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RESEARCH ARTICLE

BROIDO PLOT FOR THE EFFECT OF ACID PRETREATMENTS ON HYDROLYSIS OF OIL PALM MESOCARP FIBER

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ABSTRACT

Hydrolysis is one of the method used to produce levulinic acid. Before hydrolysis, the samples need to be pretreated to enhance the production of levulinic acid during hydrolysis reaction. Two different pretreatments, acid pretreatment and ultrasonic-assisted acid pretreatment were done followed by acid hydrolysis on oil palm mesocarp fibre (OPMF). For acid pretreatment, the parameter involved was temperatures (60 ^{0}C, 80 ^{0}C and 100 ^{0}C) while the effect of sonication powers (40%, 60% and 80%) was investigated for ultrasonic-assisted acid pretreatment. Acid hydrolysis reaction was performed at the temperature of 140 ^{0}C for 3 hours. The samples from hydrolysis were then prepared for thermo gravimetric analysis (TGA) and analysis by high performance liquid chromatograph (HPLC). TGA analysis revealed that the pretreated sample which produced the highest amount of levulinic acid based on HPLC result gave the lowest activation energy based on TGA result. This sample produced 11.45% levulinic acid and the activation energy for decomposition of this sample was only 15.16 kJ/mol. This indicates that the lowest energy was needed for decomposition of this treated sample due to the efficiency of acid pretreatment with its excellent condition towards fiber.

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INTRODUCTION

Levulinic acid has been identified as promising platform chemicals and this acid can be generated from biomass (Schmidt *et al.*, 2017). Levulinic acid can be applied in many industries, for example medicinal, food and cosmetic industries (Runge and Zhang, 2012). During biomass conversion, the content of lignocellulosic materials in biomass can influenced the yield of products and also optimal conversion methodology (Acquah *et al.*, 2017). Due to the recalcitrance of lignin during biochemical conversion of biomass, lignocellulosic biomass is usually need to be pretreated to enhance the production of levulinic acid. The purpose of thermo gravimetric analysis (TGA) is to find out kinetic of oxidation and pyrolysis or thermal events of the solid biomass. This analysis can determine the measurement of weight loss of the biomass as a function of temperature and time. TGA analysis can provide the information related to mass fraction of volatile matter, fixed carbon, water and ash. Biomass which contains high volatile matter is easier to ignite and generates higher amount of liquid products. In contrast, biomass which contains higher amount of fixed carbon gives more solid products. Basically, the kinetic of thermal behavior can be evaluated by the application of the Arrhenius equation which presented by the slopes of constant mass degradation in each thermal event with different frequency factor, activation energy and reaction order. The analysis by TGA can be performed isothermally or non-isothermally. Thermal evaluation method developed by Broido (Broido *et al.*, 1969) shows that TG curves provides the information to find out thermodynamic or kinetic parameters. The weight at any time is linked in proportionality with the fraction of initial biomass weight for this method. The parameters such as enthalpy, activation energy, free energy changes and entropy can be determined using this method. This paper only focus on one parameter which is activation energy. The activation energy presents an excellent understanding of the thermal decomposition of biomass.

MATERIALS AND METHOD

Biomass Preparation: Oil Palm Mesocarp Fiber (OPMF) was collected from Felda Sungai Tengi in Selangor. To prevent any microbial growth, the sample was packed in a sealed plastic bag and stored in a freezer. When ready to use, the sample was

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defrosted and sun-dried before washed several times to remove any unwanted foreign materials. The sample was dried overnight at 105 °C to remove moisture and grounded into approximately 0.5 mm particle size. The dried OMPF was stored in sealed plastic bags again at room temperature before being used for experiments.

Biomass pretreatments and hydrolysis: Two different pretreatments, acid pretreatment and ultrasonic-assisted acid pretreatment were done followed by acid hydrolysis on oil palm mesocarp fibre (OPMF). For acid pretreatment, the parameter involved was temperature (60 °C, 80 °C and 100 °C) while the effect of sonication powers (40%, 60% and 80%) was investigated for ultrasonic-assisted acid pretreatment. All pretreatments used 15g of OPMF as raw materials and was added into 500mL of 2% sulfuric acid as catalyst. Pretreatments were performed for 3 hours for all samples. After pretreatments, all samples undergoing acid hydrolysis reaction without separate the biomass from the pretreated solution. Acid hydrolysis reaction was performed at the temperature of 140 °C for 3 hours. The samples from hydrolysis were then prepared for thermo gravimetric analysis (TGA) and analysis by high performance liquid chromatograph (HPLC).

Sample Analysis: The effect of pretreatments was evaluated based on the product generated during acid hydrolysis. The effects of different pretreatments were investigated from the result of acid hydrolysis which was carried out after each pretreatment. No TGA analysis was carried out for the pretreated sample before hydrolysis. The thermal analysis of OPMF was performed using Thermogravimetric Analyser (TGA) at the Institute of Advance Technology (ITMA), Serdang. This TGA is a Mettler Toledo Model 851E with high temperature furnace controlled by an IBM compatible PC. The weight changes of material as a function of time or temperature were measured by TGA. After acid hydrolysis, activation energy (Ea) for a major stage of decomposition were determined by Broido's method (Broido et al., 1969) using Eq. (3.8).

$$\ln(\ln\left(\frac{1}{y}\right)) = -\frac{Ea}{RT} + Constant \qquad (2.1)$$

Where, y refers to the normalized weight (w_t/w_i), w_t is the weight of the sample at any time t, w_i is the initial weight of the sample, T indicate the temperature in Kelvin and R refer to the gas constant (8.32 J/mol K). A plot of ln(ln(1/y)) against 1/T gives a straight line, the slope of which gives E_a. Although by using multiple heating rate methods, the kinetic parameters are better estimated, single heating rate methods are being used in several studies (Adel *et al.*, 2011; Madani, 2011; Spencer and Kohl, 2011). Furthermore, the TGA analysis was also used to estimate the amount of cellulose, hemicelluloses and lignin in OPMF. In this analysis, 10 mg of OPMF was heated from 30 °C to 900 °C at a heating rate of 15 K/min under 50 ml/min air purging in the nitrogen atmosphere.

The thermogravimetric curves of lignocellulosic biomass can be divided into four stages of primary decompositions based on the weight loss of the biomass materials. These decomposition activities occurred in the temperature range of 30 °C to 900 °C. Moisture removal occurred at 50 °C to 125 °C, decomposition of hemicellulose at 180 °C to 320 °C, decomposition of cellulose at 320 °C to 400 °C and decomposition of lignin occurred at the temperature above 360 °C, corresponding to the four stages (first, second, third and fourth stages) respectively (Braga *et al.,* 2014; Chen *et al.,* 2010; Phitsuwan *et al.,* 2016). The conversion of cellulose was calculated based on the Eq. (2.2) below:

$$Conversion\ (\%) = \frac{Initial\ cellulose - cellulose\ after\ reaction}{Initial\ cellulose}\ x\ 100\% \qquad (2.2)$$

A high performance liquid chromatograph (HPLC) equipped with Refractive Index Detector (RID) was used to measure the concentration of furfural and main product for this research which was levulinic acid. The column used was a Rezex RFQ Fast Acid column from Phenomenex, (California, USA), a cation guard cartridge (Bio-Rad Laboratories). 0.01 N sulfuric acid at a flow rate of 1.0 mL/min was used as the mobile phase. Before the samples being analyzed, the samples were neutralized and diluted with $CaCO_3$ to pH 5 to 6.

RESULT AND DISCUSSION

Figure 3.1 shows the TGA curves from thermogravimetric analysis which calculate the derivatives weight loss characteristic at a heating rate of 15 K/min under 50 ml/min air purging in the nitrogen atmosphere. The chromatograms are for raw OPMF and pretreated samples after direct hydrolysis. It is observed that each samples exhibited unique combustion profiles. The weight retention rates of the raw OPMF are significantly higher than those of the pretreated samples. Yu *et al.,* (2018) suggested that the low weight retention rate of the OPMF pretreated samples were due to the diminishing of the crystalline structure and the expansion of the cellulose amorphous structure. The derivative weight loss was used to estimate the content of cellulose left in the samples after hydrolysis as shown in Table 3.1. In this table, levulinic acid content was obtained from analysis by HPLC. About 77.87% of cellulose conversion took place in this sample. Muranaka *etal.* (2014) reported that only 10% was solubilized in the reaction from the sample which pretreated at 160 °C. The conversion of cellulose for the hydrolysed sample which was pretreated at 60% and 80% sonication power was quite high which were at 73.09% and 72.32% conversion. However, the content of levulinic acid from both samples were very low. It is suggested that, even though high conversion of cellulose occurred in both samples, the pathway of production of levulinic acid from cellulose required degradation of some intermediates from cellulose such as glucose and HMF.

Table 3.1. Cellulose conversion of hydrolysed samples

Pretreatment condition of hydrolysed samples	Cellulose after reaction (%)	Conversion (%)	Levulinic acid content (%)
40% sonication power	8.00	73.09	7.38
60% sonication power	8.23	72.32	8.21
80% sonication power	9.52	67.98	8.75
Temperature of 60°C	8.94	69.93	9.38
Temperature of 80°C	8.05	72.92	10.94
Temperature of 100°C	6.58	77.87	11.45

Senthamaraikannan and Kathiresan (2018) reported that the minimum energy needed to initiate degradation of fiber is called as activation energy (E_a). Activation energy can be calculated from the slope of the appropriate linear plot based on Figure 3.2 and 3.3 by using Broido equation. As reported from Manimaran *et al.* (2018), normally the kinetic activation energy of plant fibers situated between 60-170 kJ/mol. However, the activation energy for OPMF from this study is low (35.76 kJ/mol) and this value is comparable with

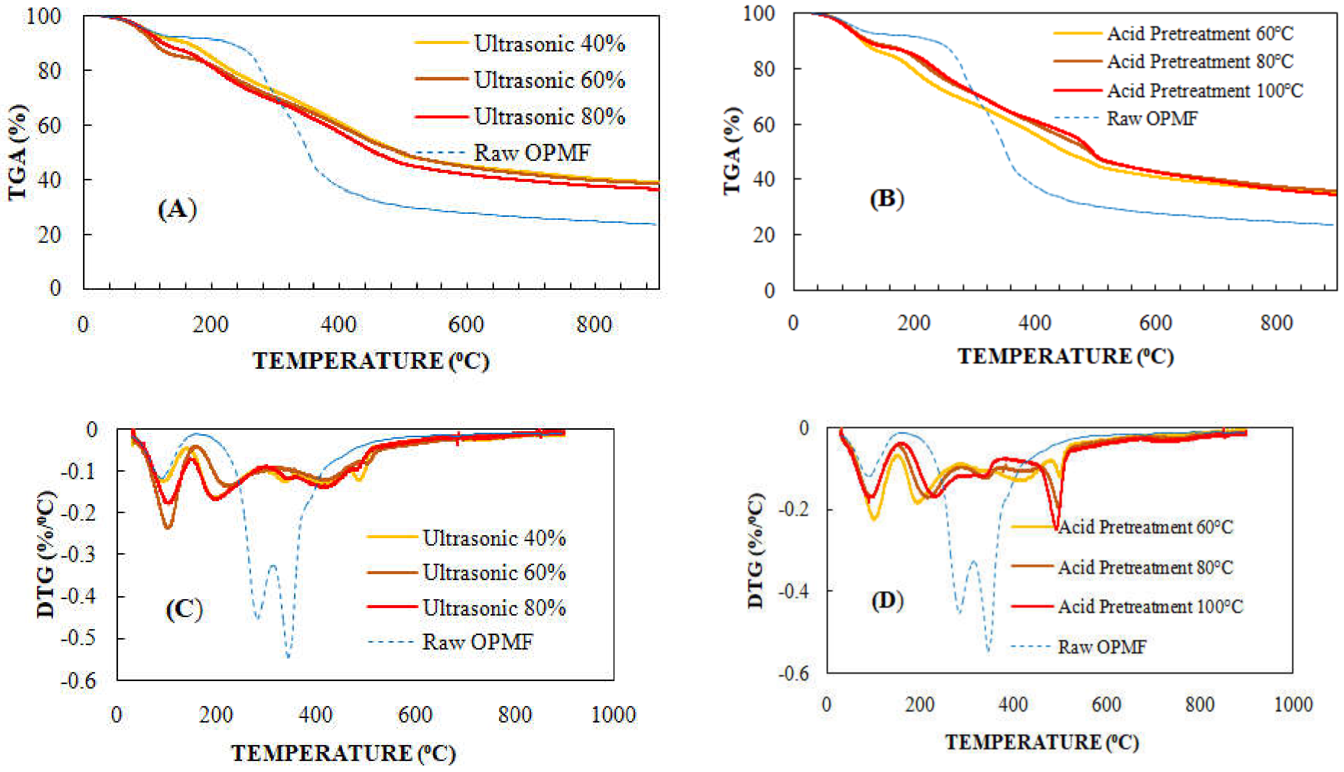

Figure 3.1. TGA and DTG curves of the hydrolysed samples after pretreated with ultrasonic-assisted acid pretreatment (A and C) and acid pretreatment (B and D) without separation of biomass and pretreated solution.

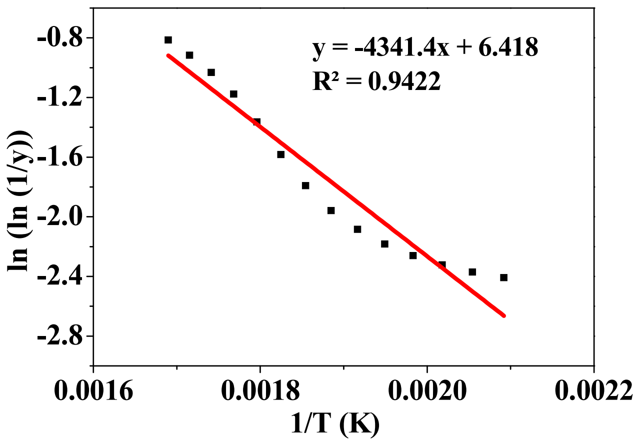

Figure 3.2. Broido's plot of raw OPMF

activation energy for combustion of OPMF from research by Asadieraghi and Wan Daud (2014) which was about 26.11 to 52.66 KJ/mol. Table 3.2 compared the activation energy value for the samples. In this table, levulinic acid content was obtained from analysis by HPLC. Based on Table 3.2, lower activation energy was observed at the pretreated samples compared to raw materials. This trend is similar to a study by Shinoj *et al.,* (2011) which found that chemical pretreatment on oil palm fibre resulted in lower activation energy. This is due to the lower energy needed to degrade lignocellulosic materials such as cellulose and hemicellulose at this decomposition stage and proved that pretreatment favoured the conversion of these materials. Jamaludin *et al.* (2017) found that the condition of polysaccharides decomposition in biomass can influence the activation energy. The material in biomass which decomposed in this range of temperature is hemicellulose. Xylose is a product from hemicellulose while furfural is product of degradation of xylose. The highest activation energy was obtained from sample A (17.73 kJ/mol) which was pretreated by ultrasonic-assisted acid pretreatment at 40% power. The low content of furfural in this sample can be related to the high activation energy produced.

As expected the low content of furfural is due to the slow degradation of other products such as xylose which is produced from hemicellulose. To the best of our knowledge, there is no other study to calculate the activation energy of OPMF after pretreatment to evaluate the degradation of polysaccharide. Based on Table 3.1, the sample which produced the highest content of LA at the same time contained the lowest content of furfural. Furfural is one of the product from xylose degradation. Runge and Zhang (2012) suggested that residual xylose in biomass could influence the content of LA due to the polymerization of

Table 3.2. Activation energy of direct hydrolysed OPMFs (acid-pretreated biomass)

Samples code	Temperature Range (°C)	Mass Loss (%)	E_a (kJ/mol)	Mass at 600 °C (mg)	Furfural content (%)	Levulinic acid content (%)
Raw	205-318	35.7624	36.12	2.92	-	-
A	136-289	26.4503	17.73	4.73	13.54	7.38
B	155-326	30.2753	15.82	4.63	15.13	8.21
C	146-300	31.1618	15.21	4.31	16.18	8.75
D	148-289	25.4361	16.16	4.52	15.68	9.38
E	148-292	28.4064	15.70	4.40	16.48	10.94
F	155-317	31.0394	15.16	4.42	18.30	11.45

*Samples which pretreated by ultrasonic-assisted acid pretreatment (A) 40% power, (B) 60% power, (C) 80% power and acid pretreatment (D) 60 °C (E) 80 °C (F) 100 °C.

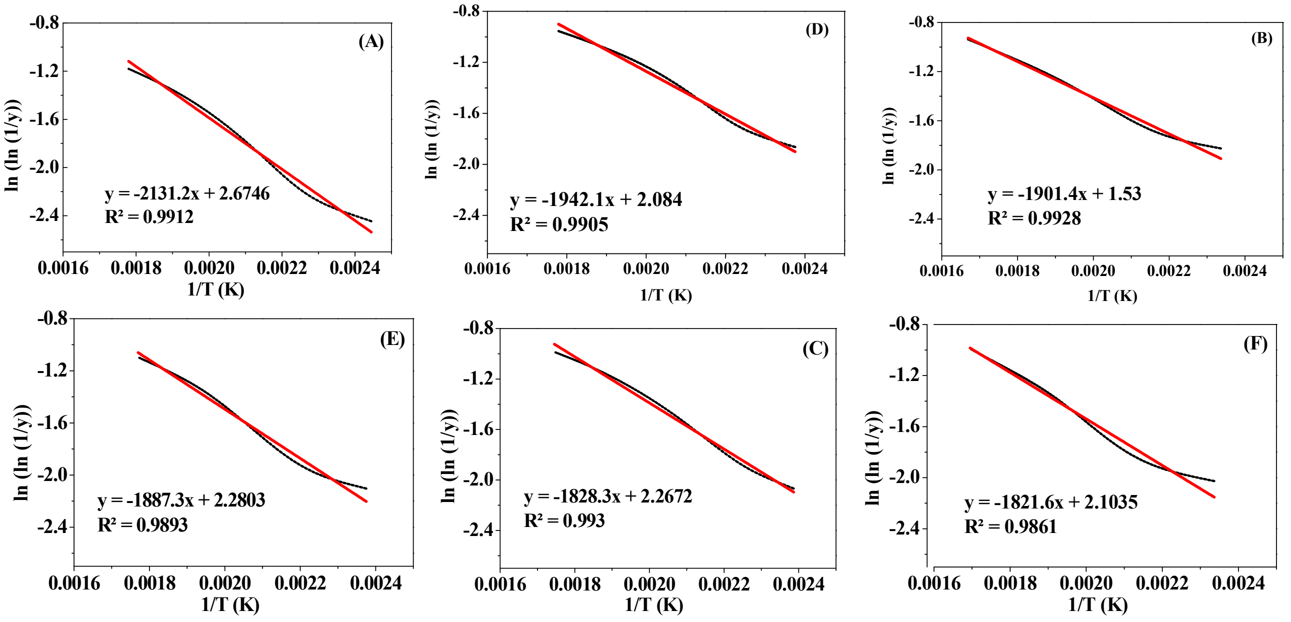

Figure 3.3. Broido's plot of direct-hydrolysed samples which pretreated by ultrasonic-assisted acid pretreatment. (A) 40% power, (B) 60% power, (C) 80% power and acid pretreatment (D) 60 °C (E) 80 °C (F) 100 °C

furfurals with saccharides and formed insoluble humins. Therefore, lignocellulosic biomass pretreatment motivationally which leads to reconstruction of fibre for removal of recalcitrance is more required, particularly during furanic compound compared to delignification.

Conclusion

TGA analysis revealed that the pretreated sample which produced the highest amount of levulinic acid gave the lowest activation energy. This sample produced 11.45% levulinic acid and the activation energy for decomposition of this sample was only 15.16 kJ/mol. This indicates that the lowest energy was needed for decomposition of this treated sample due to the efficiency of acid pretreatment with its excellent condition.

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