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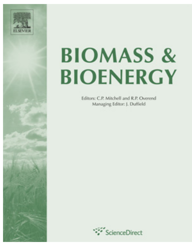

Characterisation of lignins isolated from sugarcane bagasse pretreated with acidified ethylene glycol and ionic liquids

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ABSTRACT

Sugarcane bagasse pretreatment processes using acidified aqueous ethylene glycol (EG) and ionic liquids (ILs) have been reported recently. In this study, recovery of lignins from these processes was conducted, as well as determination of their physico-chemical properties. The amount of lignins recovered from 1-butyl-3-methylimidazolium chloride ([bmim]Cl) with HCl as a catalyst and [bmim][CH_3SO_3] was ~42%, and ~35%–36% by EG with HCl or H_2SO_4 as a catalyst, respectively. The isolated lignins were characterised using wet chemistry, spectroscopy and thermogravimetry analysis (TGA), and the results compared to soda lignin from NaOH pretreatment of bagasse. The IL and EG lignins contained no or trace amounts of carbohydrates, slightly lower hydrogen content but slightly higher oxygen contents than soda lignin. The IL and EG lignins contained more C-3 and C-5 reactive sites for Mannich reaction and had more *p*-hydroxypheny propane unit structures than soda lignin. Two-dimensional heteronuclear single quantum coherence (2D HSQC) nuclear magnetic resonance (NMR) identified the major substructural units in the lignins, and allowed differences among them to be studied. As EG lignins were extracted in very reactive environment, intermediate enol ethers were formed and led to cleavage reactions which were not apparent in the other lignins. ^{31}P NMR and infra-red spectroscopy results showed that IL and EG lignins had lower total hydroxyl content than soda lignin, probably indicating that a higher degree of self-polymerisation occurred during bagasse pretreatment, despite the use of lower temperature and shorter reaction time. On the basis of the salient features of these lignins, potential applications were proposed.

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1. Introduction

Lignocellulosic biomass is the most abundant renewable resource on Earth. It has the potential to partly replace fossil-based resources (*e.g.*, coal, crude oil) for the production of fuels and chemicals. This will reduce the levels of greenhouse gas emissions and alleviate the pressure on depletion of the fossil-based non-renewable resources. Lignocellulosic biomass generally consists of three major components, namely, cellulose, hemicellulose and lignin. Bioconversion of carbohydrates (*i.e.*, cellulose and hemicellulose) in lignocellulosic biomass requires pretreatment followed by enzymatic hydrolysis of the biomass to release sugars which can be fermented by microorganisms [1]. The aim of pretreatment is to change the structure and/or the composition of biomass so that the subsequent enzymatic hydrolysis can efficiently and cost-effectively produce fermentable sugars [1,2].

Lignin is a heterogeneous, aromatic and amorphous copolymer binding hemicellulose and cellulose by ester linkages and hydrogen bonds, respectively [3]. Lignin has three monolignol monomers, methoxylated to various degrees: *p*-coumaryl, coniferyl and sinapyl alcohols [4], which exist in lignin as three basic substructure units: *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units respectively [5,6]. The degree of lignin polymerisation in nature is difficult to measure and the exact structure of lignin is still unknown since it is fragmented during delignification/extraction processes [4]. The presence of lignin in biomass reduces the efficiency of enzymatic hydrolysis of carbohydrates due to the formation of physical lignin barriers. These limit the access of cellulases to cellulose [7,8], and/or the non-productive cellulases binding with lignin [7,9]. Therefore, biomass delignification is the target of many pretreatment processes.

Lignin is a potential raw material for the production of lignin-based polyesters and polyurethanes, carbon-fibres, plastics, surfactants, adhesives and so on [10,11]. The properties of lignin largely depend on the fractionation process and the type of biomass involved [4,12–15], which influence potential lignin applications [14]. Lignin of herbaceous crops typically contains all three basic units whereas softwood lignin is composed mainly of G units and trace amounts of H units and hardwood lignin contains mainly G and S units and minor amounts of H units [12]. Mansouri and Salvado found that the contents of phenolic hydroxyl, aliphatic hydroxyl, and methoxyl groups and the weight average molecular weight (M_w) and number average molecular weight (M_n) varied among five lignins produce by the Kraft, lignosulfonate, soda-anthraquinone, organosolv and ethanol processes [14], which affected the type of application. They suggested that Kraft and soda–anthraquinone lignins are good candidates for producing lignin-based phenol–formaldehyde resins since they have a higher proportion of phenolic hydroxy group, and hence are more reactive towards modification [14].

A number of analytical techniques have been developed to determine the properties of lignin. Some basic properties such as thermostability, molecular weight and elemental composition can be measured by thermogravimetric analysis (TGA), gel permeation chromatography (GPC) and elemental analysis respectively [4,16]. Specific functional groups and structural moieties can be determined by wet chemistry methods such as nitrobenzene oxidation (NBO), thioacidolysis (TA), derivatization followed by reductive cleavage (DFRC) [17]. Furthermore, nuclear magnetic resonance (NMR) spectroscopy including proton-, carbon-, phosphorous-, and two-dimensional heteronuclear single quantum coherence (H, ^{13}C, ^{31}P and 2D HSQC) NMR enables to reveal the general picture of lignin structure [5,6,12,18,19]. One dimensional (1-D) NMR techniques (*i.e.*, ^{1}H and ^{13}C NMR) usually suffer from severe signal overlap issues [12] while 2D HSQC NMR is able to solve this problem especially in the determination of lignin subunits and the presence of lignin–carbohydrate complexes although the latter technique only provides relative proportions of the detected structures rather than the absolute values [12,19]. ^{31}P NMR has also been widely used to quantitatively determine the amount of hydroxyl groups in lignin after phosphitylation of lignin [12].

In the last decade, the use of ionic liquids (ILs) for pretreatment (including dissolution and fractionation) of lignocellulosic biomass to produce enzyme digestible carbohydrates has received wide research attention [20–22]. Lignin, as the major by-product of the IL process, has also been recovered and characterised [16,23–25]. The most studied IL for biomass dissolution and lignin extraction is 1-ethyl-3-methylimidazolium acetate ([emim][Ac]) or 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) [16,23,24,26–29], although other ILs such as 1-butyl-3-methylimidazolium chloride ([bmim]Cl), alkylbenzenesulfonate IL and nitrile-based ILs were also used [30–32]. Studies have shown that the lignin isolated with [emim][Ac] from poplar wood and lignin extracted from sugarcane bagasse by [bmim]Cl had similar structural features to milled wood lignin [16,30]. Other studies reported selectively removal of G units and increase in S/G ratio in the wood (Birch and Eucalyptus) lignin fractions extracted by [emim][Ac] [23,25].

A common feature for the majority of these reported IL processes is that biomass was first dissolved in the IL prior to the extraction and recovery processes. The dissolution processes are generally carried out at very low or zero water content [33]. Recently, several processes using acidified aqueous ILs and polyols (*e.g.*, EG) solutions for pretreatment of sugarcane bagasse have been developed [34–36]. The aqueous IL-based pretreatment process is different from most IL-based biomass dissolution processes in that: (1) the process includes significant amounts of water (up to a mass fraction of 30%) in the IL solutions, and (2) cellulose dissolution is insignificant. The use of aqueous solvents especially in ILs and polyols significantly reduces the solvent recovery costs (as complete removal of water is unnecessary). The aqueous solutions have low viscosities which will allow the use of high biomass loading necessary for industrial applications. Although polyols have long been used for biomass pulping [37], no detailed studies have been undertaken on recovered lignins from these processes.

To further improve the economics of the aqueous IL and polyol-based processes, effective recovery of the major by-products (*i.e.*, lignins) as well as characterisation of the isolated lignins are essential prior to identification of their potential applications. The lignin recovery process from our IL- and EG-based pretreatment processes was compared to

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