxyl groups of the cellulose [9]. It is found that the phosphonate and chloride imidazolium-based ionic liquids displayed higher β and π^* values if compared to other ionic liquids. It was found that the solubility of sugars is related to the hydrogen bond basicity and the polarizability of the ionic liquids.

Physical properties	BMIMCl	EtOHMIMCl	BMPyCl	EMIMSCN	DMIMMPh
Color and shape at 25°C	White powder	Yellow solid	White powder	Red liquid	Colorless liquid
Molecular formula	C ₈ H ₁₅ ClN ₂	C ₆ H ₁₁ ClON ₂	C ₉ H ₂₀ ClN	C ₇ H ₁₁ N ₃ S	C ₆ H ₁₃ N ₂ PO ₃
Purity (%)	98	98	98	95	98
Molecular weight	174.7	162.61	177.71	162.25	192.15
Melting point (°C)	65	80	114	-6	-20
Density (g/cm ³)	1.0528 at 80°C	n.d	n.d	1.114 at 25°C	1.18 at 25°C
Viscosity (cP)	142 at 80°C	n.d	n.d	20 at 25°C	50.3 at 25°C
Decomposition temp. (°C)	250	>200	210	>200	>200
Water content (ppm)	<1000	<1000	<1000	<1000	450
Solubility in water	Miscible	Miscible	Miscible	Miscible	Miscible
Solubility in ethanol	Miscible	Miscible	Miscible	Miscible	Miscible

Table 1. Physical properties of studied ionic liquids.

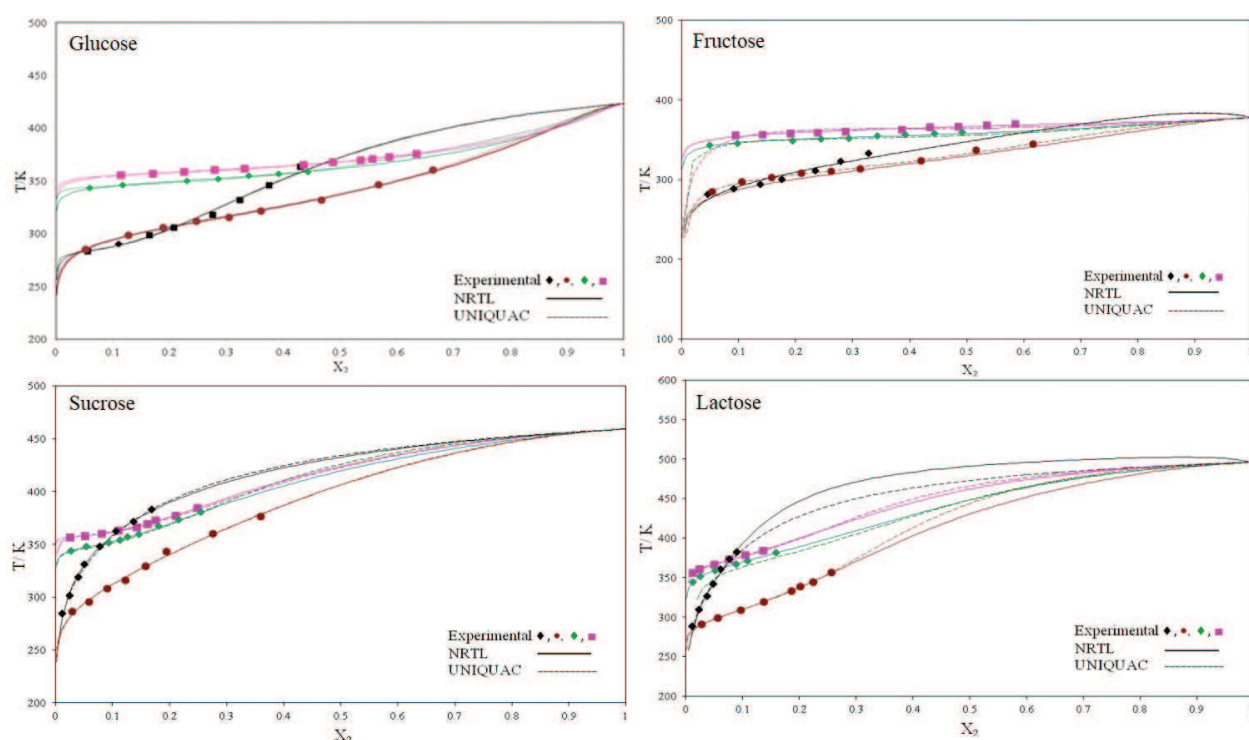


Figure 1. Plot of the experimental and calculated SLE of {IL + sugar} binary systems: ♦ EMIMSCN; ● DMIMMPh; ◆ BMIMCl; ■ EtOHMIMCl. The solid lines have been calculated using NRTL and UNIQUAC models, where X_2 is the sugar mole fraction.

Figure 1 shows that solubility of carbohydrates is a complex process in ILs. Indeed, glucose is more soluble in EMIMSCN than in DMIMMPh up to 310 K. At higher temperatures, the opposite effect is observed. The main key factors of solubility of biomass components in ILs are physicochemical properties such as viscosity, basicity and polarity. Experimental data on the solubility of glucose in thiocyanate-based ILs proved that the solubility of glucose increases

with a decrease of the alkyl chain length [15, 16]. **Figure 1** points out the importance of the influence of functional group in ILs [17]. As an example, the presence of a hydroxyl group in ILs may lead to hydrogen bond formation with the anion or the cation and then modify the behavior of the solvent with carbohydrates.

Experimental data found in the literature on the solubility of fructose and sucrose in ILs proved that their solubility is strongly affected by the alkyl chain length attached on the IL but also the basicity and the polarity. The solubility of sucrose increases with increasing the hydrogen bond basicity and polarity of the anion of the ionic liquid in the following order: C(CN)₃ < BF₄ < CF₃SO₃ < CH₃SO₃ < SCN < HSO₄ < Cl < CH₃HPO₃ [10, 11, 15, 18]. Moreover, the solubility data of sucrose in dialkylimidazolium thiocyanate measured in this work, found in the literature [15] and confirmed that the solubility of carbohydrates decreases with an increase of the alkyl chain length grafted in the cation.

2.2. Estimation of the solubility of carbohydrates in ILs

It is well established that solid-liquid equilibria of systems containing ILs can be well represented with thermodynamic models such as nonrandom two-liquid equation (NRTL) [19] or the UNiVersal QUAsiChemical (UNIQUAC) theory [20]. The solubility of the carbohydrates in the ILs was determined from an expression based on the symmetric convention for the calculation of the activity coefficients, that is, the pure liquid at the solution temperature as a standard state for the carbohydrate, together with their fusion enthalpy, $\Delta_{fus}H$ and melting temperature, T_{fus} . For a general case, this equation can be derived through an idealized thermodynamic cycle between the solid and liquid carbohydrate phase states, under this assumption: The solvent does not appear in the solid phase. Thus, the resulting expression to the calculation of the solubilities is [21] as follows:

$$\ln(x_2\gamma_2) = \frac{-\Delta_{fus}H_2}{R} \cdot \left(\frac{1}{T^{SLE}} - \frac{1}{T_{fus,2}} \right) \quad (1)$$

where $\Delta_{fus}H_2$ and $T_{fus,2}$ denote melting enthalpy and temperature of the sugar and x_2 stands for the solubility of the sugar at the saturated temperature T^{SLE} .

2.2.1. NRTL model

For the NRTL model, the activity coefficient γ_i , for any component i of the ternary system, is given by:

$$\ln\gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (2)$$

with $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$, $\tau_{ji} = \frac{g_{ji}-g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}$ and $\alpha_{ji} = \alpha_{ij} = \alpha$

where g is an energy parameter characterizing the interaction of species i and j , x_i is the mole fraction of component i . In this work, the nonrandomness parameter α was set equal to 0.2 according to the literature [22].

2.2.2. UNIQUAC model

For the UNIQUAC model, the activity coefficient γ_i for any component i of the binary system, is given by:

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^m x_j l_j - q_i \ln(\theta_j \tau_{ji}) + q_i - q_i \sum_{j=1}^m \frac{\theta_j \tau_{ji}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad (3)$$

where $\Phi_i = \frac{r_i x_i}{\sum_{j=1}^m r_j x_j}$, $\theta_i = \frac{q_i x_i}{\sum_{j=1}^m q_j x_j}$, $l_j = \frac{z}{2} (r_j - q_j) - (r_j - 1)$ and $\tau_{ji} = \exp\left(\frac{-\Delta u_{ij}}{RT}\right)$

Here, the lattice coordination number z is assumed to be equal to 10. Parameters r_i and q_i are, respectively, relative to molecular van der Waals volumes and molecular surface areas of the pure component i . The binary parameters for sugars were taken from the literature [12]. The required van der Waals parameters r_i and q_i of the UNIQUAC model for the ionic liquids were estimated with the correlation proposed by Domanska [23].

$$r_i = 0.029281 \times V_i (\text{cm}^3 \cdot \text{mol}^{-1}), \quad q_i = \frac{(z-2) \times r_i}{z} + \frac{2}{z} \quad (4)$$

where V_i is the molar volume of the ionic liquid at $T = 298.15$ K and z is the coordination number assumed to be equal to 10.

To obtain a better description of the (solid + liquid) phase equilibrium simultaneously, temperature-dependent model parameters (Δg_{ij} or Δu_{ij}) were assumed:

$$\Delta g_{12} (\text{J} \cdot \text{mol}^{-1}) = g_{12} - g_{11} = a_{12} + b_{12} \cdot T(\text{K}), \quad \Delta g_{21} (\text{J} \cdot \text{mol}^{-1}) = g_{21} - g_{22} = a_{21} + b_{21} \cdot T(\text{K}) \quad (5)$$

Each thermodynamic model requires four adjustable parameters per binary (Δg_{ji} or Δu_{ji}). The adjustable parameters were determined by minimization of the following objective function (OF):

$$OF = \sum_{i=1}^n (T_{\text{exp},i} - T_{\text{calc},i})^2 \quad (6)$$

The root-mean-square deviation (RMSD) of temperature, σ_T , was calculated according to the following definition:

$$\sigma_T = \left(\sum_{i=1}^n \frac{(T_{\text{exp},i} - T_{\text{calc},i})^2}{n-2} \right)^{1/2} \quad (7)$$

As can be seen in the results depicted in **Figure 1**, both thermodynamic models correlate well with the experimental data.

2.3. Solubility of carbohydrates in a binary mixture of (IL + EtOH)

2.3.1. Effect of the structure of the carbohydrate

Figure 2 shows the solubility of glucose, fructose, sucrose and lactose in a binary mixture of (BMIMCl + EtOH) for the following experimental conditions: mixture ratio by weight = 10, time = 300 min. The solubility increases in the following order lactose < sucrose < glucose < fructose. This behavior agrees well with the literature [24]. As expected, the solubility of disaccharides in ILs is higher than monosaccharides [15].

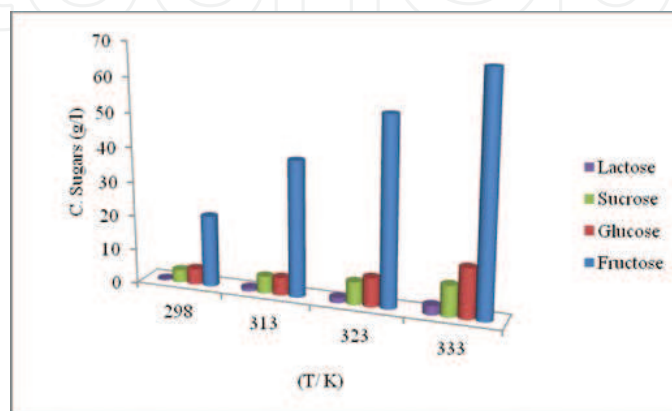


Figure 2. Solubility of carbohydrates in a binary mixture of (BMIMCl + EtOH).

2.3.2. Effect of ethanol/ionic liquid ratio and temperature

Figure 3A presents the effect of (ethanol/ionic liquid) ratio by weight on the solubility of the studied sugars in the binary mixture. It is shown that the solubility of the sugars increases with decreasing (ethanol/ionic liquid) ratio for the studied ionic liquids. This behavior can be related to the polarity and the hydrogen bond basicity of binary mixtures (cosolvent + IL) [25]. Introducing ethanol in IL leads to a reduction in polarity and hydrogen bond. Therefore, the affinity of polar compounds with (cosolvent + BMIMCl) mixtures is lower than in pure IL. A high ethanol/ionic liquid ratio is recommended for the satisfactory extraction of carbohydrates from their mixtures.

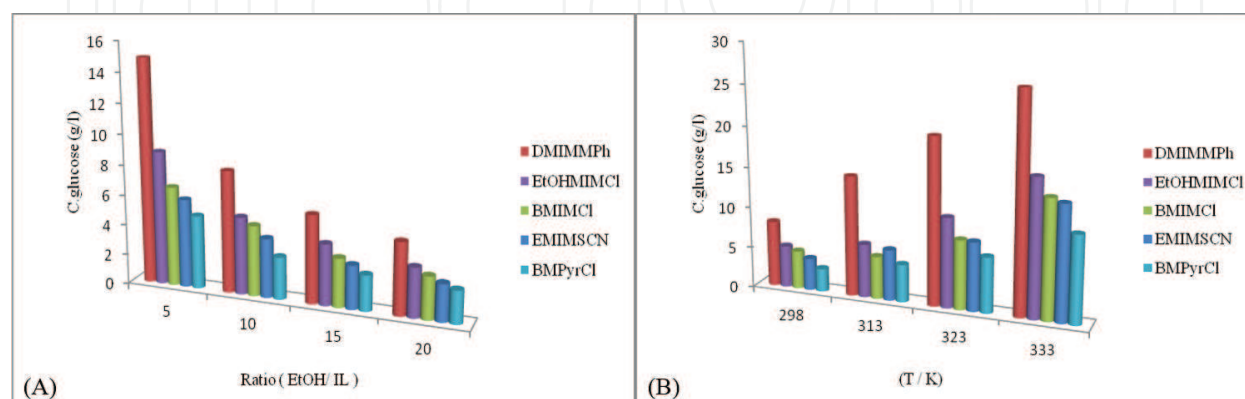


Figure 3. The effect of (A) ethanol/ionic liquid ratio and (B) temperature (K) on the solubility of glucose in the (IL + EtOH) mixture.

On the other hand, the effect of temperature on the solubility of the studied sugars in a mixture of {IL + ethanol} is illustrated in **Figure 3B**. The solubility of carbohydrates is directly proportional to the temperature for the used ionic liquids mixtures. Increasing temperature increases the molecular thermal motion of the entire system and the volatility of solute [26]. Hence, low temperature is highly recommended for a good extraction of carbohydrates.

2.3.3. Applying 2^3 full-factorial design

An experimental design technique, 2^3 full-factorial design, was used to determine the optimal parameters for the extraction of glucose from IL using ethanol and to evaluate the interaction between different parameters. Analysis of variance (ANOVA) data for the system indicates the well fitting of the experimental results to the factorial model equation and hence accuracy of this model. The interaction between the different factors and their effect on the solubility of glucose in this system are shown in **Figure 4**. It is found that there is no interaction between the different factors. As expected, the solubility of glucose increases with increasing temperature and water content and with decreasing the EtOH/IL ratio. The main effective parameter on the glucose solubility is the temperature.

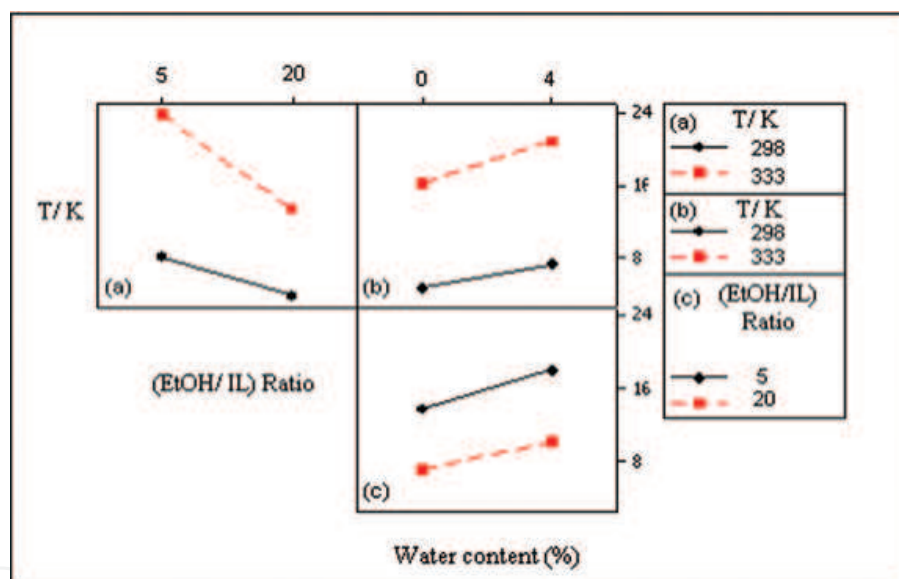


Figure 4. The interaction between different variables on the solubility of glucose in a binary mixture of (BMIMCl + EtOH) at time 300 min: (a) at water content = 2%, (b) at EtOH/IL ratio by weight = 12.5, (c) at temperature = 315.5 K.

2.4. Extraction process using the antisolvent method

Table 2 presents results of the extraction of sugars from five ionic liquids using the antisolvent method with the following characteristics: an {ethanol/ionic liquid} ratio equal to 10, neglected water content and a decrease in temperature from 313 K (or 323 or 333) to 298 K. Results indicate that the extracted percentage increases in the following order fructose < sucrose < glucose < lactose. The performance of different antisolvent on the extraction of sugars from IL using the antisolvent method was evaluated. Results are given in **Table 3**. For these extractions, a solution containing 0.20 wt% of sugar was prepared in BMIMCl at 373 K. After the complete dissolution of sugar, an antisolvent is added at 298 K.

Binary mixture of ethanol + IL	EMIMSCN	DMIMMPh	BMIMCl	EtOHMIMCl	BMPyrCl
Glucose					
Ex.% (from 313 to 298 K)	37.15	45.13	21.91	21.76	39.05
Ex.% (from 323 to 298 K)	53.33	60.39	51.89	53.21	58.63
Ex.% (from 333 to 298 K)	72.08	69.58	72.03	69.39	73.71
Sucrose					
Ex.% (from 313 to 298 K)	29.715	31.593	37.313	24.919	31.283
Ex.% (from 323 to 298 K)	43.223	49.062	52.689	41.640	42.939
Ex.% (from 333 to 298 K)	67.190	65.168	71.286	60.036	66.124

Table 2. The extraction% of the sugars from binary mixtures of the ILs.

Antisolvents	Glucose extracted %	Fructose extracted %	Sucrose extracted %	Lactose extracted %
BMIMCl				
Ethanol	99	80	99	99
Dichloromethane	99	85	99	99
Acetonitrile	99	80	99	99

Table 3. The extraction% of sugars from BMIMCl with different antisolvents.

To conclude this part, a successful extraction process requires high ethanol/IL ratio, low temperature and low water content. The addition of ethanol in mixtures strongly decreases the solubility of carbohydrates in the binary mixtures. Therefore, ethanol is strongly recommended as an antisolvent for separating sugars from ionic liquids mixtures.

3. Study of the interaction between carbohydrates and ionic liquids using ab initio calculations

Ab initio calculations are used to investigate the fundamental natures of the interaction between carbohydrates and ILs. Results were compared with experimental data.

The ab initio calculations were carried out using GAUSSIAN 98 [27]. The minimum energy geometry was determined by performing calculations with density functional theory (DFT). The hybrid Becke 3-Lee-Yang-Parr, B3LYP, exchange-correlation function with the 6-311+G(d) basis set is employed for the geometry optimizations in this work [28]. Partial atomic charges were derived from the ion pair geometries using the CHELPG method [29].

3.1. Ionic liquids structure optimization and hydrogen bond formation

3.1.1. Optimized structures of ionic liquids

The interaction energy ΔE can be calculated using the following equation [30, 31]:

$$\Delta E(\text{kJ mol}^{-1}) = 2625.5 \times [E[\text{cation}]^+ [\text{anion}]^- - (E[\text{cation}]^+ + E[\text{anion}]^-)] \quad (8)$$

where $E[\text{cation}]^+ [\text{anion}]^-$ is defined as the total energy of the system and $E[\text{cation}]^+ + E[\text{anion}]^-$ is defined as the sum of the energy of the pure compositions.

The interaction energies are corrected using the basis set superposition error (BSSE) and zero-point energy (ZPE). So, the corrected interaction energy ΔE_{Corr} is calculated as follows [30, 31]:

$$\Delta E_{\text{Corr}} = \Delta E + \Delta E_{\text{BSSE}} + \Delta E_{\text{ZPE}} \quad (9)$$

where ΔE_{BSSE} is the correction of BSSE and ΔE_{ZPE} is the correction of ZPE.

To obtain the stable configurations of DMIMMPh, the anion MPh^- is located at several different positions around the cation. The initial configurations are fully optimized. Three representative configurations, A_1 , A_2 and A_3 , are chosen, where the methyl phosphonate anion (MPh^-) is placed at carbon positioned 2, 4 and 5 at the imidazolium ring in dimethyl imidazolium cation (DMIM^+), respectively. It was found that the interaction energy of A_1 conformer is higher than that of A_2 and A_3 conformers. Therefore, A_1 conformer has better probability than others and is selected as the best optimized structure for DMIMMPh.

The same observation was found with the other ILs, where the best optimized structure was found when the anion was placed at the imidazolium C2. For BMIMCl, the best optimized structure is matched with the work of Hunt et al. [32] who also found that the best optimized structure for BMIMCl is when Cl^- is placed at C2 of BMIM^+ . The best optimized structures are shown in **Figure 5**.

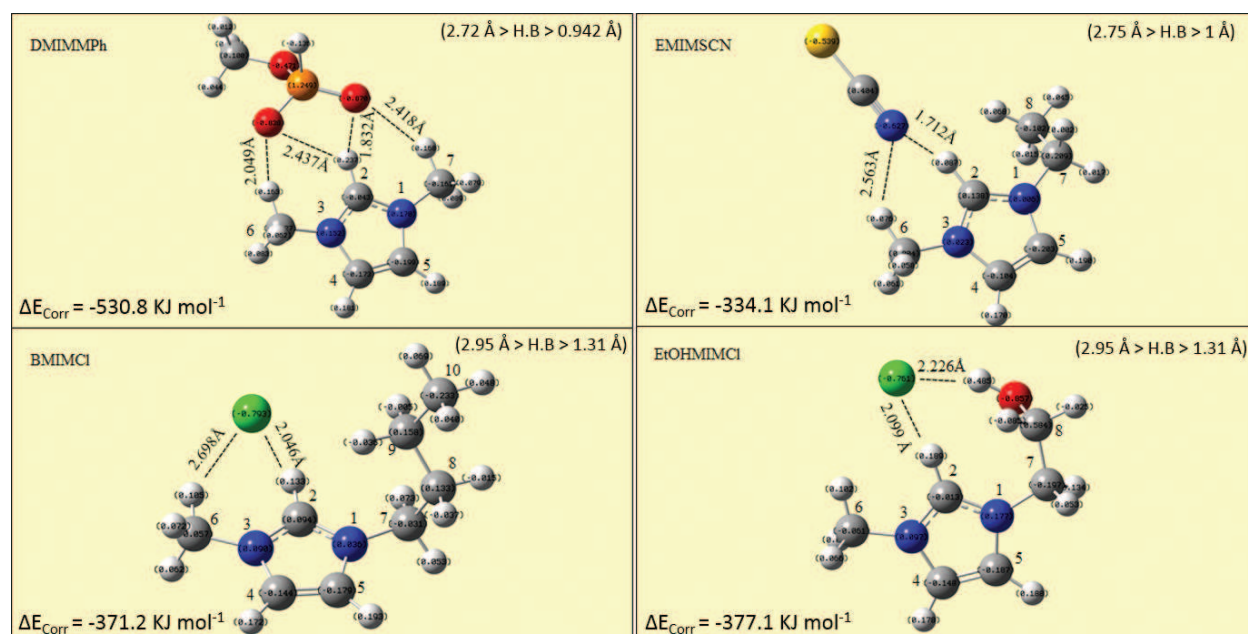


Figure 5. The most stable geometries of DMIMPh, EMIMSCN, BMIMCl, EtOHMIMCl ILs.

In fact, the most stable IL ion pairs have the position of the anion in front of the C2-H. However, the anion is shifted slightly toward the methyl group, the less bulky group, at C6 and lies slightly above the plane of the imidazolium ring.

This behavior is changed in EtOHMIMCl ionic liquid due to the presence of the hydroxyl group at C8. This makes C8 a better hydrogen bond donor than C6. Therefore, the Cl⁻ anion is shifted slightly toward the OH-C8 and this is matched with the work of Zhang et al. [33].

Ab initio calculation results for the interaction energies of the optimized ILs showed that ΔE_{Corr} increases in the following order: EMIMSCN < BMIMCl \approx EtOHMIMCl < DMIMMPh (**Figure 5**).

3.1.2. Hydrogen-bonding interaction

It is now well established that cation-anion H bonding occurs in some imidazolium-based ionic liquids [34]. Jeffrey found that a normal O...H hydrogen bond is formed when O...H < 2.7 Å and C-H...O > 90° [35]. Otherwise, a criterion that the interaction distance be less than the sum of the respective van der Waals radii has also been used.

In case of BMIMCl, the Cl...H bond length is between 2.05 and 2.67 Å. This distance is longer than the covalent bond length in H...Cl (1.31 Å), but it is shorter than the van der Waals distance of Cl...H (2.95 Å). These values approve that the Cl⁻ anion could form a hydrogen bond with the N-C-H fragments of BMIM⁺ cation (2.95 Å > H.B > 1.31 Å).

Ab initio calculations show the formation of two hydrogen bonds between BMIM⁺ cation and Cl⁻ anion. The obtained results are matched with those found in the literature [32]. Hunt et al. [32] proved that a strong hydrogen bond could be formed when the C-H...Cl length is lower than 2.3 Å, while a weak hydrogen bond is formed if 2.3 < r < 2.75 Å.

Also, the same behavior was observed with the O-H bond length in DMIMMPh ionic liquid where: 2.72 Å > H.B > 0.942 Å and also the N-H bond length in EMIMSCN ionic liquid where: 2.75 Å > H.B > 1 Å.

On the other hand, a strong hydrogen-bond interaction is observed between the Cl⁻ anion and the hydroxyl group on the cation (O-H...Cl) (**Figure 5**).

3.2. Interaction of ionic liquids with carbohydrates

Results concerning the binary systems {glucose + IL} show that the interaction of glucose-IL systems increases in the following order: glucose-BMIMCl < glucose-DMIMMPh (**Figure 6**). This observation is in good agreement with the experimental results obtained.

On the other hand, the cellulose-building unit, cellobiose, interacts similarly to glucose with anions and cations of ionic liquids (**Figure 7**). The bond strength (Å) cellulose-IL systems show that cellulose interacts with ionic liquids mainly via hydrogen-bonding formation. The interaction energies and the hydrogen-bonding formation of cellulose-IL systems increase in the following order: cellulose-BMIMCl < cellulose-DMIMMPh. This observation is in good agreement with the experimental results obtained in this work.

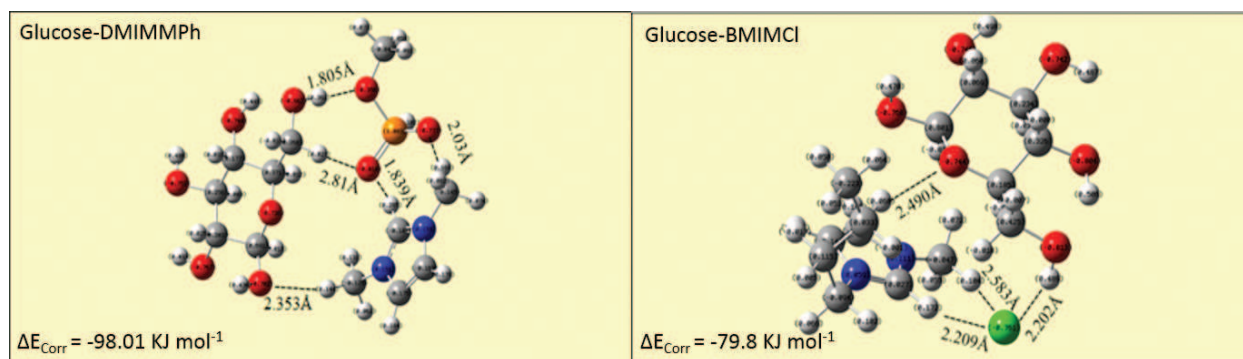


Figure 6. The interaction of glucose with (A) DMIMMPH and (B) BMIMCl.

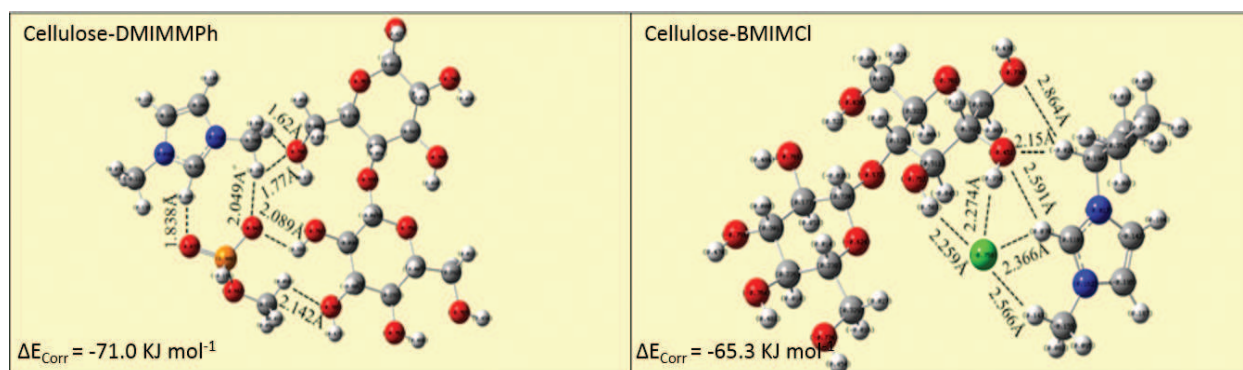


Figure 7. The interaction of cellulose with (A) DMIMMPH and (B) BMIMCl.

Comparing the values of both the interaction energy and the hydrogen bond strength of {glucose-ILs} and {cellulose-ILs} systems proved that ILs interact with glucose higher than with cellulose. This could be a result of the strong β -(1 \rightarrow 4)-glycosidic linkages between cellulose molecules compared to the linkages between glucose molecules.

3.3. Experimental study on the dissolution and regeneration of cellulose

Solid-liquid equilibria (SLE) of microcrystalline cellulose (MCC) in ionic liquids were carried out in a large range of temperature (313–393 K). Ab initio calculation results proved that ionic liquids are capable of dissolving cellulose molecules by breaking down the inter- and intramolecular hydrogen bond's network between cellulose molecules and setting up a new IL-cellulose hydrogen bond's network promoting their dissolution.

The dissolution of cellulose is higher in DMIMMPH ionic liquid, up to 13 mass fraction at 393 K, than other ionic liquids and this is matched with the theoretical results. This is maybe related to its high interaction energy, strong hydrogen bond formation, with its high hydrogen bond basicity and polarity.

It could be concluded from the analysis results, **Figures 8–10**, that DMIMMPH ionic liquid is an excellent solvent for the regeneration of cellulose from biomass feedstocks. The recovered cellulose is more accessible to the enzymes, for example, cellulose enzyme, which convert cellulose and hemicelluloses into fermentable sugars for biofuel production. These results

also proved that there are no chemical reactions occurred during the dissolution and regeneration process.

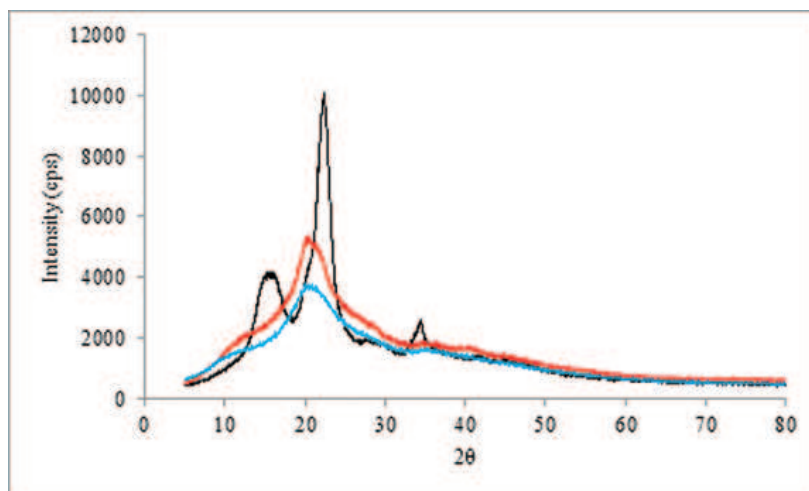


Figure 8. XRD of (■) MCC and cellulose regenerated in (■) BMIMCl and (■) DMIMMPH.

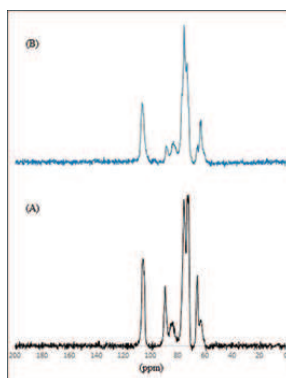


Figure 9. ¹³C CP/MAS NMR spectra of (A) MCC and (B) regenerated cellulose.

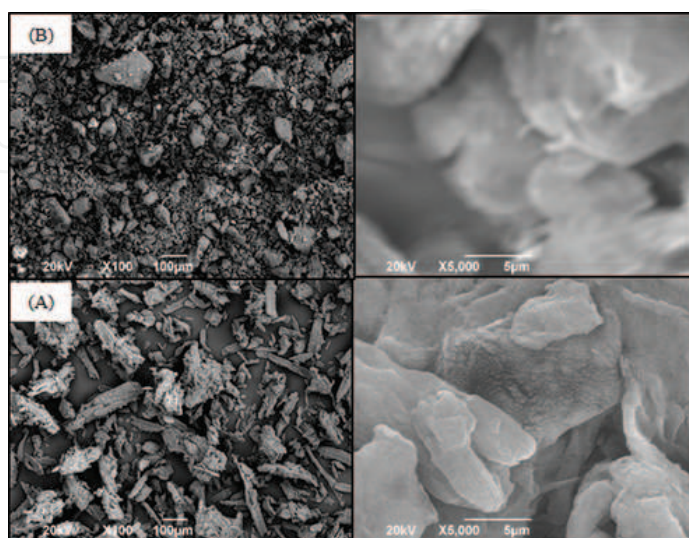


Figure 10. SEM images of (A) MCC and (B) regenerated cellulose.

4. Pretreatment of miscanthus using 1,3-dimethyl-imidazolium methyl phosphonate (DMIMMPh) ionic liquid for glucose recovery and ethanol production

Miscanthus is a promising biomass energy crop due to its relatively low maintenance and high energy content [6]. This part presents an environmentally friendly method of extracting cellulose from miscanthus using DMIMMPh ionic liquid and also provides a new approach for utilizing biomass resources.

4.1. Miscanthus solubility in ionic liquids

Imidazolium-based ionic liquids have the ability to dissolve complex macromolecules such as cellulose with high dissolution efficiency by breaking their inter- and intramolecular hydrogen bond's network [9]. The solid-liquid equilibria of {miscanthus + ILs} system were carried out in a large temperature's range (90–130°C). It is investigated that DMIMMPh has the higher dissolution efficiency than other ionic liquids **Figure 11**. This could be related to its high hydrogen bond basicity and polarity compared to other ILs. This indicates that the nature and the size of the ionic liquid's anion greatly influence the solubility of miscanthus. Strong H-bond-acceptor anions, such as phosphonate anions, effectively dissolve miscanthus. The high solubility of miscanthus in phosphonate-based ILs (DMIMMPh) may be of interest in technology of pretreatment of biomass because these ILs are free of halogens. Moreover, these ILs are less toxic, noncorrosive and biodegradable [9, 14].

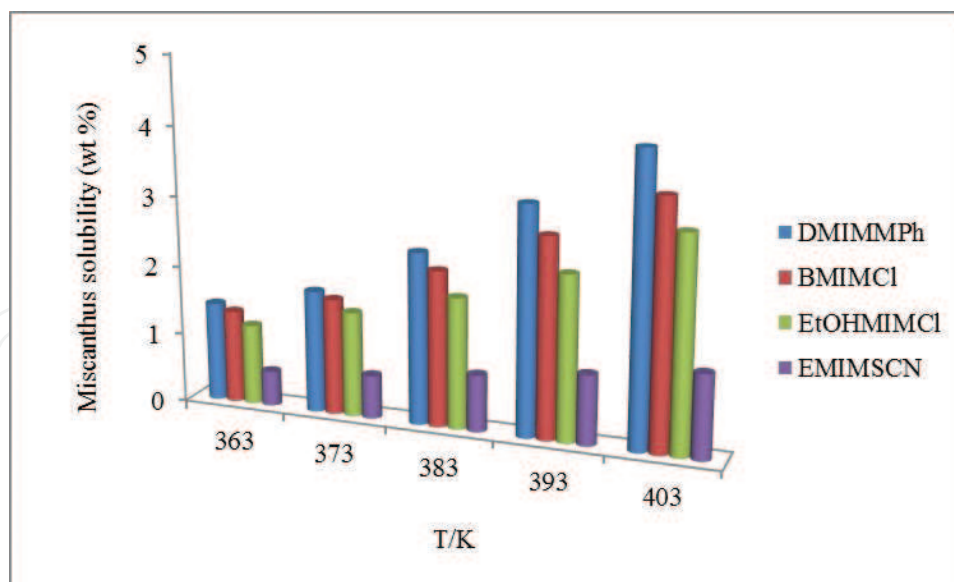


Figure 11. The solubility of miscanthus in ionic liquids.

It is suggested that, in salt solutions with small, strong polarizing cations and large polarizable anions, intensive interactions with cellulose, occur. Results obtained on the solubility of miscanthus in ionic liquids and the data published in the literature [8, 9, 14, 36] proved

that phosphonate- and chloride-based ionic liquids are good solvents for miscanthus. The presented solubility results are matched with those of Padmanabhan et al. [14].

4.2. Cellulose extraction using DMIMMPH ionic liquid

4.2.1. Effect of temperature and time

Brandt et al. [37] found that swelling and dissolution in ILs are temperature dependent and that better dissolution and regeneration rates are obtained at temperatures beyond 373 K.

Figure 12A presents the dissolution and regeneration rates as well as the cellulose grade and recovery for the {miscanthus + DMIMMPH} system with 5% miscanthus mass fraction during 6 h and using water as an antisolvent.

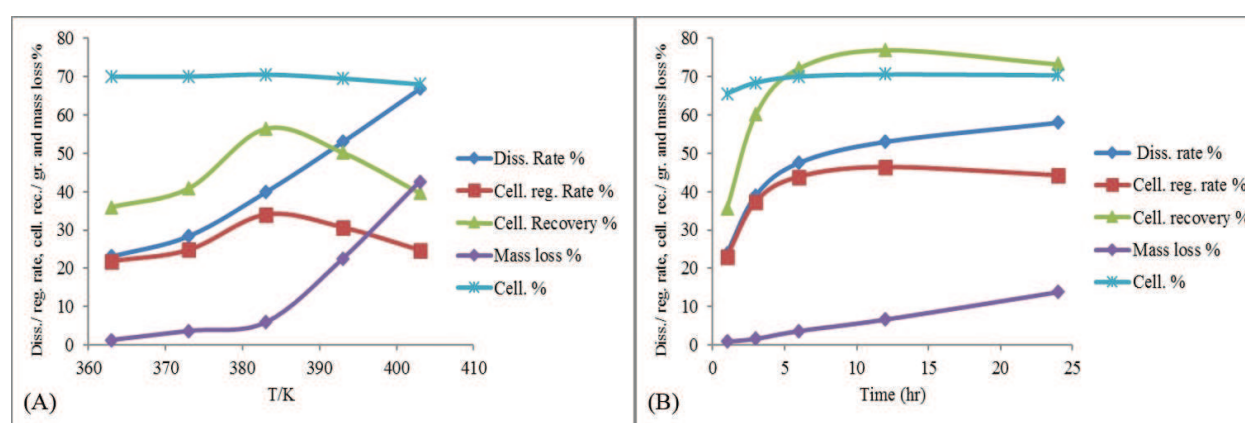


Figure 12. The effect of (A) temperature (K) and (B) time (h) on the extraction process.

Increasing the temperature, from 363 to 403 K, increases the dissolution rate and cellulose grade. Also, increasing the temperature, from 363 to 383 K, increases the cellulose recovery and regeneration rate. But at temperature higher than 383 K, cellulose recovery and regeneration rate decrease obviously due to the degradation occurrence. Mass loss proved that temperature has a significant influence on the extraction efficiency. The mass loss increased up to 30 times when increasing reaction time from 1 to 24 h. High temperature ranges, more than 380 K, lead to high degradation rates and low cellulose extraction efficiency [36].

The kinetics of the miscanthus dissolved in DMIMMPH were studied as a function of dissolution time. **Figure 12B** shows the dissolution rate%, cellulose recovery%, cellulose grade%, cellulose regeneration rate% and mass loss% miscanthus in DMIMMPH. The measurements were performed in these conditions: at 3% miscanthus mass fraction, temperature of 373 K and water is used as an antisolvent. It is obvious that increasing reaction time from 1 to 24 h increases the dissolution rate. Also, increasing reaction time from 1 to 12 h significantly increases cellulose grade, recovery and regeneration rate. On the other hand, increasing reaction time more than 12 h, the cellulose grade, recovery and regeneration rate, decreases due to the degradation occurrence. The mass loss increased up to 14 times when increasing reaction time from 1 to 24 h. Hence, polymer degradation increases with time.

4.2.2. Applying Box-Behnken experimental design on the extraction process

The results of miscanthus solubility and cellulose regeneration in DMIMMPH were evaluated using Box-Behnken experimental design. This experimental design allows the study of the effect of each factor temperature, time and miscanthus mass fraction, as well as the effects of interactions between factors on the cellulose solubility and regeneration.

According to this design, the optimal conditions were estimated using a second-order polynomial function by which a correlation between studied factors and response (mean diameter) was generated. The general form of this equation is as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (10)$$

where Y is the predicted response; dissolution rate, cellulose grade and cellulose recovery%, X_1 , X_2 and X_3 , are studied variables; temperature, time and miscanthus mass fraction; β_{ij} are equation constants and coefficients.

The analysis of variance data, ANOVA, for the system indicates the well fitting of the experimental results to the polynomial model equation and hence accuracy of this model.

Figure 13 presents the plots of the response surface of cellulose recovery. It is shown that increasing both temperature and time increase the dissolution rate and cellulose recovery. High miscanthus mass fraction decreases the cellulose recovery. No important interactions between parameters were observed. Temperature is the most effective parameter on the cellulose dissolution and regeneration.

The optimum conditions obtained from the Box-Behnken design for {miscanthus + DMIMMPH} mixture are 3.2% miscanthus mass fraction and heating up to 107°C during 6.30 h. Applying these optimum conditions resulted in the regeneration of cellulose with grade of 74.4% and recovery of 77.6% (**Table 4**). A slight decrease in efficiency was observed when using recycled DMIMMPH (**Table 4**).

4.3. Characterization of the regenerated cellulose

Analyses results, **Figures 14–17**, indicate that the regenerated cellulose-rich extract is homogeneous, dense and porous and has a higher surface area. Analyses investigations evidenced the production of amorphous cellulose almost free of lignin, which is suitable for enzymatic hydrolysis processes.

4.4. Production of bioethanol

4.4.1. Enzymatic hydrolysis

The regenerated cellulose was hydrolyzed enzymatically to produce glucose. The optimum conditions used for the enzymatic hydrolysis process were heating up to 50°C during 72 h and adding cellulase enzyme at loading 20 FPU/g of cellulose with 1:1 volume of β -glucosidase.

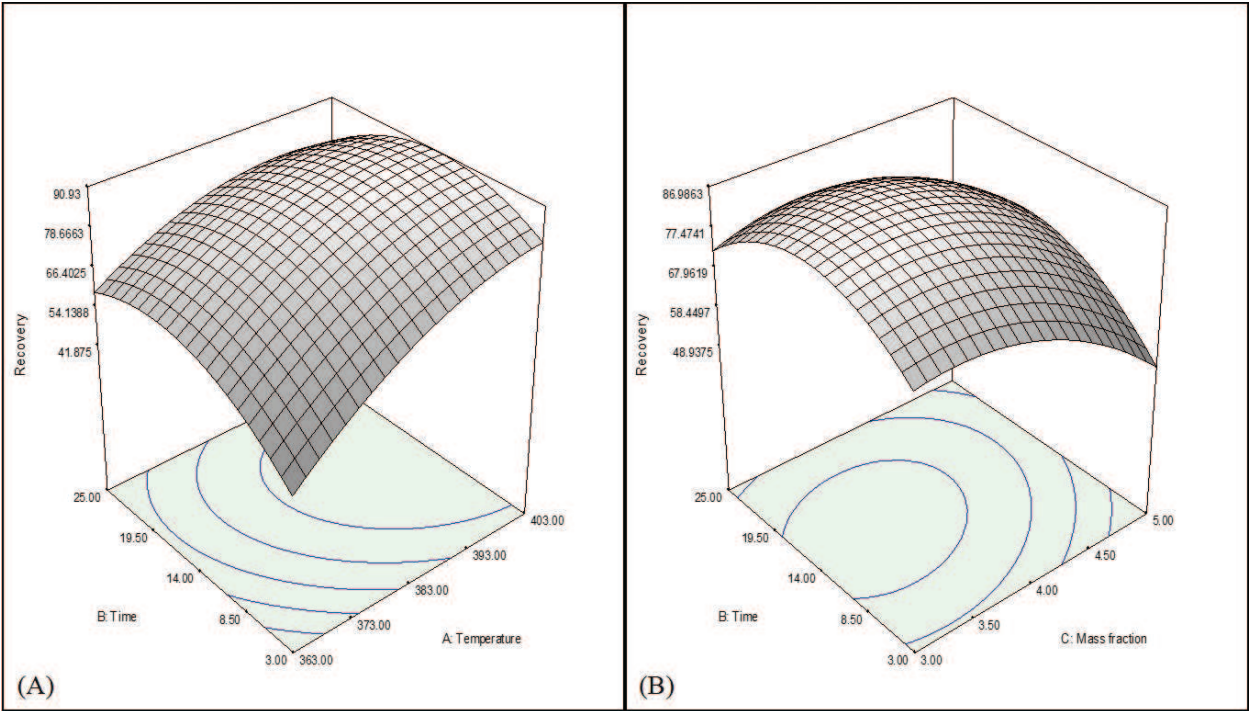


Figure 13. The response surface plots of cellulose recovery for miscanthus-DMIMMPH mixture (A) at mass fraction 4% and (B) at temperature 110°C.

Solvent	Cellulose grade %	Cellulose recovery %	Hemicell. grade %	Hemicell. recovery %	Lignin grade %	Lignin recovery %	Others (ash and unknown products) %
DMIMMPH	74.4	77.6	13.7	22.9	9.1	14.4	2.80
BMIMCl	71.8	73.8	14.9	24.6	10.5	16.4	2.90
Recycled DMIMMPH	72.3	73.5	15.1	24.9	9.7	15.0	3.00

Table 4. Applying the optimum parameters of Box-Behnken design for the miscanthus-DMIMMPH and BMIMCl mixtures.

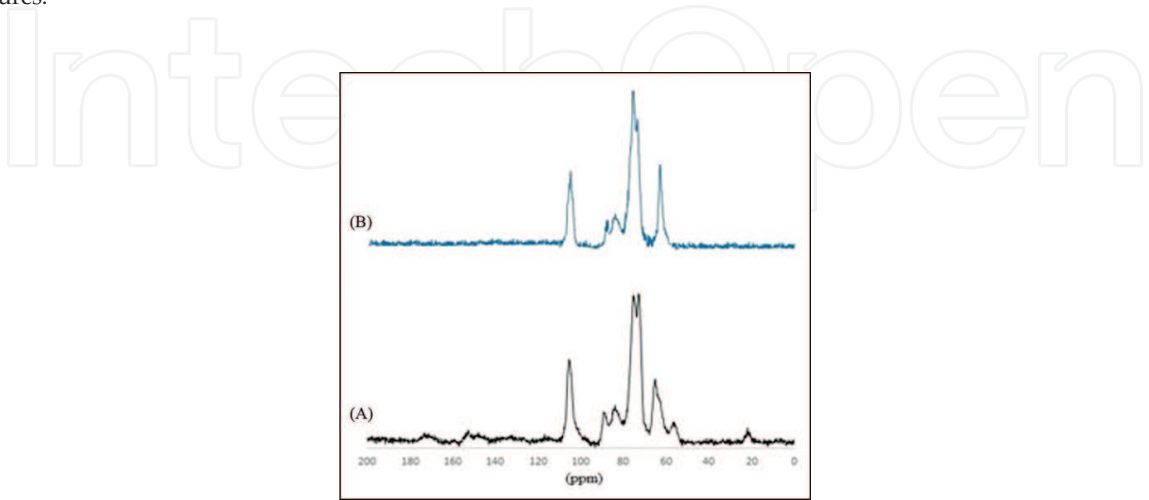


Figure 14. NMR spectra of miscanthus: (A) untreated and (B) treated with DMIMMPH IL.

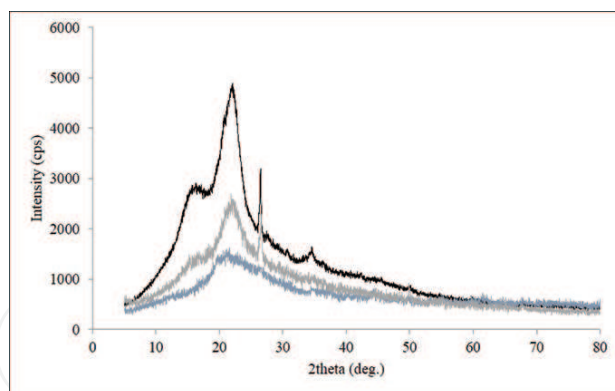


Figure 15. XRD of (■) RD miscanthus, (■) miscanthus residue and (■) cellulose-rich extract.

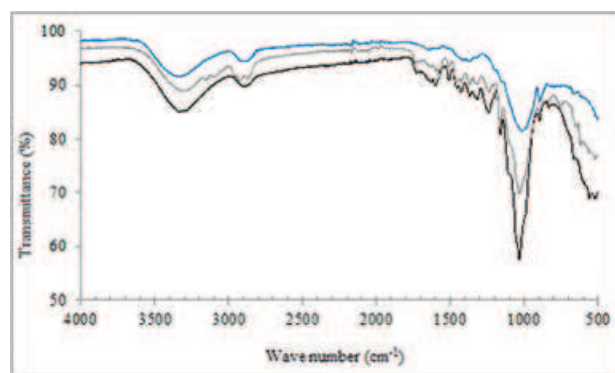


Figure 16. IR of (■) R miscanthus, (■) miscanthus residue and (■) cellulose-rich extract.

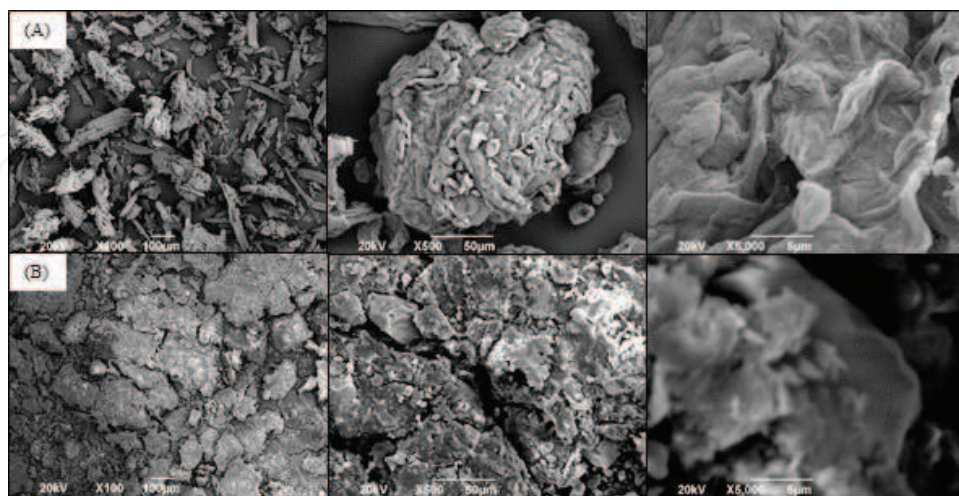


Figure 17. SEM images of (A) MCC cellulose and (B) the cellulose-rich extract with DMIMMPH.

Figure 18 represents the hydrolysis rate for the original miscanthus and the regenerated cellulose. It is obvious that the enzymatic hydrolysis rate decreases rapidly. The glucose hydrolysis efficiency reaches up to 94%.

Table 5 shows the results of different hydrolysis processes for untreated miscanthus and regenerated cellulose. Glucose hydrolysis efficiency of the untreated sample is only 11.9%, while it is more than 90% for the regenerated cellulose samples. The hydrolysis efficiency of the samples treated with DMIMMPH is higher than those treated with BMIMCl. This is maybe due to the inhibition effect of the chloride ions [14] on the cellulase enzyme.

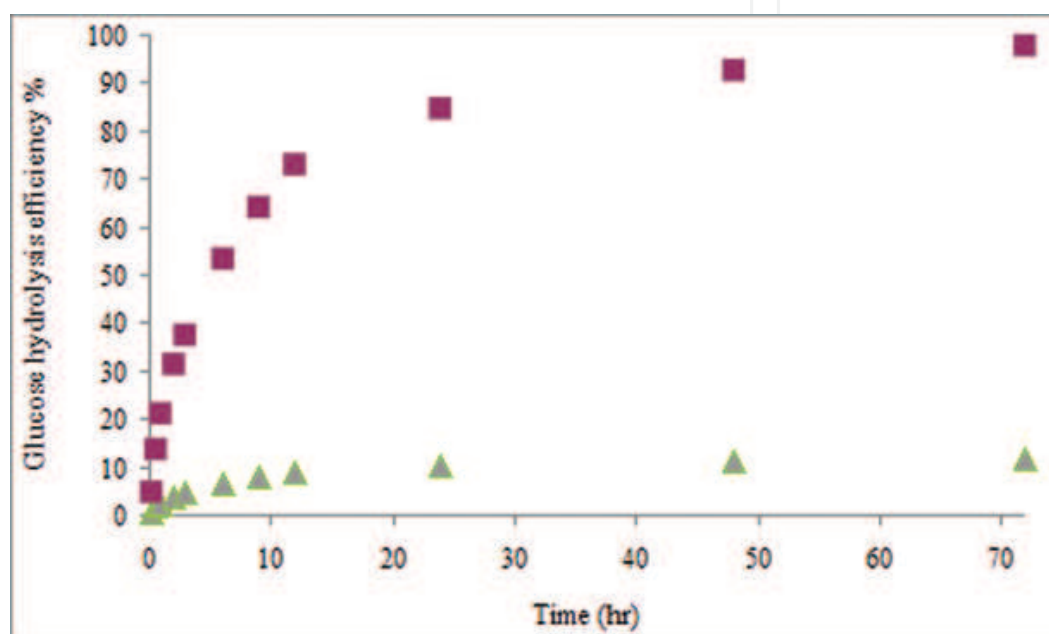


Figure 18. Glucose hydrolysis efficiency as a function of time for: (▲) untreated miscanthus, (■) cellulose regenerated with DMIMMPH.

Sample	Glucose (g/l)	Glucose hyd. effic. (%)	Xylose (g/l)	Xylose hyd. effic. (%)	Ethanol (g/l)	Ethanol conversion rate (%)	Ethanol production effic. (%)	Ethanol produced in g/kg miscanthus
Original miscanthus	1.39	11.89	0.5	6.80	0.53	55.02	4.51	17.70
DMIMMPH	41.88	93.98	5.02	61.18	20.40	85.13	66.75	148.43
Recycled DMIMMPH	37.92	87.77	3.35	43.58	16.72	79.28	55.88	119.14
BMIMCl	32.53	84.72	3.1	45.52	14.72	80.85	49.03	115.63

Table 5. Results for different hydrolysis and fermentation processes for untreated miscanthus and regenerated cellulose samples.

Furthermore, the regenerated cellulose samples have a low content of hemicellulose which could be converted into xylose during the hydrolysis process. The xylose conversion efficiency does not exceed 70%.

4.4.2. Hydrolysate fermentation

The hydrolysate solutions of the untreated miscanthus and the regenerated cellulose samples were fermented using yeast from *S. cerevisiae*. **Figure 19** shows the results of fermentation of the hydrolysate produced from the treatment of miscanthus with DMIMMPH. These results include the sugars consumption, cell growth and ethanol formation.

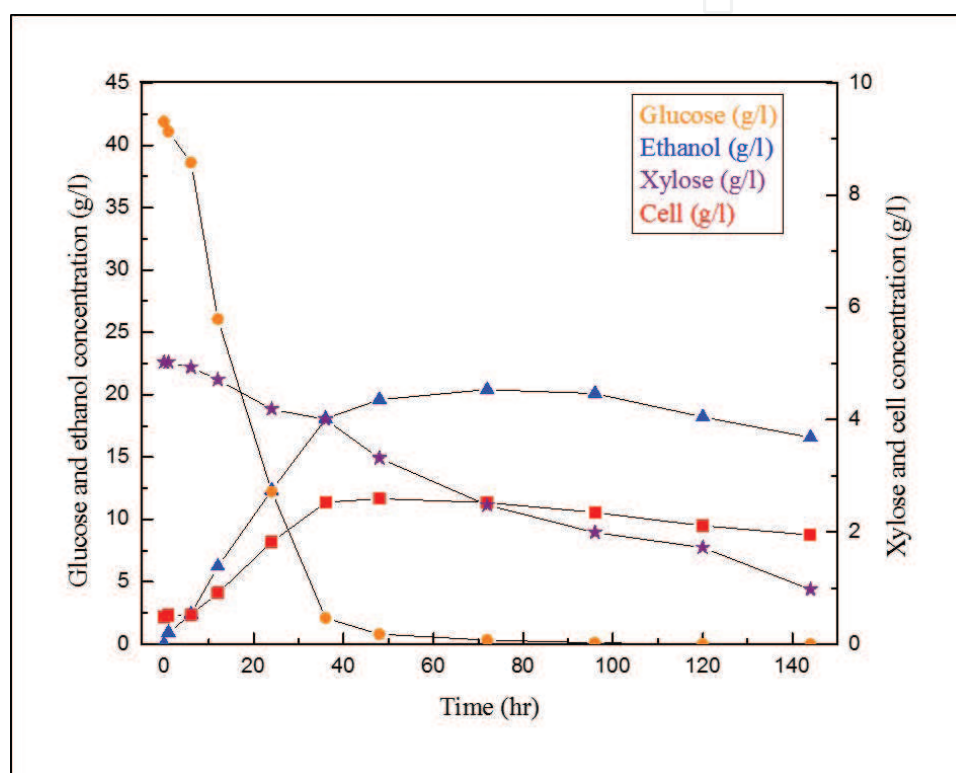


Figure 19. Fermentation results and bioethanol production.

The results indicate the formation of a typical batch growth phase. This batch includes four phases as following: lag phase (0–6 h), exponential growth phase (6–36 h), deceleration phase (36–48 h) and stationary phase (48–72 h).

At the beginning of the fermentation process, lag phase, the yeasts adapted themselves to the growth conditions and hence, the concentration of glucose is quite constant during the first 6 h. Then, after 6 h, exponential phase, both the substrate consumption and cell growth are increasing greatly with time. During the declaration phase, 36–48 h, it is observed that the growth rate is slowing down due to the glucose depletion. As expected, decreasing the glucose concentration during the fermentation process is followed by an increase in cell and ethanol production. Hence, ethanol concentration increases greatly during the exponential and declaration and

stationary phases and achieves a maximum concentration of 20.35 g/L after 72 h. Then, the ethanol concentration is decreased as it is used as a carbon source for the yeast growth when the glucose concentration is depleted [38]. The cell growth rate (μ) is 0.0677 per hour. This result is matched with the work of Cheng et al. [39].

Table 5 shows the results of the fermentation conversion rate of different hydrolysates with a maximum value of 85%. It also shows the ethanol production efficiency for carbohydrate content, cellulose and hemicellulose, in the regenerated cellulose which is calculated as following [40–42]:

$$\begin{aligned} &\text{Ethanol production efficiency(\%)} \\ &= 100 \times \left\{ \frac{\text{ethanol produced(g)}}{0.511 \times \{1.11 \times \text{cellulose content(g)} + 1.136 \times \text{hemicell.content(g)}\}} \right\} \end{aligned} \quad (11)$$

where the value 1.11 is equivalent to [molecular weight of glucose unit (180.16)/molecular weight of cellulose unit (162.14)], while the value 1.136 is equivalent to [molecular weight of xylose unit (150.13)/molecular weight of hemicellulose unit, xylan, (132.11)].

The obtained ethanol production efficiency is 66.75% **Table 5**. These values could be compared with those published in the literature for the hydrolysates based on acid and alkali pretreatments in which the ethanol production efficiency ranges from 65 to 75% [40–42].

Finally, an overall ethanol yield was calculated in order to have a complete evaluation for the production of bioethanol from miscanthus. This calculation is based on total amount of miscanthus considering the loss of carbohydrates during the pretreatment, enzymatic hydrolysis and fermentation processes. The overall ethanol yield for the miscanthus treated with DMIMPh was 148 g ethanol per kg miscanthus. This value indicates the high efficiency of the presented process when compared the values published in the literature for other biomass feedstocks [40–42].

To conclude this part, the use of DMIMPh ionic liquid in the pretreatment of miscanthus and the extraction of cellulose has been studied. Analyses results evidenced the production of amorphous, porous cellulose almost free of lignin. The glucose hydrolysis efficiency of the regenerated cellulose reached up to 94%. The IL pretreatment efficiency is determined by its ability to improve cellulose accessibility and increase overall sugars. This is confirmed with the high overall ethanol yield, up to 148 g ethanol kg⁻¹ miscanthus, produced from the fermentation of the hydrolysates.

5. Conclusions

The solubility of glucose, fructose, sucrose and lactose in ionic liquids was measured within a temperature range from 283 to 383 K. It is observed that the solubility of disaccharides exhibits a noticeably lower solubility than monosaccharides. Solubility data were successfully correlated with NRTL and UNIQUAC thermodynamic models. The possibility of extracting sugars from ILs using the antisolvent method has been evaluated. A successful extraction process requires high ethanol/IL ratio, low temperature and low water content. The considerable

decrease in the solubility of sugars in the binary mixtures proves the ability of ethanol as an excellent antisolvent [43, 44].

Ab initio calculations were used as a tool to investigate the fundamental natures of the interaction between carbohydrates and ILs. The most stable geometries ILs have been studied. The most stable IL ion pairs have the anion positioned in front of the C2-H of the imidazolium ring of cation. It was concluded that the anion plays the main role in the dissolution process of carbohydrates, in which the H-bonding forces are the major interactions. The obtained results proved that DMIMMPH is more efficient than other ionic liquids. The analyses results indicate that the regenerated cellulose is quite similar to the original one with a great decrease in its crystallinity. This proves that the treatment of cellulose with ILs is accompanied only with a physical change [45].

The use of ILs in the pretreatment of miscanthus has been studied. Extraction results were evaluated using Box-Behnken design. Analyses results evidenced the production of amorphous, porous cellulose almost free of lignin, thereby facilitating its enzymatic hydrolysis. The glucose hydrolysis efficiency of the regenerated cellulose reached up to 97.74%. The pretreatment efficiency is determined by its ability to improve cellulose accessibility and increase overall sugars yield. This could be confirmed with the high overall ethanol yield, up to 150 g ethanol kg⁻¹ miscanthus, produced from the fermentation of the hydrolysates. Alkylphosphonate anion-based ILs were proposed as excellent candidates for biomass treatment and biofuel production [46, 47].

Author details

El-Sayed R.E. Hassan^{1,2} and Fabrice Mutelet^{1*}

*Address all correspondence to: fabrice.mutelet@univ-lorraine.fr

1 Reactions and Process Engineering Laboratory (CNRS UMR 7274), University of Lorraine, Nancy, France

2 Central Metallurgical Research and Development Institute (CMRDI), Helwan, Cairo, Egypt

References

- [1] Tadesse H., Luque R., Advances on biomass pretreatment using ionic liquids: an overview. *Energy Environ Sci.*, (2011); **4**:3913–3929.
- [2] Henry R., Evaluation of plant biomass resources available for replacement of fossil oil. *Plant Biotechnol J.*, (2010); **8**:288–293.
- [3] Balat M., Balat H., Oz C., Progress in bioethanol processing. *Prog Energy Combust Sci.*, (2008); **34**:551–573.

- [4] Agbor V. B., Cicek N., Sparling R., Berlin A., Levin D. B., Biomass pretreatment: fundamentals toward application. *Biotechnol Adv.*, (2011); **29**:675–685.
- [5] Wang H., Gurau G., Rogers R. D., Ionic liquid processing of cellulose. *Chem Soc Rev.*, (2012); **41**:1519–1537.
- [6] Brosse N., Dufour A., Meng X., Sun Q., Ragauskas A., Miscanthus: a fast growing crop for biofuels and chemicals production. *Biofuels Bioprod Bioref.*, (2012); **6**:580–598.
- [7] Dadi A. P., Schall C. A., Varanasi S., Mitigation of cellulose recalcitrance to enzymatic hydrolysis by IL pretreatment. *Appl Biochem Biotechnol.*, (2007); **136–140**: 407–421.
- [8] Sun N., Rahman M., Qin Y., Maxim M. L., Rodríguez H., Rogers R., Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chem.*, (2009); **11**:646–655.
- [9] Swatloski R. P., Spear S. K., Holbrey J. D., Rogers R. D., Dissolution of cellulose with ionic liquids. *J Am Chem Soc.*, (2002); **124**:4974–4975.
- [10] Liu Q. B., Janssen M. H. A., van Rantwijk F., Sheldon R. A., Room-temperature ionic liquids that dissolve carbohydrates in high concentrations. *Green Chem.*, (2005); **7**:39–42.
- [11] Carneiro A. P., Rodriguez O., Macedo E. A., Solubility of monosaccharides in ionic liquids –experimental data and modeling. *Fluid Phase Equilib.*, (2012); **314**:22–28.
- [12] Xu H., Pan W., Wang R., Zhang D., Liu C., Understanding the mechanism of cellulose dissolution in 1-butyl-3-methyl imidazolium chloride ionic liquid via quantum chemistry calculations and molecular dynamics simulations. *J Comput Aid Mol Des.*, (2012); **26**: 329–337.
- [13] Shill K., Padmanabhan S., Xin Q., Prausnitz J. M., Clark D. S., Blanch H. W., Ionic liquid pretreatment of cellulosic biomass: enzymatic hydrolysis and ionic liquid recycle. *Biotechnol Bioeng.*, (2011); **108**:511–520.
- [14] Padmanabhan S., Kim M., Blanch H. W., Prausnitz J. M., Solubility and rate of dissolution for Miscanthus in hydrophilic ILs. *Fluid Phase Equilib.*, (2011); **309**:89–96.
- [15] Conceição L. J. A., Bogel-Lukasik E., Bogel-Lukasik R., A new outlook on solubility of carbohydrates and sugar alcohols in ionic liquids. *RSC Adv.*, (2012); **2**:1846–1855.
- [16] Fort D. A., Swatolski R. P., Moyna P., Rogers R. D., Moyna G., Use of ionic liquids in the study of fruit ripening by high-resolution ¹³C NMR spectroscopy: ‘Green’ solvents meet green bananas. *Chem Commun.*, (2006); **7**:714–716.
- [17] Zhang H., Gurau G., Rogers R. D., Ionic liquid processing of cellulose. *Chem Soc Rev.*, (2012); **41**:1519–1537.
- [18] Malgorzata E. Z., Ewa B. L., Rafal B. L., Solubility of carbohydrates in ionic liquids. *Energy Fuels*, (2010); **24**:737–745.
- [19] Renon H., Prausnitz J. M., Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.*, (1968); **14**:135–144.

- [20] Abrams D. S., Prausnitz J. M., Statistical thermodynamics of liquid mixtures: a new expression for the excess gibbs energy of partly or completely miscible systems. *AIChE J.*, (1975); **21**:116–128.
- [21] Prausnitz J. M., Lichtenthaler R. N., Azevedo E. G., Molecular thermodynamics of fluid-phase equilibria, 2nd ed.; Prentice-Hall Inc.; Englewood Cliffs, NJ, 1986.
- [22] Simoni L. D., Chapeaux A., Brennecke J. F., Stadtherr M. A., Asymmetric framework for predicting liquid-liquid equilibrium of ionic liquid-mixed-solvent systems. 2. Prediction of ternary systems. *Ind Eng Chem Res.*, (2009); **48**:7257–7265.
- [23] Domanska U., Solubility of n-alkanols (C16, C18, C20) in binary solvent mixtures. *Fluid Phase Equilib.*, (1989); **4**:6223–248.
- [24] Hyvonen L., Koivistoinen P., Fructose in food systems. Applied Science Publishers. : In Birch, G.G. & Parker, K.J. Nutritive Sweeteners. London & New Jersey; pp. 133–144. ISBN 0-85334-997-5, 1982.
- [25] Yang Q., Xing H., Su B., Yu K., Bao Z., Yang Y., et al., Improved separation efficiency using ionic liquid–cosolvent mixtures as the extractant in liquid–liquid extraction: a multiple adjustment and synergistic effect. *Chem Eng J.*, (2012); **181–182**: 334–342.
- [26] Liu W., Hou Y., Wu W., Ren S., Jing Y., Zhang B., Solubility of glucose in ionic liquid + antisolvent mixtures. *Ind Eng Chem Res.*, (2011); **50**: 6952–6956.
- [27] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., et al., Gaussian 03, revision E.01, Gaussian, Inc.: Pittsburgh, PA, 2003.
- [28] Becke A. D., Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys.*, (1993); **98**:5648–5652.
- [29] Breneman C. M., Wiberg K. B., Determining atom-centered monopoles from molecular electrostatic potentials: the need for high sampling density in formamide conformational analysis. *J Comp Chem.*, (1990); **11**:361–373.
- [30] Ji W., Ding Z., Liu J., Song Q., Xia X., Gao H., et al., Mechanism of lignin dissolution and regeneration in ionic liquid. *Energy Fuels*, (2012); **26**:6393–6403.
- [31] Zhou J., Mao J., Zhang S., Ab initio calculations of the interaction between thiophene and ionic liquids. *Fuel Process Technol.*, (2008); **89**:1456–1460.
- [32] Hunt P. A., Gould I. R., Structural characterization of the 1-butyl-3-methylimidazolium chloride ion pair using ab initio methods. *J Phys Chem A*, (2006); **110**:2269–2282.
- [33] Zhang S., Qi X., Ma X., Lu L., Zhang Q., Deng Y., Investigation of cation-anion interaction in 1-(2-hydroxyethyl)-3-methylimidazolium-based ion pairs by density functional theory calculations and experiments. *J Phys Org Chem.*, (2012); **25**:248–257.
- [34] Chiappe C., Pieraccini D., Ionic liquids: solvent properties and organic reactivity. *J Phys Org Chem.*, (2005); **18**:275–297.

- [35] Jeffrey G. A., The ups and downs of C–H hydrogen bonds. *J Mol Structure*, (1999); **485–486**:293–298.
- [36] Wanga X., Li H., Cao Y., Tang Q., Cellulose extraction from wood chip in an ionic liquid 1-allyl-3-methylimidazolium chloride. *Bioresour Technol.*, (2011); **102**:7959–7965.
- [37] Brandt A., Hallett J. P., Leak D. J., Murphy R. J., Welton T., The effect of the ionic liquid anion in the pretreatment of pine wood chips. *Green Chem.*, (2010); **12**:672.
- [38] Coppella S. J., Dhurjati P., A detailed analysis of *Saccharomyces cerevisiae* growth kinetics in batch, fed-batch and hollow-fiber bioreactors. *Chem Eng J.*, (1989); **41**:B27–B35.
- [39] Cheng N. G., Hasan M., Kumoro A. C., Ling C. F., Tham M., Production of ethanol by fed-batch fermentation. *Pertanika J Sci Technol.*, (2009); **17**:399–408.
- [40] Yue Z., Teater C., MacLellan J., Liu Y., Liao W., Development of a new bioethanol feedstock-Anaerobically digested fiber from confined dairy operations using different digestion configurations. *Biomass Bioenergy*, (2011); **35**:1946–1953.
- [41] Yue Z., Teater C., Liu Y., MacLellan J., Liao W., A sustainable Pathway of Cellulosic Ethanol production integrating anaerobic digestion with biorefining. *Biotechnol Bioeng*, (2010); **105**:1031–1039.
- [42] Tan L., Tang Y-Q., Nishimura H., Takei S., Morimura S., Kida K., Efficient production of bioethanol from corn stover by pretreatment with a combination of sulfuric acid and sodium hydroxide. *Prep Biochem Biotechnol*, (2013); **43**:682–695.
- [43] Hassan El-Sayed R. E., Mutelet F., Pontvianne S., Moise J-C., Studies on the dissolution of glucose in ionic liquids and extraction using the antisolvent method. *Environ Sci Technol.*, (2013); **47**: 2809–2816.
- [44] Hassan El-Sayed R. E., Mutelet F., Moise J-C., From the dissolution to the extraction of carbohydrates using ionic liquids. *RSC Adv.*, (2013); **3**:20219–20226.
- [45] Hassan El-Sayed R. E., Mutelet F., Bouroukba M., Experimental and theoretical study of carbohydrate-IL interactions. *Carbohydr Polym*, (2015); **127**:316–324.
- [46] Hassan El-Sayed R. E., Mutelet F., Moise J-C., The pretreatment of miscanthus using ionic liquids; a way for biofuel production, *MATEC Web Conf.*, (2013); **3**:01049.
- [47] Hassan El-Sayed R. E., Mutelet F., Moise J-C., Brosse N., Pretreatment of miscanthus using 1,3-dimethyl-imidazolium methyl phosphonate (DMIMMPH) ionic liquid for glucose recovery and ethanol production. *RSC Adv.*, (2015); **5**:61455–61464.

