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Pretreatment and Fractionation of Wheat Straw Using Various Ionic Liquids

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ABSTRACT: Pretreatment of lignocellulosic biomass with ionic liquids (ILs) is a promising and challenging process for an alternative method of biomass processing. The present work emphasizes the examination of wheat straw pretreatment using ILs, namely, 1-butyl-3-methylimidazolium hydrogensulfate ([bmim][HSO_4]), 1-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium dicyanamide ([bmim][$N(CN)_2$]). Only [bmim][HSO_4] was found to achieve a macroscopic complete dissolution of wheat straw during pretreatment. The fractionation process demonstrated to be dependent on the IL used. Using [bmim][SCN], a high-purity lignin-rich material was obtained. In contrast, [bmim][$N(CN)_2$] was a good solvent to produce high-purity carbohydrate-rich fractions. When [bmim][HSO_4] was used, a different behavior was observed, exhibiting similarities to an acid hydrolysis pretreatment, and no hemicellulose-rich material was recovered during fractionation. A capillary electrophoresis (CE) technique allowed for a better understanding of this phenomenon. Hydrolysis of carbohydrates was confirmed, although an extended degradation of monosaccharides to furfural and hydroxymethylfurfural (HMF) was observed.

KEYWORDS: *green solvents, fractionation, cellulose, hemicellulose, lignin, capillary electrophoresis*

INTRODUCTION

The undiscovered potential of lignocellulosic biomass to obtain a variety of value-added products requires broad research to ensure the feasibility of lignocellulosic biorefineries. One of the major limitations of the biorefinery concept is the lack of an efficient biomass processing tool, which could compromise investment in this sector. Therefore, studies on biomass pretreatment and fractionation were developed to efficiently overcome the recalcitrance of lignocellulose and reduce costs of biorefinery processes.[1−4]

The composition of lignocellulose is mainly ascribed to three general components, namely, cellulose, hemicellulose, and lignin. The isolation of each fraction from lignocellulose is required to achieve maximal valorization of a low-cost feedstock by producing valuable commodities, such as hydroxymethylfurfural (HMF) and levulinic acid (cellulose derivatives),[5,6] furfural and xylitol (hemicellulose derivatives),[7,8] and phenolic compounds and styrenes (lignin derivatives).[9] A new and attractive process that allows cellulose, hemicellulose, and lignin as separated fractions is the pretreatment of biomass using ionic liquids.[10,11]

Ionic liquids (ILs) are usually organic salts with melting points below 100 °C. ILs as design solvents demonstrate a great variety of physicochemical properties. The most common properties of ILs are a high polarity,[12] a great thermal stability (even above 300 °C),[13] a high conductivity and a large electrochemical window, a great solvent power,[14,15] a negligible volatility, and nonflammability.[16] The toxicity and biodegradability of ILs is an important issue, and in the past years these topics were studied extensively.[17,18]

The unique properties of ILs allow their use for biomass processing in pretreatment and/or extraction processes.[19−22] ILs have an ability to dissolve biomass by an effective disruption of the complex network of noncovalent interactions between carbohydrates and lignin.[23,24] Generally, a complete biomass dissolution should be attained during the pretreatment to improve the efficiency of the process. After pretreatment with specific conditions (temperature, residence time, and biomass/IL ratio), an antisolvent is added to the solution mixture, promoting carbohydrate precipitation as a recovered material. Lignin and other soluble compounds are partially extracted to the liquid phase.[25] Lignin can be further recovered by acidification of the antisolvent/IL medium.[26−28] From the regenerated material, hemicellulose and cellulose can be obtained as separated fractions using specific solvents to maximize the fractionation process.[26,27,29,30]

1-Ethyl-3-methylimidazolium acetate ([emim][CH_3COO]) is the most often reported IL due to its good solubility properties for biomass. Nevertheless, there is room for additional investigation of new ILs for biomass pretreatment, especially with a specific goal such as integrated biomass selective fractionation and hydrolysis.[31−33]

In a previous work a wheat straw fractionation using [emim][CH_3COO] was successfully carried out.[26] The aim of the present investigation relies on evaluation of the versatility of the previously developed method[26] using the three different ILs

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