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PRETREATMENT OF VEGETAL MATERIALS BY IONIC LIQUID DISSOLUTION

BY

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Abstract. In this work investigates effects of dissolving vegetal materials in the ionic liquids 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium chloride, 1-ethyl-2,3-dimethylimidazolium chloride, 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl) imidazolium bromide. Good solvent for cellulose is 1-butyl-3-methylimidazolium chloride, whereas for vegetal material the best solvents is 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl) imidazolium bromide. A total reducing sugar (TRS) yield of 39.75% was obtained in ionic liquid 1-butyl-3-methylimidazolium chloride at 105ºC in 300 min reaction time.

Key words: ionic liquid, vegetal materials, TRS, crystallinity index.

1. Introduction

Vegetal materials has the potential to serve as a low cost and renewable feedstock for bioconversion into sugars, which can be further utilized for biofuel production (Gomez *et al.*, 2008; Wyman *et al.*, 2005). Ionic liquids are

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also able to dissolve other biomaterials (Fort *et al.,* 2006) such as lignin and lignocelluloses (Kilpeläinen *et al.*, 2007). Dissolved cellulose can be precipitated and separated from lignin and hemicelluloses by the addition of anti-solvents, such as water (Fort *et al.,* 2006). Ionic liquids have demonstrated great promise as efficient solvents for biomass dissolution with easy recovery of cellulose upon anti-solvent addition (Dadi *et al.*, 2006; Lee *et al.*, 2009; Liu & Chen, 2006; Zhao *et al.*, 2009).

Because of the diversity properties of ionic liquids they are in the focus of the scientific interest for several uses since some years (Olivier-Bourbigou *et al.*, 2010).

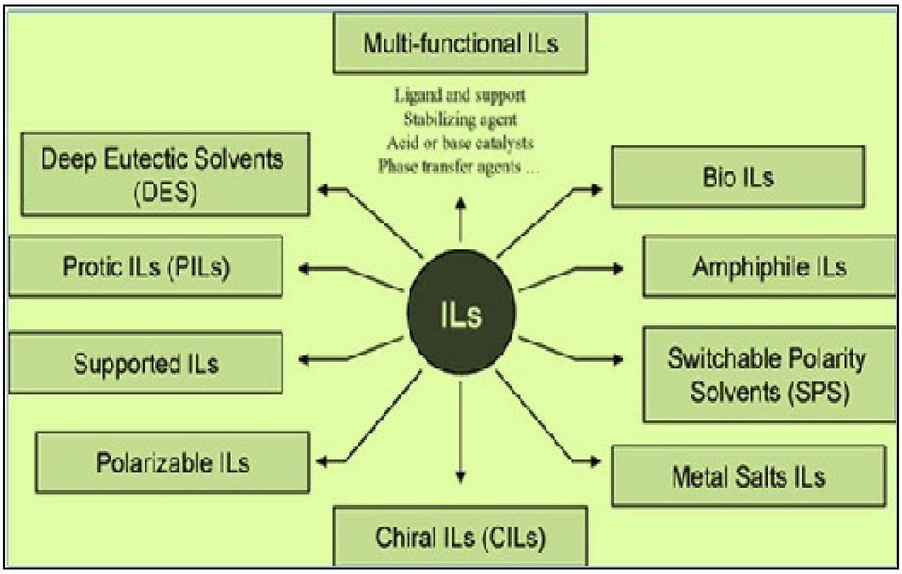

Fig. 1 − Evolution of IL generations (Olivier-Bourbigou *et al.*, 2010).

The goal of present study was to determine the effects of ionic liquids on vegetal materials and cellolignins for obtaining polysaccharides.

2. Experimental

2.1. Materials

Ionic liquids (1-ethyl-3-methylimidazolium acetate from Sigma-Aldrich), (1-butyl-3-methylimidazolium chloride from Merck), (1-ethyl-2,3-dimethylimidazolium chloride from Merck), (3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)imidazolium bromide) was purchased from Organic Chemistry Laboratories, Department of Chemistry, University “Alexandru Ioan Cuza”, Iaşi, România.

2.2. Methods

Ionic Liquid Treatment. The process of destructuration the cellulosic material with ionic liquids is exemplified: 0.06 g of *Avicel* cellulose or rapessed stalks and 1 g of ionic liquid were put in a 25 mL glass vial heated to 105°C for 6 h. Thus, at this mixture was added 60 μL HCl (1.66 M) and the reaction mixture was stirred at 130°C. After 10 min, deionized water (200 μL) was added with stirring, followed by additional aliquots at 20 min (100 μL), 30 min (150 μL), and 60 min (250 μL). After a total reaction time of 2.5 h, the precipitate collected on the filter paper was washed by additional 1.5 mL deionized water. Insoluble materials were removed by centrifugation, rinsed twice with water (400 μL) and dried. The pretreated samples solution were separated by filtration (Binder & Raines, 2010).

A series of similar experiments were carried out by using the rapeseed stalks of prehydrolysis cellolignin obtained with 0.5% concentration sulphuric acid at temperature 170°C. Thus, the cellolignin (0.06 g) was heated with 1 g of ionic liquid (chloride 1-butyl-3-methylimidazoliu) at 105°C for 4.5 h. To this mixture was added 43.5 μL HCl (1.66 M) and the reaction mixure was stirred at 130°C. After 10 min, 150 μL of deionized water was added with stirring, followed by additional 75 μL water at 20 min, 202.5 μL water at 30 min, and 210 μL water at 60 min. After 3 h total reaction time, the solution was diluted with water (900 μL) and centrifuged to sediment insoluble materials (Binder & Raines, 2010).

Analysis of total reducing sugars. The concentration of TRS (the total reducing sugars) was calculated by the DNS (3,5-dinitrosalicylic acid) assay using D-glucose as a standard (Miller, 1959). Absorbance was read against the blank reagent at 540 nm, as measured by a V-550 JASCO spectrometer.

FTIR spectroscopy. A Fourier transform infrared (FTIR) spectrometer (Digilab Scimitar FTS 2000) was used for determining changes in the structure after the pretreatments. Each spectrum was obtained with an average of 32 scans and resolution of 4 cm^{-1} from 4000–400 cm^{-1}. All spectra were normalized by the highest absorbance using a program Digilab Merlin series.

3. Results and Discussions

3.1. Analysis of Total Reducing Sugars

Different ionic liquids were tested concerning their solvent capability for *Avicel* cellulose and rapeseed stalks, whereas the pretreatment were performed with the 1-ethyl-3-methylimidazolium acetate (IL-1), 1-butyl-3-methylimidazolium chloride (IL-2), 1-ethyl-2,3-dimethylimidazolium chloride (IL-3) and 3-(2-methoxy-2-oxoethyl)-1-(3-methoxy-3-oxopropyl)-imidazolium bromide (IL-4) (Fig. 2).

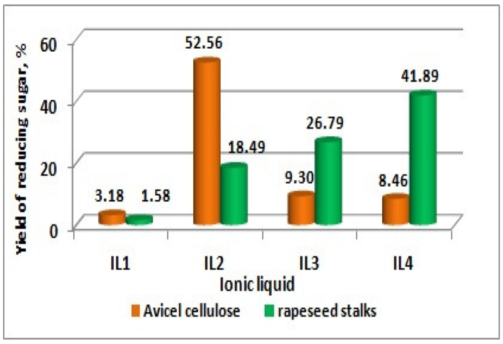

Fig. 2 - Yield of dissolved *Avicel* cellulose and rapeseed stalks produced under ionic liquid pre-treatment.

Fig. 3 summarizes the various pretreatment conditions and the yield of each sample before and after pretreatment. Results show that compared with the untreated materials, both dilute acid and ionic liquid pretreatment remove lignin and hemicelluloses ranging from 10.19% to 39.75%.

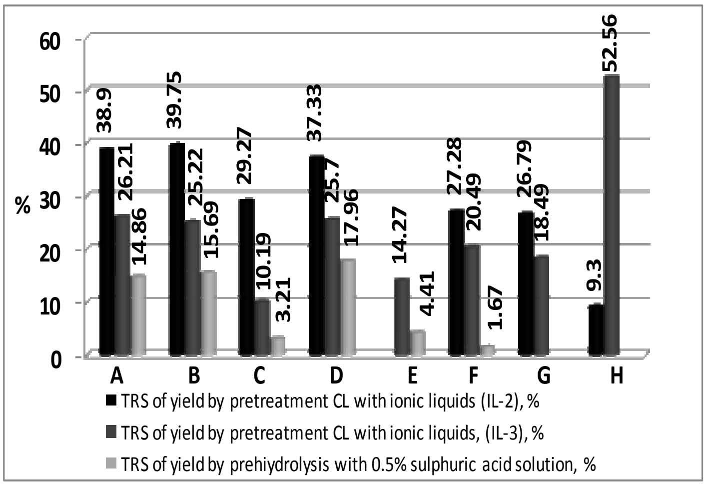

Fig. 3 − The total reducing sugars yields obtained before and after pretreatment with ionic liquids (*A* - CL obtained by prehydrolysis rapeseed stalks of H_2SO_4 0.5%, 170°C, dynamic conditions; *B* - CL obtained by prehydrolysis rapeseed stalks of H_2SO_4 0.5%, 170°C, static conditions; *C* - CL obtained by prehydrolysis rapeseed stalks of $Al_2(SO_4)_3$ solution 3%, 170°C, dynamic conditions; *D* - CL obtained by prehydrolysis rapeseed stalks of $Al_2(SO_4)_3$ solution 3%, 170°C, static conditions; *E* - CL obtained by prehydrolysis rapeseed stalks of H_2O, 170°C, dynamic conditions; *F* - CL obtained by prehydrolysis rapeseed stalks of H_2O, 170°C, static conditions; *G* - Rapeseed stalks; *H* - *Avicel* cellulose).

Ionic liquid pretreatment removes more lignin and hemicellulose than dilute acid pretreatment, TRS (total reducing sugars) yield ranges between 17.96% (prehydrolysis rapeseed stalks of $Al_2(SO_4)_3$ solution 3%, 170°C, static conditions) to 39.75% (pretreatment of 1-butyl-3-methyl imidazolium chloride and cellolignin (CL) obtained by prehydrolysis rapeseed stalks of H_2SO_4 0.5%, 170°C, static conditions).

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Compared to the untreated sample, results are summarized shown ionic liquid (1-butyl-3-methylimidazolium chloride – IL-2) pretreatment decreases the polyssacharides (Pz)/lignin (L) ratio from 2.10 (rapeseed stalks) to 1.44 (pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of H_2O, 170°C, static conditions).

Table 1
Absorbance Ratio of Cellolignins Determined by FTIR Spectroscopy

Sample	Pz/L ($1060\ cm^{-1}/1510\ cm^{-1}$)
rapeseed stalks	2.10
pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of $Al_2(SO_4)_3$ solution 3%, 170°C, dynamic conditions	2.63
pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of $Al_2(SO_4)_3$ solution 3%, 170°C, static conditions	3.21
pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of H_2SO_4 solution 0.5%, 170°C, dynamic conditions	4.00
pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of H_2SO_4 solution 0.5%, 170°C, static conditions	8.33
pretreatment of IL-2 and CL obtained by prehydrolysis rapeseed stalks of H_2O, 170°C, static conditions	1.44

CL - cellolignin
IL-2 - 1-butyl-3-methylimidazolium chloride

4. Conclusions

Avicel cellulose and rapeseed stalks have been performed with different ionic liquids. The results of the comparative analysis, both dilute acid and ionic liquid pretreatment show that the remove lignin and hemicelluloses ranging from 10.19% to 39.75%. FTIR analysis indicated that ionic liquid treated vegetal materials exhibited a significant loss of native cellulose crystalline structure (the cellulose/lignin ratio from 2.10 to 1.44).

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PRETRATAREA MATERIALELOR VEGETALE PRIN DIZOLVAREA ÎN LICHIDE IONICE

(Rezumat)

În această lucrare se investighează efectele de dizolvare a materialelor vegetale în lichide ionice: acetat de 1-etil-3-metilimidazoliu; clorură de 1-butil-3-metilimidazoliu; clorură de 1-etil-2,3-dimetilimidazoliu; bromură de 3-(2-metoxi-2-oxoetil)-1-(3-metoxi-3-oxopropil) imidazoliu. Bun solvent pentru celuloza s-a dovedit a fi clorura de 1-butil-3-metil-imidazoliu, în timp ce pentru materialul vegetal este bromura de 3-(2-metoxi-2-oxoetil)-1-(3-metoxi-3-oxopropil)imidazoliu. Un randament total de zaharuri reducătoare (TRS) de 39,75% a fost obținut prin utilizarea clorurii de 1-butil-3-metil imidazoliu la 105°C, timp de reacție 300 min.