Industrial Crops and Products 85 (2016) 389–402

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Multi response optimization of oil palm frond pretreatment by ozonolysis

Wan Nor Nadyaini Wan Omar, Nor Aishah Saidina Amin*

Chemical Reaction Engineering Group, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

ARTICLE INFO

Article history:
Received 28 July 2015
Received in revised form 10 January 2016
Accepted 12 January 2016
Available online 16 February 2016

Keywords:
Biomass pretreatment
Ozonolysis
Lignin degradation
TRS recovery
Oil palm frond
Multi response optimization

ABSTRACT

Oil palm frond (OPF) is a promising feedstock for the second-generation biofuel. However, the recalcitrant lignin layer conceals the cellulose component in the OPF and thus, curtails the conversion of cellulose to the value-added chemicals. The ozonolysis pretreatment is envisaged as an effective method for lignin degradation. This study investigated the influence of OPF particle size, moisture content, reaction time, ozone flowrate as well as their interaction, on lignin degradation and total reducing sugar (TRS) recovery by response surface methodology (RSM). The experiments conducted were based on Box-Behnken design (BBD). The process condition for the optimum lignin degradation and TRS recovery was determined by desirability function. The RSM analysis revealed that the interaction of particle size–moisture content was important for the lignin degradation while the interaction of moisture content–reaction time during ozonolysis was crucial for TRS recovery. Both the lignin degradation and TRS recovery at 84.7 wt.% and 99.9%, respectively were optimized simultaneously under the recommended optimum conditions. The pre-treated OPF under the optimum conditions yield the levulinic acid equivalent to the commercial cellulose.

1. Introduction

The whole plant, "non-food" perennial crops (woody biomass and tall grasses), lignocellulosic biomass residue, and wastes (woodchips from forest thinning and harvest residues, surplus straw from agricultural) have become potential feedstocks for second-generation biofuel (Centi and van Santen, 2007). The oil palm industry in Malaysia is the second largest in the world which has generated an abundance of sustainable biomass materials. In 2008, based on replanting regime of 1.8% of total oil palm (*Elaeis guineensis*) planted area of 4.5 million hectares, 71.33 million tonnes of biomass were available. Out of the total number, about 1.16 million tonnes and 64 million tonnes of oil palm frond (OPF) were produced during the palm felling and pruning, respectively. Hence, other than the empty fruit bunch (EFB), the oil palm frond (OPF) is a promising feedstock for biofuel (Wan Asma et al., 2012). In addition, the OPF is a highly attractive feedstock since it is composed of high cellulose content and is available at a low cost (Goh et al., 2010).

However, the pretreatment of lignocellulosic biomass is needed in biorefinery to improve the cellulose digestibility into sugar monomer structure. The main objective of the pretreatment is to disintegrate biomass structure into fibrous components. The lignin structure, which hinders the possibility of sugar recovery via enzymatic or acid hydrolysis, would be the main component to be removed in the pretreatment process. Lignin, consisting of cross-linked polymers of phenolic monomers, is a complex molecular structure. Lignin functions like a glue where it attaches the hemicellulose and cellulose structure into the complex matrix biomass structure (Benjamin et al., 2013; Conde-Mejía et al., 2012; Kumar et al., 2009; Villa-Vélez et al., 2015; Zikeli et al., 2014). The degradation or removal of lignin during the pretreatment would lead to the breakdown of the complex matrix biomass structure (Cardona et al., 2010) to produce a substrate riches with cellulose (glucan) and hemicellulose (xylan).

The degradation or delignification of lignin can be performed by physically (milling, grinding and electrical), chemically (alkali, dilute acid, oxidizing agents, and organic solvents), and biologically methods or a combination of these techniques (steam pretreatment/autohydrolysis, hydrothermolysis, and wet oxidation, ozonolysis,) (Agbor et al., 2011; Kumar et al., 2009; Pandey et al., 2015; Taherzadeh and Karimi, 2008). Among these methods, ozonolysis is acclaimed as an effective method to remove lignin from biomass (García-Cubero et al., 2009; Lee et al., 2010; Li et al., 2015; Panneerselvam et al., 2013; Travaini et al., 2013). In ozonolysis chemical reaction, it was reported that the glycosidic bond could

* Corresponding author. Fax: +60 7 5588166.
E-mail address: noraishah@cheme.utm.my (N.A.S. Amin).

http://dx.doi.org/10.1016/j.indcrop.2016.01.027
0926-6690/

be cleaved by ozone as the conjugated of carbon-carbon double bond functional group was attacked (Travaini et al., 2015; Zaikov and Rakovsky, 2009).

The ozonolysis method has been proven to remove lignin with a slight degradation of hemicellulose and almost without any effects on cellulose (Kumar et al., 2009; Li et al., 2015). Meanwhile, Quesada et al. (1999) reported that the ozonation of corn stalks affects the polymer of lignin initially, followed by the hemicellulose and cellulose. The lignin is rapidly oxidized by ozone and generates oxyaromatics (Mamleeva et al., 2009), which would transform into short-chain aliphatic acids. In addition, the sugar monomer (glucose or xylose) yield increases after the ozonolysis pretreatment (García-Cubero et al., 2009, 2012; Lee et al., 2010).

Ozone has been recognized as a powerful and green oxidant because it can be decomposed to form oxygen (O_2), and discharged into the environment safely. The filtrate from the washing step could also be retrieved for lignin recovery. Thus, no toxic is produced from the ozonolysis process. In addition, the ozonolysis process is performed under ambient temperature and pressure (Kumar et al., 2009; Panneerselvam et al., 2013). Hence, the possibility to employ ozonolysis method for the pretreatment of biomass is substantiated.

The enhanced biodegradability of the treated biomass by the ozonation during the enzymatic hydrolysis has been proven by previous studies (Binder et al., 1980; Kumar et al., 2009; Neely, 1984; Shefet and Ben-Ghedalia, 1982; Vidal and Molinier, 1988). However, industrial implementation of the method was limited since ozone production was not yet economical at that time. Recently, the cost of ozone production has been decreasing with the advent of a new technology (Lee et al., 2010). Therefore, researchers have reconsidered the ozonolysis for biomass pretreatment. Nonetheless, Binder et al. (1980) recommends the economics of the process may be improved by reducing the ozone production costs and optimizing the ozonation process for the pretreatment of biomass.

A number of studies have been carried out to investigate the influence of the ozonolysis process variables on the biomass conversion (Barros et al., 2013; García-Cubero et al., 2009, 2012; Lee et al., 2010; Li et al., 2015; Neely, 1984; Panneerselvam et al., 2013). Previously, the details of the variables affecting lignin degradation and enzyme digestibility during the ozonolysis were discussed by Neely (1984). Kojima and Yoon (2008) reported that the ozonolysis would increase the total pore volume and specific surface area of pulp besides reducing the lignin content. This resulted in the access of cellulase to the pulp fiber surface and improved enzymatic hydrolysis. García-Cubero et al. (2009) studied the influence of the process variables on the effectiveness of the ozonolysis treatment for the enzymatic digestibility of wheat and rye straw in a fixed-bed reactor using the factorial design approach. They found that the ozonation of biomass solubilizes the lignin with partial effect on hemicelluloses and exerted no effect on the cellulose structure. Similar trends were reported by Barros et al. (2013) and Li et al. (2015) recently. In addition, the moisture content and biomass type with different amounts of lignin were the most important variables in the ozonolysis process (García-Cubero et al., 2009; Mamleeva et al., 2009). Mamleeva et al. (2009) clarifies that the presence of water would stimulate the wood swelling and provide an access for the ozone into the internal surface of the wood cells. Meanwhile, Li et al. (2015) explains the interaction effect of particle size and moisture content for the ozonolysis treatment of maize stover was significant on the lignin degradation.

The optimization of biomass pretreatment by ozonolysis using mathematical approach such as response surface methodology (RSM) has never been reported before until recently (Al Jibouri et al., 2015). The optimization study of process conditions would save the time and cost as suggested by Binder et al. (1980) especially by using the RSM approach. However, the simultaneous multi-response optimization of lignin degradation and TRS recovery from treated solid has not yet been studied. Mostly lignin degradation and hydrolysis sugar yield were identified separately as the main responses to investigate the effectiveness of the ozonolysis pretreatment in previous studies (Al Jibouri et al., 2015; Barros et al., 2013; García-Cubero et al., 2009, 2012; Miura et al., 2012). Wan Omar and Amin (2015) discovered that higher lignin degradation of OPF did not necessary yield high sugar recovery. This is due to the fact that excessive exposure of biomass would lead to carbohydrates degradation into soluble compounds and possibly be lost during the washing step (Pandey et al., 2015). The loss in the total weight after the pretreatment might affect the TRS recovery from biomass.

The objective of this work is to investigate the influence of particle size, moisture content, reaction time, and ozone flowrate in the ozonolysis pretreatment of OPF on lignin degradation and TRS recovery using the RSM approach. The experiments were designed by employing a three-level factorial Box-Behnken design (BBD) with three replicates center point at selected experiment range. The predicted model developed from the RSM approach, would elucidate the effect of the process variables on the response. In addition, multi-objective responses for lignin degradation and TRS recovery of OPF for the ozonolysis pretreatment were optimized using desirability function in *STATISTICA* software tools. The recommended optimum condition for the ozonolysis pretreatment of OPF was verified experimentally. The levulinic acid production from optimized pre-treated OPF was demonstrated.

2. Experimental

2.1. Materials

The OPF, supplied by KESEDAR Renok Baru Plantation, Kelantan, Malaysia, was grounded and meshed at the Polymer Laboratory, N29, Faculty of Chemical Engineering, UTM, Malaysia to obtain a particle size between 0.3 and 0.8 mm. The OPF was then stored in a sealed container at room temperature for further characterization and subsequent reaction.

Chemicals such as sulphuric acid, H_2SO_4 (95–98%) (Qrec, NZ), sodium carbonate (Qrec, NZ), potassium iodide (Qrec, NZ), and potassium permanganate (Fisher Brand, UK) were in analytical reagent grade. Oxygen gas (170 bar, 8.4 m^3) was supplied by Mega Mount Gases Sdn Bhd, Malaysia. Cellulose (Sigma–Aldrich, USA) and D-glucose (Qrec, NZ) were selected as the model compound.

2.2. Characterization of the OPF

The compositions of cellulose and hemicellulose were determined by cellulose isolation method and modification of chlorination method respectively. The method was slightly modified from Tan and Lee (2012). The lignin was determined by Klason lignin method and the ash content was measured by LAP 005 method (Rowell, 2005).

The crystallinity of OPF was determined by powder X-ray diffraction (XRD). The XRD patterns were taken with a Bruker D8 Advance diffractometer, which has a Dynamic Scintillation Detector with low background (0.4 cps) and high dynamic range (up to 2×106 cps), allowing rapid data acquisition for most samples. The diffractometer used *Cu K* α radiation (40 kV 40 mA) with a wavelength (λ) of 1.54 Å. The samples were recorded from 15° to 50° (2θ) with a step scan of 0.05° every 1s. The phases were identified using the power diffraction file (PDF) database (JCPDS, International Centre for Diffraction Data).

The Brunauer–Emmet–Teller (BET) specific surface areas, pore volume, diameter of pore as well as the structure of the micro-