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Pretreatment of empty palm fruit bunch for production of chemicals via catalytic pyrolysis

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A B S T R A C T

The effect of chemical pretreatments using NaOH, H_2O_2, and $Ca(OH)_2$ on Empty Palm Fruit Bunches (EPFB) to degrade EPFB lignin before pyrolyis was investigated. Spectrophotometer analysis proved consecutive addition of NaOH and H_2O_2 decomposed almost 100% of EPFB lignin compared to 44% for the $Ca(OH)_2$, H_2O_2 system while NaOH and $Ca(OH)_2$ used exclusively could not alter lignin much. Next, the pretreated EPFB was catalytically pyrolyzed. Experimental results indicated the phenolic yields over Al-MCM-41 and HZSM-5 catalysts were 90 wt% and 80 wt%, respectively compared to 67 wt% yield for the untreated sample under the same set of conditions. Meanwhile, the experiments with HY zeolite yielded 70 wt% phenols.

1. Introduction

Biomass utilization as a source of clean energy and chemicals has attracted many research attentions in recent years amid to fossil fuel energy crisis and clean energy drive (Aho et al., 2008; Ji-Lu et al., 2008). Conversion of non-edible biomass such as agriculture residues, wood chips, and fruit bunches, stalks, industrial and municipal wastes into fuels and useful chemicals would solve waste disposal and energy issues (Baratieri et al., 2008).

Generally cellulose, hemicellulose, and lignin are the three major biomass components. Due to the crosslinking, lignocellulosic materials are insoluble in all solvents and are hard to degrade at typical biomass pyrolysis temperature (300–500 °C) (Aguado et al., 2006; Boateng et al., 2006). Hence, pretreatment of EPFB to dissolve lignin structure and cleave the chains seem to be a promising option before the pyrolysis process in order to avail important chemicals from biomass.

Pretreatments of lignocellulosic biomass have been investigated in many recent studies, for example in production of pulp kraft, lactic acid and bioethanol (Karin et al., 2007; Rebecca et al., 2007; Xu et al., 2006). Pretreatments are sometimes needed to make material handling easier through subsequent processing steps.

Chemical pretreatments have been widely reported as a potential technique for lignin degradation using acid and alkaline pretreatment, liquid hot water, pH controlled hot water and flow-through liquid hot water (Mosier et al., 2005). Effect of sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2) in decomposing cotton stalks lignin has been reported (Rebecca et al., 2007). $Ca(OH)_2$ has also been reported (Chang et al., 2001) for chemical pretreatment owing to its low cost and recovery from water as insoluble calcium carbonate by reacting with CO_2.

Pyrolysis is a thermal degradation of biomass under moderate temperature over short residence time in the absence of oxygen. Pyrolysis products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char (Boateng et al., 2006). Zeolite catalysts employed to pyrolysis of biomass have excellent performance as solid acid cracking catalysts due to their higher selectivity (Tamunaidu and Bhatia, 2007). Among the most industrially favored zeolite catalyst is HZSM-5. As a matter of fact, HZSM-5 has been used commercially in synthetic fuels, petrochemicals and petroleum refining (Xu et al., 2005). Besides, HY and Al-MCM-41 zeolites are also widely used in the production of bio-oil (Habib et al., 2008). Compared with microporous zeolites, mesoporous Al-MCM-41 provides a larger surface area and more accessible reaction sites.

The objective of this study is to investigate the performance of different chemical pretreatment methods in degrading EPFB lignocellulose structure. It is envisaged that degrading the rigid and complex structures of lignin before pyrolyzing the EPFB would improve the quality of the bio-oil. In addition, this study also intends to investigate the effects of pretreatment process on the chemical compositions produced through catalytic pyrolysis. Product distributions from HZSM-5, HY and Al-MCM-41 catalyzed pyrolysis were also investigated for qualitative measurement.

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2. Methods

2.1. Materials

Seasoned EPFB sample aged approximately 6–12 months was obtained from the Faculty of Mechanical Engineering, Universiti Teknologi Malaysia and was crushed in a high-speed rotary cutting mill to give particle size in the range of 0.1–0.5 cm. The sample was dried at 105 °C for 24 h prior to the experiments. The EPFB contained 18.1 wt%, 59.7 wt%, 22.1 wt% of lignin, cellulose and hemicellulose, respectively. Its high heating value (HHV) was reported to be 16.74 MJ/kg. Elemental analysis has verified the EPFB contains 47.89% carbon, 45.41% oxygen and 6.05% hydrogen.

The catalysts used in the EPFB pyrolysis were HZSM-5, HY and Al-MCM-41. Both HZSM-5 and HY catalysts were obtained from Zeolyst International, while Al-MCM-41 was synthesized at the Faculty of Science, Universiti Teknologi Malaysia. The characteristics of the catalysts are displayed in Table 1. The structural characteristics of the zeolites (pore area, pore volume, and pore diameter) were measured using nitrogen isothermal adsorption at 77 K in AUTOSORB-6 Quantachrome equipment.

2.2. Pretreatment condition

Three chemical pretreatment methods were employed in this study. NaOH and $Ca(OH)_2$ at a concentration of 100 mM were used to pretreat 5 g of the EPFB samples in each method. The samples were treated in a 250-mL Erlenmeyer flask under constant stirring at 200 rpm and temperature being 27 °C.

The first method was exclusively conducted over one type of chemical, either using NaOH or $Ca(OH)_2$. In the second and third methods, H_2O_2 was added simultaneously and consecutively, respectively. All experiments were conducted within 48 h of the pretreatment period. At the end of the reaction, the pretreated samples were washed and dried overnight at 100 °C. A total of seven experiments were performed to investigate the effects of chemical pretreatment method on lignin degradation. Controls were carried out at the same operating conditions but in the absence of any chemicals.

2.3. Pyrolysis experimental procedure

The pyrolysis experiments were conducted in a semi-batch stainless steel reactor using the pretreated EPFB (30 g) mixed with 5 wt% HZSM-5 catalyst. The experimental system was initially purged with inert nitrogen for approximately 30 min. The reactor was externally heated by an electrical furnace at a fixed temperature of 300 °C, which was monitored by a *K*-type thermocouple. Vapors produced from the reaction chamber were collected as liquid products in a round bottom flask while non-condensable gaseous components were collected into a gas sampling port. The effect of HZSM-5, HY and Al-MCM-41 catalysts on the production of important chemicals at the same pyrolysis operating conditions was also notified.

Table 1
Characteristics of zeolite catalysts used in catalytic cracking.

Characteristics	HZSM-5	HY	Al-MCM-41
SiO_2/Al_2O_3 (w/w)	30	30	N/A
Particle size (nm)	14.3	14.5	19.5
Micro pore area (m^2/g)[a]	444.8	1375	1859
Micro pore volume (cc/g)[a]	0.16	0.49	0.66
Total pore volume (cc/g)	0.17[b]	0.34[c]	0.97[d]
Micro pore width (Å)[a]	8.2	0.22	0.51
Average pore diameter (Å)	1.55	15.39	43.43
Total weight loss at 50–150 °C (%)	9.45	19.07	36.76

[a] DR Method.

[b] With diameter less than 15.4 Å at $P/Po = 0.09442$.

[c] With diameter less than 14.3 Å at $P/Po = 0.07472$.

[d] With diameter less than 3192.7 Å at $P/Po = 0.99395$.

2.4. Lignin content determination

An amount of 0.1 g EPFB was added into a mixture of 20 mL of 0.02 mol/L potassium permanganate ($KMnO_4$) with 5 mL of 2.0 mol/L sulfuric acid (H_2SO_4) and mixed well for three minutes. Solid sample was separated from the solution through filtration, while the filtrate was measured using UV-Spectrophotometer (Shimadzu, USA) at 546 nm of wavelength. The one-point calibration method was carried out to determine the value of Kappa number (Chai and Zhu, 1999), as shown in Eq. (1).

$$K = \frac{a}{w}\left(\frac{A_o - A_e}{A_o}\right) \tag{1}$$

where, K is Kappa Number, a is the volume of $KMnO_4$ used in the solution, w is weight of moisture-free sample used, A_o is spectral intensities at time $t = 0$ (before sample is being added) and A_e is spectral intensities at the end of the reaction.

Accordingly, lignin content in the sample was calculated from the values of Kappa Number, K using Eq. (2), where the percent of lignin degradation is illustrated in Eq. (3) (Ohra-aho et al., 2005).

$$\text{Lignin Content } (wt\%) = 0.15\,\text{K} \tag{2}$$

$$\text{Lignin degradation} = \frac{\text{Lignin}wt\%\ (\text{untreated}) - \text{Lignin}wt\%\ (\text{treated})}{\text{Lignin}wt\%\ (\text{untreated})} \tag{3}$$

2.5. Characterization of bio-oil

The functional groups of bio-oils were analyzed by using Fourier Transform Infrared (FTIR) spectrophotometer. The absorption frequency spectra were recorded and plotted. The standard IR-spectra of organic compounds were used to identify the functional groups of the bio-oil.

The chemical compositions of the bio-oil were analyzed using Gas Chromatography (GC), and the compounds were determined using Mass Selectivity (MS) detector equipped with a 30.0 m × 250 μm × 0.25 μm nominal column HP-5MS. Helium gas was employed as a carrier gas at a constant flow rate of 1 ml/min. The heating of the column started at 80°C, and programmed to 250 °C by a rate of 10 °C/min and held for 5 min. Finally, the temperature was ramped to 300 °C at the same rate and kept isothermal for 15 min. The compounds obtained were grouped as aldehydes, acids, alcohols, ketones, phenols and polyaromatic hydrocarbons.

The test of basic fuel properties includes pH, density, kinematic viscosity and higher heating value (HHV). The pH value was measured by a pH probe with digital meter (Lab 850 Schott). The density of bio-oil was determined using ASTM 4052 method in Picnometer. The kinematic viscosity at 40 °C of bio-oil was analyzed using ASTM D445-94 in kinematic viscosity bath and viscometer capillary, while the HHV was determined via bomb calorimeter.

The yield of EPFB conversion and product yield of gaseous and liquid oils obtained in the pyrolysis reaction were calculated on weight basis according to Eqs. (4)–(6):