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Fractionation of Oil Palm Fronds (OPF) by Ozonolysis for Enhanced Sugar Production

Wan Nor Nadyaini Wan Omar, Nor Aishah Saidina Amin*

Chemical Reaction Engineering Group (CREG). School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM, Johor Bahru, Johor
noraishah@cheme.utm.my

This study investigates the potential of ozonolysis pretreatment on oil palm frond (OPF) for enhancing total reducing sugar (TRS) recovery. The OPF is pretreated by ozonolysis prior to two-step acid hydrolysis. The effect of ozonolysis pretreatment on the physico-chemical properties of OPF is scrutinized followed by the effect of process parameters on lignin degradation and TRS recovery. The presence of lignin-rich and cellulose-rich fractionates are proven by TGA. The XRD reveals crystallinity after pretreatment is increases while crystal size reduces indicating the removal of amorphous lignin region. The structure of OPF is disrupted during the pretreatment revealing the cellulose rosette structure in treated OPF as shown by FeSEM. Ultimately, TRS recovery increases up to 62.3 % with 90 % lignin degradation. This testifies ozonolysis is pertinent for enhancing sugar yields in acid hydrolysis. Among the process parameters, OPF particle size is the most significant followed by reaction time, moisture content, and ozone flowrate. The findings of this work contribute to new information about the pretreatment of biomass by ozonolysis.

1. Introduction

Sugar derived from oil palm frond (OPF) by hydrolysis holds the key to waste to wealth concept except that there are needs to deconstruct and fractionate the complex structure of lignocellulosic biomass (LB) to increase the efficiency of a biorefinery (Bardone et al., 2014). The dominant reducing sugar (RS) produced is glucose and xylose – two valuable chemical blocks for various biochemical and biofuel industries (Mahmood et al., 2019). Thermochemical acid hydrolysis has high commercial potential due to the high conversion rate and RS recovery at milder operating conditions (Ko et al., 2020). Besides, the physico-chemical properties such as surface area, crystallinity, and porosity of the LB would be affected by the pretreatment (Rezania et al., 2020). Other LB pretreatment method such as physical (milling and grinding), physicochemical (steam pretreatment/autohydrolysis, hydrothermolysis, and wet oxidation), chemical (alkali, dilute acid, oxidizing agents, and organic solvents), biological, electrical or a combination of these techniques have been studied. The drawbacks of these method deter the commercialization process (Bhatia et al., 2020). Recently, ozonolysis pretreatment appears as a promising green method to degrade lignin in biomass with minimum RS loss (Mardawati et al., 2019). The ozone (O_3) is highly reactive towards compounds incorporating conjugated double bonds (C=C) and functional groups with high electron densities such as lignin (Perrone et al., 2017). The process is operated at ambient condition and there is no toxic waste produces since excess ozone is decomposed into oxygen before discharge (Cubero et al., 2012). The potential of ozonolysis as an effective pretreatment method on Malaysia's biomass for RS production by acid hydrolysis is scarcely reported. OPF which contributes to 78 % of total LB from oil palm sector consists of high holocellulose and small amount of lignin compared to other oil palm waste (Khan et al., 2010). This study investigates the potential of ozonolysis pretreatment on OPF for enhancing the TRS recovery by acid hydrolysis. The alteration of physico-chemical properties due to pretreatment is scrutinized, and the effects of process parameters during pretreatment are screened to provide insights about the reaction.

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2. Experimental

2.1 Design of experiment (DOE)

A two-level factorial with full resolution designed by STATISTICA *ver.* 8 software is applied due to the limitation of feedstock homogeneity. Four independent process parameters: moisture content (X_1), particle size (X_2), reaction time (X_3), and ozone flow rate (X_4), and response: Lignin degradation (Y_{LD}) was studied at all levels (low, -1 and high, +1) by considering part of OPF as the blocking parameter (Table 1).

Table 1: Design of Experiment (DOE) and lignin degradation

Part of OPF	Moisture content (wt%), X_1	Particle size (mm), X_2	Reaction time (min), X_3	Ozone flow rate (mL/min), X_4	ODT yield (%)	Lignin degradation (wt%)	
						Observed	Predicted
Petiole, P (-1)	30 (-1)	0.25 (-1)	30 (-1)	90 (+1)	74.8	85.1	83.7
	65 (+1)	0.25 (-1)	30 (-1)	60 (-1)	59.8	48.6	55.9
	30 (-1)	0.63 (+1)	30 (-1)	60 (-1)	59.2	98.7	94.9
	65 (+1)	0.63 (+1)	30 (-1)	90 (+1)	63.4	73.8	81.1
	30 (-1)	0.25(-1)	60 (+1)	60 (-1)	66.4	83.6	76.3
	65 (+1)	0.25 (-1)	60 (+1)	90 (+1)	68.5	79.7	83.5
	30 (-1)	0.63 (+1)	60 (+1)	90 (+1)	56.5	98.1	90.8
	65 (+1)	0.63 (+1)	60 (+1)	60 (-1)	54.4	95.5	96.9
Rachis, R (+1)	30 (-1)	0.25 (-1)	30 (-1)	60 (-1)	68.0	66.7	69.4
	65 (+1)	0.25 (-1)	30 (-1)	90 (+1)	74.1	56.8	48.3
	30 (-1)	0.63 (+1)	30 (-1)	90 (+1)	63.6	89.1	91.7
	65 (+1)	0.63 (+1)	30 (-1)	60 (-1)	67.4	89.9	83.9
	30 (-1)	0.25 (-1)	60 (+1)	90 (+1)	76.6	80.7	86.7
	65 (+1)	0.25 (-1)	60 (+1)	60 (-1)	73.7	75.3	72.7
	30 (-1)	0.63 (+1)	60 (+1)	60 (-1)	61.7	67.0	75.6
	65 (+1)	0.63 (+1)	60 (+1)	90 (+1)	63.6	92.7	90.1

2.2 Ozonolysis pretreatment

Oil palm frond (OPF) obtained from Lembaga Kemajuan Kelantan Selatan (KESEDAR), Renok Baru plantation, Kelantan, Malaysia was cut into two parts known as petiole (P)-from trunks to middle of stem, and rachis (R)-from the middle of stem to the tip. The procedure of the experiment is described by Wan Omar and Amin (2016). 10 g of OPF was moisturized with distilled water (DW) before the reaction. Then, ozone gas (60 mg/L) was supplied continuously within the desired reaction time followed by mixing with 100 mL of NaOH (5 wt %) solution for 1 h at room temperature. The suspension was filtered, rinsed, and dried in an oven. The oven dried treated, ODT sample was weighed and stored for next step. The filtrate was cooked until it became solid and labelled as ODR. The ODT yield was calculated by Eq(1). The lignin content was quantified following Wan Omar and Amin (2016) and Eq(2) formulated the lignin degradation.

$$\text{ODT yield}(\%) = \frac{\text{Weight of ODT}}{\text{Weight of OPF}} \times 100 \quad (1)$$

$$\text{Lignin degradation (wt \%)} = \frac{\text{lignin content in OPF - lignin content in ODT}}{\text{lignin content in OPF}} \times 100 \quad (2)$$

2.3 RS synthesis

0.3 g of ODT and OPF sample was hydrolyzed using 3 mL of H_2SO_4 (72 %) at 30 °C for 2 h, and then immediately diluted with 84 mL of DW before boiled at 95 °C for 1 h, then the mixture was filtered. The filtrate was neutralized by sodium carbonate before the 3, 5-dinitrosalicylic acid (DNS) analysis (Wan Omar and Amin, 2016). The concentration of glucose and xylose were estimated by UV-Vis spectrophotometer at 540 nm and 510 nm, by comparing with the standards. The recovery of glucose and xylose were calculated using Eqs(3-4), here 0.9 and 0.88 are anhydro corrections for glucose and xylose (Capareda, 2013). Eq(5) is formulated for total reducing sugar (TRS) recovery.

$$\text{Glucose recovery (\%)} = \frac{\text{Glucose concentration } \left(\frac{\text{mg}}{\text{ml}}\right) \times 87(\text{ml}) \times 0.9}{300 \text{ mg of ODT}} \times \text{ODT yield (\%)} \quad (3)$$

$$\text{Xylose recovery (\%)} = \frac{\text{Xylose concentration } \left(\frac{mg}{ml}\right) \times 87(ml) \times 0.88}{300 \text{ mg of ODT}} \times \text{ODT yield (\%)} \quad (4)$$

$$\text{TRS Recovery (\%)} = \text{Glucose recovery(\%)} + \text{Xylose recovery (\%)} \quad (5)$$

2.4 Physico-chemical analysis of OPF and ODT samples

Thermal gravimetric analysis (TGA) (Perkin Elmer, STA 6000) identified the chemical compositions and thermal characteristics of the samples at 10 °C/min heating rate under ambient nitrogen. The surface morphology of samples was captured by field emission scanning electron microscopy (FeSEM, ZEISS SUPRA 35VP) at 1,000x and 2,500x magnification (20-10 kV). Powder X-ray diffraction (XRD) performed by Bruker D8 Advance diffractometer with a step scan of 0.05 s^{-1} identified the crystal structure, and estimated the crystallinity index (Cr*I*) and crystal size according to Ling et al. (2017).

3. Results and discussions

3.1 Effects of ozone pretreatment on the structure of OPF by TGA

Figure 1 portrays the TGA analysis of OPF, ODT and ODR. All the samples unveil three stages of mass loss due to degradation of their component. The first stage is below 100 °C (<10 wt%) for all sample signifying the evaporation of physisorption water from the surface (Kumneadklang et al., 2019). The second stage loss about 55 wt% of OPF and ODT in between 150-350 °C denoting the holocellulose- hemicellulose and cellulose region. The DTG curve of OPF presents a slight shoulder peak at 240 °C indicating the hemicellulose decomposition, and 312 °C is cellulose (Kumneadklang et al., 2019). In contrast, the single sharp DTG curve at 330 °C shows risen of onset temperature in ODT because of an amorphous region removal. Besides, the ODR DTG peak presence at 133, 215, and 263 °C with a total of ≈20 wt% renders the amount of sugar loss during swelling activity. The third stage of the TG curve starts slowly at 400-900 °C represents the lignin because it is stable and difficult to decompose (Burhenne et al., 2013). ≈ 25 wt% loss is perceived for the OPF between 400-600 °C region. There is no DTG peak detected for ODT while the peak appears at 700-800 °C with ≈50 wt% loss for ODR. The weight loss continues until the non-volatile components remain about 5 wt% OPF and 15 wt% ODT as the temperature increases to 900 °C.

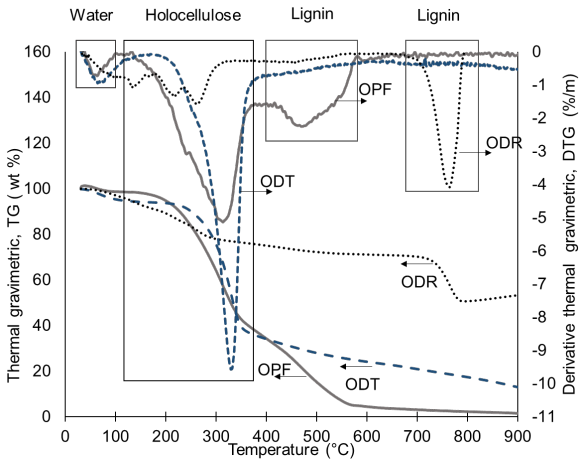

Figure 1: TGA Analysis of OPF, ODT and ODR

3.2 The effect of ozone pretreatment on physico-chemical properties of OPF

Figure 2 shows the OPF has a well-organised primary cell wall plasma membrane (Figure 2a and 2b) and the primary cell wall is disrupted for ODT. The lignin in ODT is removed and reveals the holocellulose microfibril strands that protect the cellulose rosette. The cellulose rosette structure is spotted at the rupture microfibril surface. The XRD analysis show the structure of OPF and ODT is para-crystalline with the crystal lattice of cellulose II polymorph. The ODT confers higher crystallinity and smaller crystal size (36.1 % and 4.94 nm) than OPF (44.68 %, 1.95 nm). the same trend is reported by (Hashim et al., 2017). This infers that the amorphous region is mainly attributed to lignin being removed leaving the para-crystalline cellulose structure with strong hydrogen bonding. This also show that the ODT have a potential to be converted into nanocellulose.

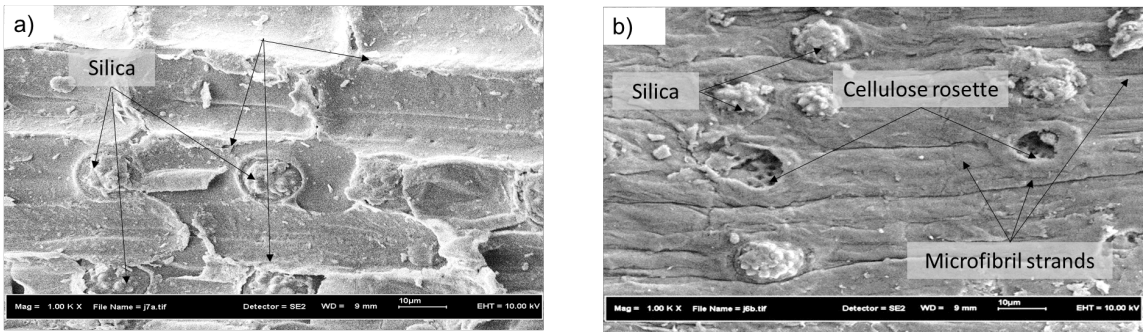

Figure 2: FeSEM image of sample at 1000x resolution, (a) OPF, (b) ODT

3.3 Effects of process parameter during ozonolysis treatment on lignin degradation, ODT yield and TRS recovery

The relationship between the process parameters ($X_{0\text{-}5}$) and lignin degradation (Y_{LD}) is expressed by Eq(6). All the data fall into a normal distribution with *R*-Square = 0.8478 at 5 % level of significance. The OPF particle size is the most significant parameter at over 95 % significance level followed by reaction time, moisture content, and ozone flow rate as analyzed by the Student *t*-distribution analysis. All the terms are studied to verify the analysis is precise and no important parameters are omitted (Antoy, 2014).

$$Y_{LD}= 59.68-2.81X_0 -0.78+94.81X_2-0.71X_3+0.50X_4+1.03X_1X_2+0.02X_1X_3-0.01X_1X_4-1.32X_2X_3 -0.56X_2X_4+0.01X_3X_4 \quad (6)$$

Figure 3 and 4 visualize the effect of process parameters on lignin degradation with a stationary point at a low level. The *petiole* part of OPF registers higher lignin degradation compared to *rachis* as the lignin content in *petiole* is lower than *rachis* (Figure 3). It implies that different types of feedstock would perform differently based on lignin content as report by Cubero et al. (2009). The forward analysis considers the *petiole* part only. Figure 4 indicates higher OPF moisture for all particle size (Figure 4a) requires longer reaction time (Figure 4b) and slower ozone flowrate (Figure 4c). Larger particle size leads to higher lignin degradation (Figure 4a, 4d and 4e) following interfacial tension theory. More energy is required for ozone transfer into the water film for smaller particle size as the surface tension of OPF increases with surface area (Razavi et al., 2019). Increasing the ozone flow rate (Figure 4c, 4e and 4f) could minimize the reaction time and maximize the efficiency of ozone consumption by supplying sufficient ozone for the reaction (Neely, 1984). Longer reaction time could lead to the degradation of holocellulose components (Figure 4d).

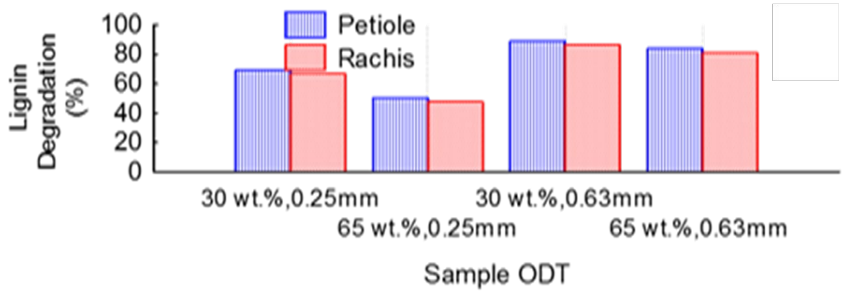

Figure 3: Lignin degradation with various moisture content and particle size of petiole and rachis

Figure 5 exhibits the effect of lignin degradation on ODT yield, sugar yields and TRS recovery at different pretreatment condition. More than 60 wt% of ODT yield is attained and have no direct relationship with lignin degradation since hemicellulose degrades along with lignin. The sugar yields increase for ODT compared to 0.85 and 0.96 mg/mL of glucose and xylose obtained from OPF hydrolysis. The xylose yield is higher than glucose since hemicellulose is easily hydrolyzed at mild reaction condition. Smaller OPF particle size (Figure 5a), higher moisture content (Figure 5b), prolonged ozonolysis time (Figure 5c), and faster ozone flow rate (Figure 5d) is unfavourable pretreatment condition since the hemicellulose could break and produce carboxylic acid leading to sugar loss. TRS recovery has a similar performance with lignin degradation (Figure 5a-5c), but

have no direct relation for ozone flowrate (Figure 5d). The TRS recovery for ODT increases to 75.8 % compared to 46.7 % for OPF- an increment of 62.3 % as observed by Cubero et al. (2009).

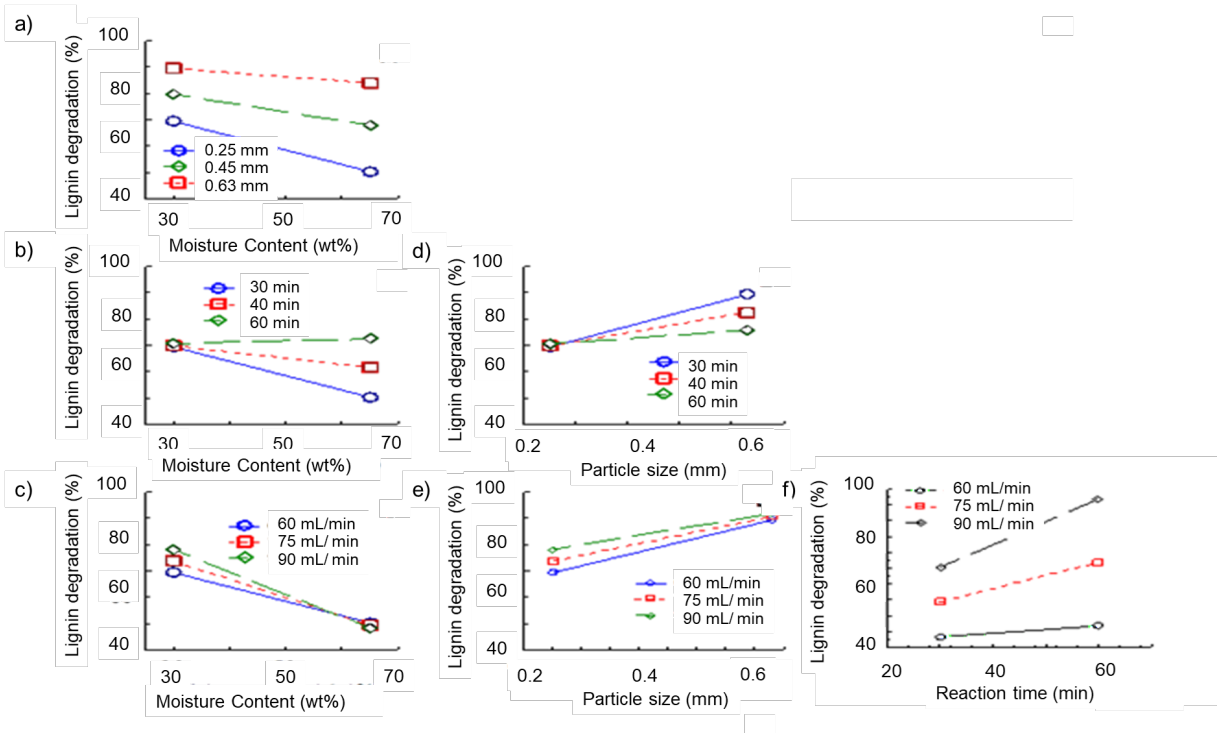

Figure 4: Main effect and interaction of process parameters on lignin degradation, (a) Moisture content and particle size (X_1X_2), (b) Moisture content and reaction time (X_1X_3), (c) Moisture content and ozone flowrate (X_1X_4), (d) Particle size and reaction time (X_2X_3), (e) Particle size and ozone flowrate (X_2X_4),(f) Reaction time and ozone flowrate (X_3X_4).

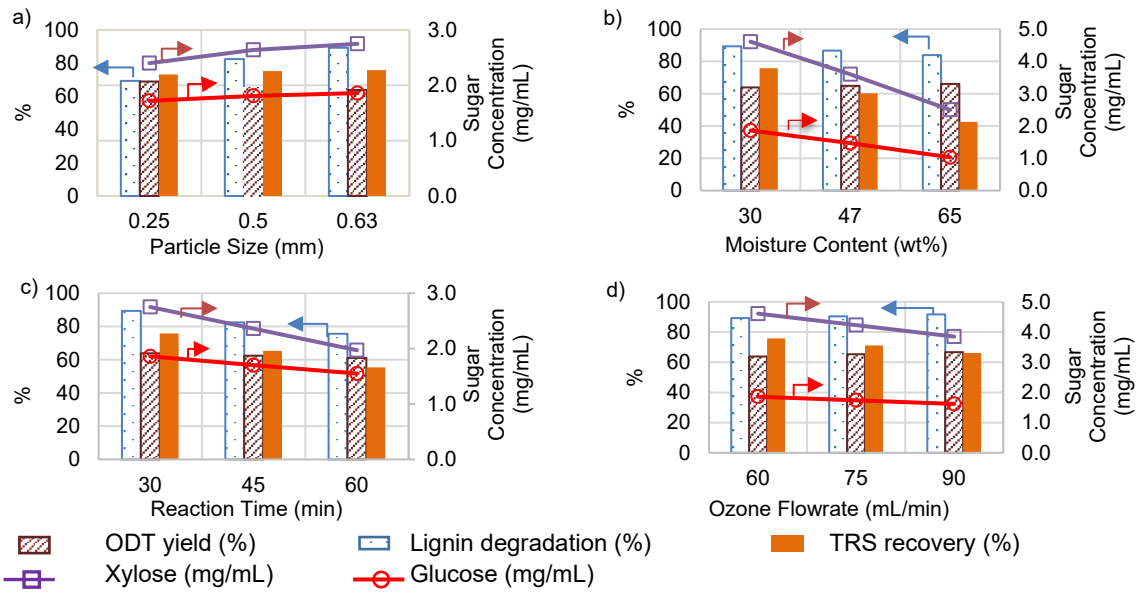

Figure 5: The ODT yield, lignin degradation and TRS recovery based on different ozonolysis process condition, (a) X_1=30 wt %, X_3=30 min, X_4= 60 mL/min, (b) X_2=0.63 mm, X_3=30 min, X_4=60 mL/min (c) X_2=0.63 mm, X_1=30wt%, X_4=60 mL/min, (d): X_2=0.63 mm, X_1=30 wt %, X_3=30 min

4. Conclusions

90 % of lignin contained in petiole OPF has been removed by ozonolysis pretreatment with enhanced recovery of TRS up to 62.3 %. The ozonolysis pretreatment fractionates the OPF sample allowing separation of lignin and cellulose rich fractions. The ODT mixture is rich with cellulose as proven by TGA, and FeSEM. Large OPF particle size, lower moisture content, shorter ozonolysis time, and slower ozone flow rate are the favourable pretreatment conditions for enhanced sugar recovery.

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