Comparison of delignification of Oil Palm Empty Fruit Bunch (EFB) by Microwave assisted alkali / acid pretreatment and Conventional Pretreatment Method

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Abstract**—**Pretreatment of lignocellulosic biomass are key technologies for the production of fermentable sugars to produce biofuels and high value added organic acids. Microwave-Alkali (MW-A) pretreatment is an efficient, time saving and fast method to remove a high amount of lignin. Lignin content of the oil palm biomass was determined after Microwave-Alkali (Mw-A) pretreatment and conventional pretreatment methods. In conventional pretreatment, empty fruit bunches (EFB), was soaked in 2.5 M NaOH for 2 hours in autoclave. While, in microwave assisted dilute acid/ alkali, the EFB was soaked in dilute sulphuric acid by conventional autoclave heating which remove 90 % of hemicellulose. In the second step, acid treated EFB was soaked in 2.5 M NaOH solution, and applied for microwave pretreatment. The amount of acid insoluble lignin was determined by klason's method. The results revealed that lignin obtained from untreated EFB was 24.87, conventional heating autoclave pretreatment 16.34, microwave- alkali dilute acid/alkali treated 8.67 (g/100gm). The results showed that a high amount of lignin 71.91% of lignin has removed by microwave assisted alkali/acid pretreatment as compared with conventional heating (34.65 %).

Keywords**—**Microwave-Alkali (MW-A)**;** microwave assisted alkali/acid pretreatment; Dilue acid pretreatment (DA); Oil palm biomass; Empty fruit Bunches (EFB); cellulose; hemicellulose; lignin

I. Introduction

THE oil palm biomass comprising of palm empty fruit bunches (OPEFBs), oil palm fronds (OPFs), oil palm trunks (OPTs) and palm kernel shells (PKSs) produced approximately 59 million tonnes every year in Malaysia [1] which is the world second largest producer oil palm. Current studies shows that lignocellulosic biomass including oil palm biomass has a potential to produces industrially important compound succinic acid [2].

Recently, a combination of microwave-alkali (MW-A) pre-treatment of lignocelluloses material has been performed as an alternative method over conventional heating. Application of such pre-treatment on lignocellulosic material has been reported on rice straw [3-5], rice straw [4], switch grass [6] and empty fruit bunches fibre [7]. It is interesting to note that, most of the silicon in the lignocellulosic fibre is removed during microwave irradiation pre-treatment as reported by [7] on morphology study of EFB. Dilute acid pretreatment remove maximum amount of hemicellulose and only a small amount of lignin. While, microwave alkali pretreatment resut in high delignification. Hence, combination of dilute acid with microwave alkali pretreatment can remove maximum amount of hemicellulose and lignin, thus resulting high amount of cellulose for organic acids production The morphology of non-treated EFB, dilute acid/ alkali treated EFB and conventional pretreated EFB are shown in fig 1

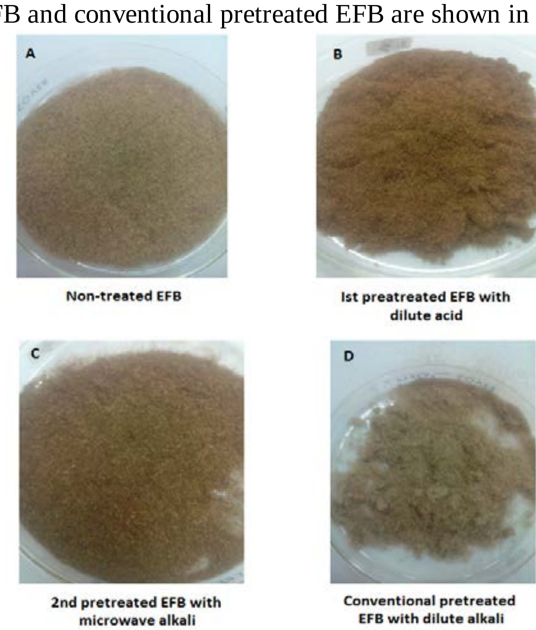

Fig. 1. Morphologies of the EFB samples (A) the non-treated EFB (B) the first dilute acid-pretreated EFB (C) the second sequential acid/alkali- pretreated EPFB fiber (D) Conventional dilute alkali pretreated EFB

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II. METHODOLGY

2.1 Raw Material

The EFB biomass was collected from FELDA palm oil mill Semenchu, Kota Tinggi, Johor, Malaysia. The EFB samples were washed with tap water to remove soil, dust and other unwanted materials prior to air-drying under sunlight. The biomass was grinded 0.5 x 1.0 cm size using disk mill model FFC-15, China and was sieved by using a Restuch sieve shaker (AS 200 basis, Germany) into a particle size less than 1.0 mm (mesh size < No.18). Prior to the analysis, the powdered sample was dried in an oven at 60 °C for 24 h and stored in an air-tight container at room temperature. The SINEO's microwave model (MAS-II, China) used in the pretreatment were purchased from China.

2.2 Chemical reagents

The chemical reagents used were of analytical grade. They were ethanol (C_2H_5OH), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), sodium hydroxide (NaOH), and toluene (C_7H_8), sodium chlorite ($NaClO_2$) and sodium hypochlorite (NaClO) solution.

2.3.1 Conventional pretreatment

20g of dry EFB (20% w/v) with no physical treatment was soaked 2.5 M solutions of NaOH for two hours then heated in an autoclave at 121^{o}C, 15 psi for 1 h. The alkali-treated EFB (EFBacid) was then obtained in the alkaline solution, washed with tap water followed by distilled water, filtered and dried at 90 ^{o}C overnight which can be stored for further analysis.

1) Dilte acid (DA) pretreatment & Microwave/alkali pretreatments of EFB

In sequential acid/microwave alkali-pretreatment, 20g of dry EFB (20% w/v) with no physical treatment was soaked in H_2SO_4 solutions within the concentration 8.0% (v/v) and heated in an autoclave at 121^{o}C, 15 psi for 1 h. After dilute acid the EFP were washed with water and dried in an oven. The dried EPB acid was then soaked in 2.5 N NaOH solution in the ratio of 10:1 and then applied microwave. The conditions set for microwave pretreatment are as follows: microwave power 700 W, temperature 80 °C; and duration 60 min, respectively [7]. The microwave treated biomass were washed with water and then dried in an oven prior to subsequent analysis.

2.4 Analytical procedures

The amount of extractives was measured by soxhlet extraction (tappi-1997;T 204 cm-97), Klason's lignin (tappi 2002;T 222 om-02), holocellulose content [8]. The TAPPI test method T 203 cm-09, with slightly modified version was employed to determine α-cellulose content. Meanwhile, the hemicellulose amount of EFB sample was calculated as the difference between holocelulose and cellulose [8].

III. RESULTS & DISCUSSION

The results for the removal of lignin and constituent of oil palm lignocellulosic biomass empty ruit bunches (EFB) are listed in table 1. Delignification in conventional pretreatment of EFB was absorbed

TABLE 1
CHEMICAL COMPOSITION OF RAW AND TREATED EFB BIOMASS (G/100GBIOMASS)

Pretreatment	(g/100g biomass)
Type	Lignin
Raw	18.87 ± 0.19
DA	12.34 ± 0.30
DA + Mw-A	5.67 ± 0.10

All measurements were duplicated and within the relative percentage difference below 5%.
Mw-A: Microwave-alkali, AAC: Alkali-autoclave-chemical

The lignin content was also examined after pretreatment dilute acid pretreatment and combinaction of dilute acid and alkali microwave pretreatment. In DA and DA + Mw-A pretreatments, both treated OPF samples contained (g/100g biomass): 12.34 and 5.67 klason's lignin, respectively. There was a high reduction of hemicellulose 90% and 10 % lignin in dilute acid pretreatment while in combination of dilute acid and microwave can attained maximum delignification of around 71.91%. Different paremeters such as microwave power, temperature and time duration were studied to attained maximum delignification as shown in table. 2. Dilute NaOH 2.5M were used in dilue acid and Mw-A pretreatment.

TABLE II
EFFECT OF THE MICROWAVE POWER, TEMPERATURE AND TIME ON THE DELIGNIFICATION OF THE EMPTY FRUIT BUNCH (EFB) BY MICROWAVE WITH 2.5M NAOH

Run NaOH 2.5 M	Temperature T (°C)	Duration, t (min)	Microwave power, MW (watt)	Lignin (g/100g)
1	80	60	700	13.40
2	90	70	800	9.30
3	100	80	900	5.67
4	110	90	1000	5.30

Using a combination of dilute acid and + Mw-A remove 90% of hemicellulose in the first step. While in the second step Mw-A, different parameters such as temperature (80-90°C), time (60-90min) and microwave power (700-1000 watt) were studied. The reulsts show that microwave power is great effect on delignification. Same effect was observed when the time or temperature is increase. Maximum delinification of 71.91% were attained at microwave power 900 watt, time 80 minutes and tepm 110°C. Hence, more lignin was eliminated in dilute acid + Mw-A pretreatment as compared with conventional pretreatment.

IV. CONCLUSION

The present study focus on the comparison of conventional autoclave pretreatment method and combination of dilute acid and microwave pretreatment. Using conventional pretreatment remove 34% of lignin. While using dilute acid in the first can remove 10% of lignin and 90% of hemicellulose. However, dilute alkali and microwave power 900 watt, time 80 minutes and temp 110 ^{O}C attained 71% delignification. Lignin and hemicellulose shield cellulose and is a major obstacle in enzymatic hydrolysis. Hence, removal of maximum hemicellulose and lignin can improve the enzymatic hydrolysis rate and result in high amount of organic acids production.

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