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Blended ionic liquid systems for macroalgae pretreatment

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ABSTRACT

A novel ionic liquid (IL) blend system, consisted of a solvent IL for biomass dissolution and an acidic IL for acid-catalyzed hydrolysis of the released polysaccharides into simple sugars, was developed for the pretreatment of macroalgae *Gelidium amansii*. Acidic ILs with varying Hammett acidities were screened; among which, 1-*n*-butyl-3-methylimidazolium hydrogen sulfate was found most suitable as it provided the highest sugar yields with lowest propensity to degrade the produced sugars. On the other hand, 1-*n*-butyl-3-methylimidazolium chloride was found the most effective solvent IL for *G. amansii*. A compositional balance between the solvent IL and AIL was found critical to achieve the highest sugar yields. Interestingly, it was notable that the macroalgae was more efficiently dissolved in the selected IL blend than in the most effective pure solvent IL. Pretreatments can be accomplished under atmospheric environment but temperature control and timely reaction termination were both important in order to maximize the sugar yields and minimize the subsequent sugar degradation. Overall, the developed IL blend system proved to be viable for the pretreatment of macroalgae, an abundant renewable resource of fermentable sugars as valuable precursors for biofuel or biochemical production.

1. Introduction

Macroalgae has become a viable resource of sugars as precursors for the production of biofuels and platform chemicals owing to its abundance, ease of cultivation and high photosynthetic efficiency [1–4]. Pretreatment studies reported the high carbohydrate contents of several red and brown seaweeds like *Gelidium amansii*, *Undaria pinnatifida*, *Laminaria japonica*, *Sargassum fulvellum* and other species, from which simple sugars have been successfully recovered [5–7].

Chemical saccharification of macroalgae is typically performed in an aqueous environment which involves initial biomass dissolution to depolymerize its fibrillar matrix followed by an acid-catalyzed hydrolysis of the liberated polysaccharides into simple sugars [8–10]. Despite its simpler chemical and structural properties than lignocellulosic biomasses, macroalgae is sparingly soluble in water thus necessitates heated and pressurized systems (i.e. up to 10 bars) to accomplish the pretreatment [5,6,11]. For a more expedient method under relatively milder pretreatment conditions, recent studies focused on environmentally benign ionic liquids (ILs) in which a myriad of cation/anion pairs have been combined and tuned to function as (1) biomass solvents, (2) acid catalysts or as (3) media with dual properties as solvent and acid catalyst [5,11–14].

A recent review reported that majority of the most effective biomass solvent ILs are imidazolium-based cations with counterions having high hydrogen bond accepting abilities [11,12,15]. The high solvency power of certain ILs is associated with their ability to disrupt the Van der Waals and hydrogen bond interactions within the biomass matrix [11,12,15–17]. However, most of the known effective solvent ILs are neutral hence require mineral acids or solid acid catalysts addition for the hydrolysis step [5,7,18–21]. Meanwhile, ILs with acidic properties (AILs) have been utilized as catalysts for the hydrolysis of macroalgae; early reports demonstrated better sugar yields in AIL-catalyzed systems than those with mineral acids [11,14]. However, AILs have only been used as mineral acid substitutes in aqueous systems hence its application in conventional energy-demanding pretreatment systems remains an issue.

More recent development in IL-based pretreatment systems involves the utilization of ILs with dual functionalities as a solvent and as an acid catalyst (i.e. solvent AIL). Solvent AIL eliminates the necessity of mineral acid addition, post-treatment neutralization or separation of spent solid acid catalysts [14]. But the availability of task specific solvent AILs for biomass pretreatment remains limited.

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Furthermore, solvent AIL lacks tunability; utilization of a pure solvent AIL may result in an extreme chemical environment (i.e. excessive acidity) unfit for macroalgae pretreatment. The difficulty to control the conditions could lead to sugar degradations which may compromise the reaction selectivity towards sugar production [3,22–26].

Alternatively, blending two IL components, (1) a biomass solvent IL and (2) an acidic IL catalyst, is a convenient technique to produce an IL mixture with similar features as those of a solvent AIL. Apart from the dual property of the blend, IL mixture properties such as solvency power and acidity levels can be easily tuned by simply changing the component ratios. As far as is known, this is the first report on IL blend systems for biomass pretreatment application.

In this study, the potential of blended ILs as alternative biomass pretreatment systems is investigated. With the current interest on galactose and glucose as renewable chemical precursors, *G. amansii* was selected as a substrate due to its high carbohydrate content. *G. amansii* is particularly abundant in warm shallow coastal areas in sub-tropical countries [19].

Specifically, the current work addresses the following objectives: (1) to develop a suitable blended IL system by screening several choices and pairs of imidazolium-based ILs as solvent IL or AIL components (Fig. 1), (2) to identify the critical reaction parameters (i.e. blend composition, temperature, time) which could facilitate high sugar yields and high hydrolysis selectivity (i.e. minimization of sugar degradation) and (3) to propose a tentative biomass pretreatment mechanism involved in a blended IL system.

2. Materials and methods

2.1. Materials

Dried *G. amansii* was supplied by Natural Food (http://0808.or.kr) from Sanjeong-dong, Mokpo, South Korea. The raw sample was washed with deionized water (DI) to remove residual salts and then dried at 40 °C until ≤10 wt% of moisture content was achieved. The dried red algae was then pulverized and stored in a desiccator at room temperature when not in use.

All ILs were kept in a drying oven when not in use. Ionic liquids bearing 1-*n*-butyl-3-methylimidazolium (BMIM) cations with counterions such as chloride (≥98% [BMIM]Cl), hydrogen sulfate (≥94.5% [BMIM]HSO_4) and tetrafluoroborate (≥98% [BMIM]BF_4) were purchased from Sigma Aldrich (Mo., USA) whereas [BMIM] with acetate anion (≥98% [BMIM]OAc) was supplied by C-TRI (South Korea). Other ILs, 1-*n*-ethyl-3-methylimidazolium chloride (97% [EMIM]Cl) and 1-allyl-3-methylimidazolium chloride (>98% [AMIM]Cl), were from Acros Organics (Belgium). Other [BMIM]-based ILs with dihydrogen phosphate ([BMIM]H_2PO_4), nitrate ([BMIM]NO_3) and p-Toluenesulfonate ([BMIM]pTsO) anions were synthesized in the laboratory according to the methods described elsewhere [27–29].

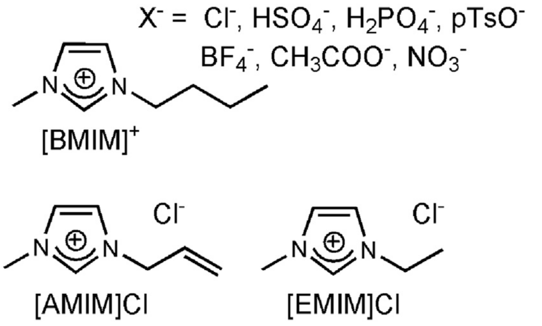

Fig. 1. Imidazolium-based ILs used either as solvent IL or AIL in this study.

Other reagents such as phosphoric acid (85% H_3PO_4), sulfuric acid (H_2SO_4), dichloromethane, para-toluenesulfonic acid (pTSA), 4-nitroaniline, D-Galactose (≥99%) and 5-hydroxymethylfurfural (≥99% 5-HMF) were procured from Sigma–Aldrich (Mo., USA). D-Glucose was purchased from Acros Organics (Belgium).

2.2. Chemical composition of *G. amansii*

The biomass moisture content was maintained <10 wt% prior to characterization [30]. The carbohydrate content of *G. amansii* was determined using a two-step acid hydrolysis reaction according to the National Renewable Energy Laboratory (NREL) protocol TP-510-42618 [31]. The NREL protocol was designed for lignocellulosic biomass hence was modified for samples more amenable to hydrolysis like *G. amansii*. Particularly, the reaction time of the first hydrolysis step was shortened from 60 ± 5 min to 30 min as it afforded maximum release of sugars and minimum sugar degradation products (Supporting information Fig. S1). Contents of *G. amansii* components such as D-Glucose, D-Galactose, 3,6-anhydro-L-Galactose (AHG), protein, lipid, ash content, residual moisture, acid soluble- and insoluble lignin were measured according to the analytical methods described in Section 2.5.

2.3. *G. amansii* pretreatment experiments

The pretreatments were performed under atmospheric pressure. In a 20 mL vial, a solvent IL and an AIL were blended at an appropriate mass ratio via magnetic stirring for 30 min in an oil bath kept at constant temperature (i.e. 120 °C). Dried biomass sample was then added at 3 wt% with respect to the mass of the IL mixture. Hydrolysis was initiated upon addition of 155 mg DI water. Aliquots of the reaction mixture were taken periodically, weighed (M_1) and immediately quenched with chilled DI water (V_1). The sample mixture was centrifuged for 10 min at 10,000 rpm then passed through a 0.22 μm syringe filter prior to sugar and decomposition products analysis as detailed in Section 2.5.

2.4. Pretreatment conditions

Five AILs were screened to determine the most suitable acid catalyst for *G. amansii* pretreatment. AIL candidates [BMIM]HSO_4, [BMIM]pTsO, [BMIM]H_2PO_4, [BMIM]OAc and [BMIM]BF_4 were individually blended with [BMIM]Cl at a fixed mass ratio of 1:1. [BMIM]Cl was initially selected as the solvent IL as it effectively dissolved cellulose and brown macroalgae in previous studies [7,12]. The pretreatment experiments were carried out at 120 °C based on an earlier investigation [7]. The most suitable AIL was identified in terms of: (1) maximum sugar yields, (2) sugar degradation product formation and (3) kinetic analysis.

With the selected AIL, other solvent ILs containing different cation and anion components were also evaluated. Pretreatment efficiencies of six solvent ILs (blended individually with the selected AIL at 1:1 mass ratio) were determined. The most suitable solvent IL/AIL blends were identified in terms of maximum sugar yields. Further optimization of the selected IL blend was performed by varying the IL component mass ratio, temperature (120 °C–150 °C) and reaction period (15 min–5 h).

2.5. Analytical methods

Sugar and decomposition products from hydrolysis reactions and compositional analysis were quantified using High