

NEW FINDINGS ON THE DELIGNIFICATION OF AUSTRALIAN RICE HUSK USING LOW-COST AMINO ACID BASED IONIC LIQUID

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ABSTRACT

In this work, two choline-based low-cost ILs (i.e., [Ch][Gly] and [Ch][Cl]) were synthesised in laboratory and applied for the delignification treatment of "Rice Husk (RH)", an abundantly available lignocellulosic biomass in Australia. The synthesised choline based ILs were compared with commercially available imidazolium based IL ([Emim][OAc]). Among the all ILs studied, [Ch][Gly] outperformed over others in terms of degree of delignification. In addition, it has been established for the first time that *RCRM* produced from the choline-based ILs has higher porosity, crystallinity and thermal stability compared to imidazolium based ILs. The findings from this work recommends that pre-treatment with choline-based ILs is highly favorable for the production of platform chemicals from lignocellulosic biomass.

Keywords: Low-cost ionic liquids; Lignocellulosic biomass; Pre-treatment; Biofuels; Biochemicals.

NOMENCLATURE

Abbreviations

[Emim][OAc]	1-ethyl-3-methylimidazolium acetate
<i>RCRM</i>	Regenerated cellulose-rich material
<i>DoD</i>	Degree of delignification
ChOH	Choline hydroxide
[Ch][Gly]	Choline glycinate
[Ch][Cl]	Choline chloride
XRD	X-ray powder diffraction
FTIR	Fourier-transform infrared
TGA	Thermogravimetric analysis
DTG	Differential thermogravimetric
SEM	Scanning electron microscope
<i>CrI</i>	Crystallinity index
RCCI	Relative change in <i>CrI</i>

1. INTRODUCTION

The utilisation of lignocellulosic biomass on the production of biofuels and biochemicals has gained

tremendous attention because of high level of emissions from fossil fuel based technologies and rapid depletion of fossil fuels [1]. In lignocellulosic biomass, the lignin along with the cellulose and hemicellulose makes the lignocellulosic structure complex and rigid which limits its possibility to be transformed into energy and value-added materials [2–4].

The pre-treatment of lignocellulosic biomass can alter the structure of biomass and the biomass derived fractions become ready for further processing into biofuels and biochemicals. Considering the capital and operating costs, the chemical pre-treatment methods (i.e., dilute acid treatment, alkali treatment and organic solvent treatments) have been found superior over physical and biological pre-treatment methods [2,5,6]. However, the chemicals used in these pre-treatment methods are highly flammable and volatile and therefore their applications have severe environmental, health and safety consequences. In addition, the low recovery of the treating chemicals is a significant shortcoming of the chemical pre-treatment processes.

Recently, the chemical pre-treatment of lignocellulosic biomass employing ILs is gaining tremendous interest because of the environmental benefits [7]. The imidazolium cation based ILs are commercially available and their potentiality as a solvent for lignocellulosic biomass dissolution and lignin separation is proven [2,7]. However, the synthesis cost of these ILs are high and this is considered to be the main bottleneck on their application in industrial-scale IL pre-treatment processes [2]. While the recycling of ILs are often considered as the solution to optimise cost for IL pre-treatment processes, there is also cost associated with the recycling of ILs. In addition, the performance of ILs is degraded after several recycling. Therefore, it is important to develop environmentally friendly and economically viable ILs for the pre-treatment of lignocellulosic biomass. Choline-based ILs is considered

as low-cost and biodegradable solvent for the effective pre-treatment of lignocellulosic biomass [8,9].

The aim of this work is to synthesise choline-based low-cost ILs and compare their pre-treatment performance with a commercially available imidazolium-based IL in terms of *DoD* and the quality of *RCRM*.

2. MATERIALS AND METHODS

2.1 Materials and pre-treatment experiments

The *RH* sample was sourced from a Victorian local supplier. Acetone (purity \geq 99.9%), choline hydroxide (46 wt% in water), glycine (purity \geq 99%) and [Emim][OAc] (purity 95%) were purchased from Sigma Aldrich. Sulphuric acid (72 w/w%) and hydrochloric acid (32 w/w%) was obtained from RCI Labscan.

Choline-based ILs were synthesised with a slight modification of the method presented in the previous literature [10]. In the synthesis of [Ch][Gly], equimolar ChOH and glycine were mixed in water where the ratio of water and glycine was 4:1. The mixture was heated at 70 °C with continuous stirring for 5 h. For [Ch][Cl] synthesis, equal molar amount of hydrochloric acid was added drop-wise into the ChOH at room temperature with continuous stirring. The ILs were then heated to evaporate moisture.

The pre-treatment experiments were conducted following our previous study [11]. Briefly, 0.5 g *RH* was pre-treated with 5 g IL at 120 °C and 500 rpm for 5 h. Each pre-treatment experiment was repeated for three times. The pre-treated solution was diluted with 50% (v/v) aqueous acetone and centrifuged to separate *RCRM*. The *RCRM* was washed with distilled water, dried overnight at 90 °C and then quantified. The filtrate was then concentrated by evaporating acetone and the pH was of the filtrate was maintained at 2. The solution was centrifuged and lignin was separated by filtration. The solid lignin was washed with distilled water and dried overnight at 90 °C. Finally, the dried lignin was quantified to estimate *DoD*.

2.2 Characterisation techniques

The quality of *RCRM* samples was assessed by their detail characterisations using XRD, FTIR, TGA and SEM analysers. The crystallinity of *RCRM* samples were analysed by XRD, while the thermal stability of those samples were studied by TGA. The variations in the surface morphologies of the *RCRM* samples were investigated using SEM instrument.

3. RESULTS AND DISCUSSION

3.1 Degree of delignification investigation

Table 1 shows the influence of various IL pre-treatments on the recovery yield of *RCRM* and *DoD*. As can be seen from the experimental investigation, [Ch][Gly] pre-treatment of *RH* extracted more lignin compared to other pre-treatments with a value of 63.2%. According to the data of Table 1, *DoD* capabilities of the ILs can be ordered as follows: [Ch][Gly] > [Ch][Cl] > [Emim][OAc]. However, the ILs showed the reverse order for *RCRM* yields. For instance, [Ch][Gly] yielded the lowest (66.1%) *RCRM* due to its strong ability to remove lignin and hemicellulose.

Table 1 *RCRM*, *DoD*, *CrI* and *RCCI* of various pre-treatment

Condition	<i>RCRM</i> yield (%)	<i>DoD</i> (%)	<i>CrI</i> (%)	<i>RCCI</i> (%) ^a
Untreated <i>RH</i>	-	-	42.3 \pm 0.9	-
[Emim][OAc] treatment	77.2 \pm 3.4	47.5 \pm 3.1	26.3 \pm 1.6	37.9 \pm 2.5
[Ch][Gly] treatment	66.1 \pm 1.4	63.2 \pm 2.9	44.3 \pm 1.3	-4.8 \pm 0.5
[Ch][Cl] treatment	72.5 \pm 2.4	55.1 \pm 4.1	43.1 \pm 0.6	-1.7 \pm 0.3

^a(-) indicates the increase in *CrI*

The colour of the *RCRM* samples changed after the pre-treatments as shown in Fig. 1. In the case of [Ch][Gly] pre-treatment, the colour of the *RCRM* was whiter compared to the other *RCRM* samples and this is due to the higher amount of lignin removal by [Ch][Gly]. This observation is consistent to the *DoD* values of the pre-treatments.



Fig 1 Images of untreated *RH* and *RCRM* samples

3.2 XRD and crystallinity analysis of *RCRM* samples

Fig. 2 illustrates the XRD spectra of untreated *RH* and *RCRM* samples obtained from the pre-treatment of *RH* using [Emim][OAc], [Ch][Gly] and [Ch][Cl]. The major peaks at I_{101} , I_{002} and I_{040} indicate crystalline Cellulose I

structure in native biomass. The *CrI* of untreated *RH* was about 42.3% and it was found to be increased to 44.3 and 43.1% for [Ch][Gly] and [Ch][Cl] treatments respectively. This increase in *CrI* was most likely associated with the removal of amorphous lignin and hemicellulose which outplayed the degree of Cellulose I to amorphous Cellulose II transformation. Another reason for this increase in *CrI* might be the accumulation of degraded products during the pre-treatment. In the case of [Emim][OAc] pre-treatment, the *CrI* value of *RCRM* sample was observed to be reduced by 37.9%. In this case, the crystalline peak at 22.2° shifted to lower angle at 20.8°. The peak at 16.2° was completely disappeared and this was linked to the transformation of crystalline Cellulose I to amorphous Cellulose II.

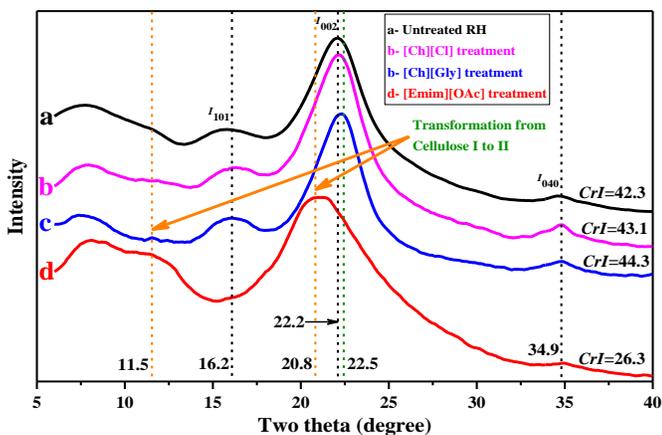


Fig 2 XRD patterns of untreated *RH* and *RCRM* samples

3.3 Thermal stability of *RCRM* samples

The changes in thermal stability of *RCRM* samples after pre-treatment of *RH* were analysed. TGA and DTG profiles were developed as illustrated in Fig. 3 (A) and (B), respectively. The thermal profile of *RCRM* samples was significantly different from the untreated *RH*. The major decomposition temperature for untreated *RH* was about 352 °C. In the case of [Emim][OAc] pre-treatment, the peak decomposition temperature shifted to lower temperature (312 °C) indicating relatively lower thermal stability. This alteration of the thermal stability of *RCRM*, in the case of [Emim][OAc] pre-treatment, was most likely due to the presence of amorphous Cellulose II in the *RCRM* and reduced crystallinity. On the contrary, the DTG peak temperature for *RCRM* samples from choline-based IL pre-treatments shifted towards higher temperatures. The higher thermal stability of *RCRM* samples, in the case of choline-based IL pre-treatments, was associated with the removal of amorphous components of lignocellulosic structure.

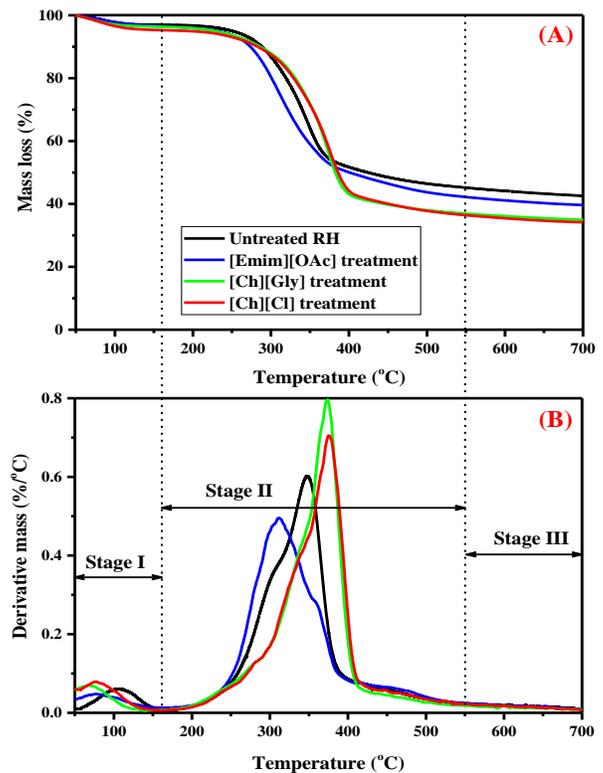


Fig 3 Thermal profiles of untreated *RH* and *RCRM* samples

3.4 FTIR spectroscopic analysis of *RCRM* samples

Fig. 4 shows the FTIR spectroscopic analysis of untreated *RH* and *RCRM* samples. Some noticeable differences were observed between the untreated *RH* and *RCRM* samples. In the case of [Emim][OAc] pre-treatment, the OH stretching peak of cellulose at 3310 cm^{-1} shifted to 3385 cm^{-1} demonstrating the Cellulose I to II transformation. The unconjugated C=O stretch vibration in hemicellulose and lignin at 1718 cm^{-1} , C=O unconjugated stretching in hemicellulose at 1718 cm^{-1} , C=C stretching in lignin and hemicellulose at 1421 cm^{-1} and the aromatic skeletal of lignin at 1585 cm^{-1} almost disappeared from *RCRM* samples due to the removal of lignin and hemicellulose during IL pre-treatment.

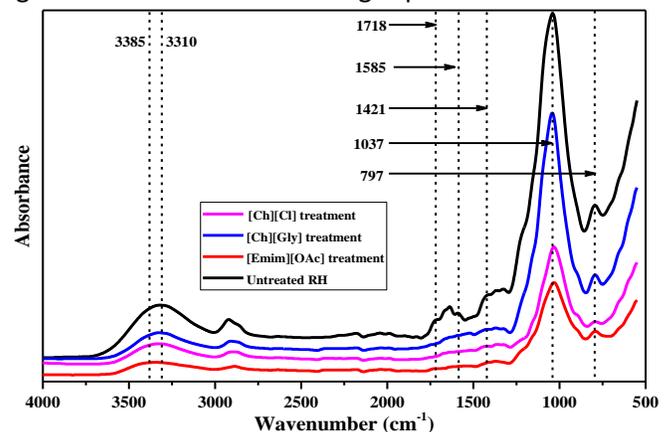


Fig 4 FTIR spectra of untreated *RH* and *RCRM* samples

3.5 Surface morphology analysis of RCRM samples

The surface morphology of untreated *RH* and changes in surface morphology of *RCRM* samples are illustrated in Fig. 5. It can be seen from the SEM images that the morphology of *RH* greatly altered after IL pre-treatments. The untreated *RH* was observed to be intact and compact lignocellulosic structure. The *RCRM* samples exhibited different structural morphology when compared to untreated *RH*. The lignocellulosic structure of *RH* was largely destroyed upon the IL pre-treatments as evident in SEM images. [Emim][OAc] pre-treatment produced *RCRM* with large pores whereas the *RCRM* samples produced from the [Ch][Gly] and [Ch][Cl] pre-treatment contained fibers.

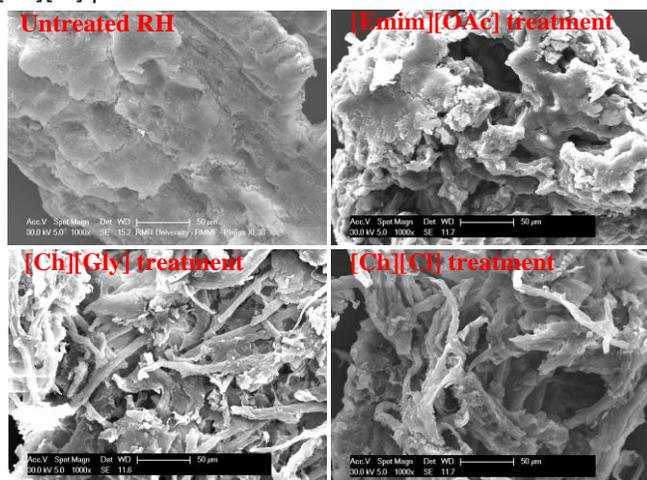


Fig 5 SEM images of untreated *RH* and *RCRM* samples

4. CONCLUSIONS

Choline-based ILs was found to be efficient low-cost green solvent for the extensive removal of lignin and hemicellulose from lignocellulosic structure of *RH*. Amino acid-based [Ch][Gly] was the most favorable for lignin extraction and this IL demonstrated 63.2% lignin removal from *RH*. Although, the *CrI* and thermal stability of *RCRM* samples increased after choline-based ILs pre-treatment, high *DoD* can be favorable for the production of glucose and anhydrosugars. Therefore, choline-based low-cost ILs showed promising delignification efficiency and opportunities to develop techno-economically viable integrated processes such as IL pre-treatment–pyrolysis on the transformation of *RH* into cellulose based various biochemicals.

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