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Enhanced lignin extraction from different species of oil palm biomass: Kinetics and optimization of extraction conditions

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ABSTRACT

Lignin from industrial crops is a renewable bioresource which can be used for a variety of value-added applications, however effective separation of lignin from lignocellulosic biomass is still an ongoing challenge. The present study involves the selective extraction of lignins from three different morphological parts of oil palm biomass plant, namely empty fruit bunches (EFB), palm mesocarp fiber (PMF) and palm kernel shells (PKS) using Pyridinium Formate [PyFor], a Protic ionic liquid under mild extraction conditions compared to the conventional chemical processes. The effect of initial lignin contents and parameters (namely, particle size range, extraction temperature, time and solid loading) influencing the lignin extraction efficiency were analyzed and optimized using response surface methodology. The experiments conducted at the estimated optimum conditions gave the maximum lignin extraction of 92.01%, 91.23% and 90.70% at lowest process temperatures 351.5 K, 361.9 K and 370.8 K for EFB, PMF and PKS respectively. In a second-stage the extraction experiments were conducted to study the kinetics of extraction process under selected conditions and results were well correlated using pseudo-second order kinetics model. The theoretical lignin concentration at saturation (C_s), rate constant (K) and initial rate of extraction (h) at various temperatures ranging from 323 to 373 K were determined. The nature of biomass source and initial lignin content were found to have major impact on the extraction kinetics. Furthermore, the present estimated activation energies of 12 kJ mol^{-1}, 23 kJ mol^{-1} and 28 kJ mol^{-1} for the present extraction of lignins from EFB, PMF and PKS respectively are remarkably lower as compared to those reported in literature for traditional wood pulp processes. The extracted lignins were successfully characterized using FTIR and ^{1}H NMR analysis. The regeneration and recyclability of [PyFor] is also tested and the sustainability of the solvent for commercial application is proved.

1. Introduction

Oil palm biomass is considered as a renewable biomass resource for the biofuel production (Basiron, 2004; Putro et al., 2016). Lignocellulosic biomass consists of three basic macromolecular components namely cellulose, hemicellulose and lignin, which are the potential building blocks for the production of biofuels, biochemicals, and biodegradable products (Korotkova et al., 2015; Zhang, 2008). Among these lignin is the second most essential polymer in the plant world with distinctive properties (Korotkova et al., 2015; Sun and Cheng, 2002). Lignin is linear polymer containing branching points where chemical linkages to hemicellulose and cellulose do exist. (Ralph et al., 2007). Lignin can be considered as a potential source of many value-added products such as lignin based carbon fibers, isocyanate binders, biodispersants, phenolic and thermosetting resins etc. (Kadla and Kubo, 2004; Lora and Glasser, 2002). Lignin extraction from wood is a complex phenomenon, it involves the breaking of intermolecular bonds present between lignin and the plant matrix along with diffusion of lignin into the solvent (Korotkova et al., 2015). The most common separation techniques for commercial delignification of wood are kraft pulping (Abdul-Karim et al., 1995), sulfite pulping (Mansouri and Salvado, 2006), acid hydrolysis (Kumar et al., 2009) and organosolv pulping (Lu and Ralph, 2010). Due to the severity of the process conditions involved during the delignification process, such as; high temperatures and pressures, long dissolution times induce severe changes to the original lignin structure (Rashid et al., 2016; Wang and Chen,

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2016). Thus, in spite of the value-addition and attractive applications, only 1–2% of lignin is considered for valuable applications and the rest is being burnt as a low-grade fuel (Lora and Glasser, 2002; Putro et al., 2016; Zhang, 2008). Hence, the effective separation technique to break the compact network structure of lignocellulosic biomass, while preserving its biopolymers (cellulose, hemicellulose and lignin) from degradation is an essential feature, prior to its further utilization for the bio-refinery concept (Ho et al., 2011; Korotkova et al., 2015).

Recently protic ionic liquids (PIL's) have emerged as prospective solvents as they possess a range of distinctive properties, namely negligible vapor pressure, high thermal stability, and low chemical reactivity (Achinivu et al., 2014; George et al., 2015; Rashid et al., 2016). These unique characteristics, along with the fine tunable properties favor their application in diverse fields such as cationic surfactants, polymer membrane fuel cells, non −aqueous electrolytes etc. (Belieres and Angell, 2007). In the present study an attempt has been made to use Pyridinium Formate [PyFor] as a solvent (which is cost effective, less viscous, non-corrosive and easy to synthesize) to selectively extract lignin from biomass,.

The characteristics as well as the lignin contents of a lignocellulosic biomass would be expected to vary depending on the type and age of plant, weather and growing conditions etc. and above all the techniques employed for the separation (Esteves Costa et al., 2016; Tejado et al., 2007). Lignin is an amorphous tridimensional polymer consisting of three primary units: syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units, joined together by ether and C—C linkages (Nada et al., 1998; Tejado et al., 2007). The structure of lignin obtained from oil palm biomass (OPB) is more complex than the structure of wood lignin due to a complex arrangement of these (S), (G) and (H) units in the OPB fiber and shells (Sidik et al., 2013; Singh, 1999).

From our previous work it is evident that lignin extraction using [PyFor] is purely physical (Rashid et al., 2016) and the original lignin structure is not disturbed. To the best of our knowledge, there exists a gap in literature data regarding the kinetics of physical lignin extraction process (solid-liquid extraction) from biomass using [PyFor] as a solvent. An important engineering tool in order to design a process is the mathematical modeling to achieve reduced energy, time and solvent consumption (Kitanovic et al., 2008). Generally, kinetic models are categorized as physical and empirical. Physical models deal with the mass transfer phenomenon through plant tissues into the bulk of solvent, while empirical models explain the quantification of solute extracted by a specific solvent with respect to time (Kitanovic et al., 2008; Piwowarska and González-Alvarez, 2012). Though empirical models are simpler than physical models, but they still provide useful information related to the better understanding of the process and hence for upscaling (Abdul-Karim et al., 1995). Although there are a few literatures on empirical delignification kinetics using organic acids and soda pulping (Dang and Nguyen, 2006; Dapıa et al., 2002; Park et al., 1999), nevertheless these separation techniques are more concerned on efficient recovery of cellulose only. Few studies regarding delignification kinetics of wheat straw, bagasse and rice husk biomass have also been reported in literature (Abdul-Karim et al., 1995; Correia et al., 2001; Ho et al., 2011; Korotkova et al., 2015; Park et al., 1999; Tu et al., 2008; Yiwen, 1986). These studies can be summarized as following; Yiwen (1986) studied the mechanism and kinetics of delignification from rice husk and suggested that the whole phenomenon can be divided into three phases i.e. (i) bulk phase (90 °C); (ii) supplementary phase (90–150°C) and (iii) final phase at much higher temperature i.e. (≥150 °C). based on the studies on kraft pulping, Abdul-Karim et al. (1995) concluded that the delignification is governed by first order chemical reaction. Park et al. (1999) systematically analyzed the kinetics and mechanism of delignification as well as silica removal from rice straw and suggested that both process follows first order kinetics, which are similar to that of formic acid pulping of bagasse (Tu et al. (2008)). Correia et al. (2001) studied soda pulping delignification kinetics and calculated the activation energies for lignin removal from Canadian hemp. Two phases of delignification were identified by Ho et al. (2011) and respective equations for the transition times at various temperatures and catalyst dosages were reported. Korotkova et al. (2015) studied the isolation of lignin from spruce wood and analyzed the extraction kinetics, with respect to the alkali concentration. A comprehensive list of literature involving the kinetics of several extraction processes are compared in Table 9. From the available literature on the lignin extrtaction, it is evident that a there exists a gap in the fundamental understanding of the impact of the initial lignin concentration of lignin and the effect of several operating parameters such as; particle size, temperature, extraction time, solid loading on the lignin extraction from three different species of oil palm biomass (OPB) namely; Empty Fruit Bunch (EFB), Palm Mesocarp Fiber (PMF) and Palm Kernell Shells (PKS). In the present research Response Surface Methodology (RSM), a statistical tool, is used to determine an appropriate experimental design protocol. RSM was effectively utilized for experimental design, by examining the effects of multiple variables and optimizing these variables for the optimal response (Dehghani et al., 2016). The Box-Behnken design was selected and the experimental data were analyzed using Statgraphics Centurion 15.2.11.0 version 8.0. The optimum conditions for lignin extraction were identified. On the basis of these facts, the main objective of this work was to establish extraction kinetics of lignin removal from oil palm biomass using [PyFor], by exploring the influence of lignin contents and various operating parameters. From the experimental data, second order extraction model was employed to provide a quantitative representation of present lignin extraction process. In addition, the extraction activation energy (E_a) for the extraction process was also calculated. This can be helpful for both fundamental and applied perspective as it can contribute to the basic understanding of the lignin extraction process using protic ionic liquids.

2. Experimental section

2.1. Materials and methods

The starting material used for the current study include, Formic Acid 99% (w/w) and Pyridine (used as precursors for [PyFor] synthesis), Karl Fischer titration standards, Dimethyl Sulphoxide (DMSO-d_6), Benzene and Ethanol, (used as a solvent for extractives estimation using soxhlet extraction), Acetone (99% purity), Sulphuric acid 98% (w/w), Glacial Acetic acid 99% (w/w), 17.5% sodium hydroxide solution, sodium chlorite (used for the characterization of raw biomass) were purchased from Sigma Aldrich and used as received. Pyridinium formate was synthesized (Rashid et al., 2016). Fresh EFB, PMF and PKS samples were supplied by FELCRA, Nasaruddin Oil Palm Mill, Bota, Perak, Malaysia and stored at ≈5 °C. The raw biomass was washed with detergent solution (2%) in order to remove oil and greases. The washed biomass samples were dried under natural sun light for 24 h before being grinded and crushed using power cutting mill (Pulverizette 25). Subsequently, the grinded biomass samples were sieved to attain three different particle sizes of (0.1–0.3 mm), (0.3–0.5 mm) and (0.5–1.0 mm) respectively. Triple distilled water was used for the experiments.

2.2. Proximate analysis

The composition of EFB, PMF and PKS was determined based on the respective standard procedures: (i) acid insoluble and soluble lignin (TAPPI T222 om-02); (ii) holocellulose and a- cellulose (Teramoto et al., 2009); (iii) extractives ((NREL) laboratory analytical procedure (LAP-010)); (iv) moisture content (LAP-001); (v) ash content (LAP-005). All the present reported data were taken from the average of the duplicates.