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Catalytic Pyrolysis of Empty Fruit Bunch (EFB) with Cobalt Alumina Catalyst

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ABSTRACT

Empty fruit bunch (EFB) is viewed as a potential candidate for renewable energy source since it is easily available, abundant and produces less environmental pollution. Pyrolysis is a thermochemical breakdown of biomass to produce bio-oil, bio-char and gas and performs under inert environment at high temperature. Catalytic pyrolysis is a technique that assist the breakdown of biomass under desired conditions. In this study, a series of non-catalytic and catalytic pyrolysis of EFB was performed using a fixed bed reactor. The catalytic pyrolysis of EFB with cobalt oxide doped alumina (CoO/Al2O3) catalyst was performed from room temperature to 500°C in the presence of nitrogen (N2) gas. The effects of two process parameters were investigated towards distribution of pyrolysis product yields. The effects were different catalyst to biomass ratio in the range of 0-20 wt% and different percentage composition of Co in CoO/Al2O3 catalyst in the range of 0-25 wt% towards pyrolysis product yields. For non-catalytic EFB pyrolysis, the product yields were 32.90, 25.65 and 41.45 wt% respectively for bio-oil, char and gas productions. When CoO/Al2O3 catalyst to biomass ratio was increased to 10 wt% with 5 wt% Co addition into CoO/Al2O3 catalyst, the highest bio-oil yield of 44.28 wt% was attained with bio-char and gas yields of 24.00 wt% and 34.12 wt% respectively. It can be concluded that the addition of CoO/Al2O3 catalyst into EFB pyrolysis had actually increased the bio-oil production by 11.38 wt%.

Keywords:
Catalytic pyrolysis, empty fruit bunch, cobalt alumina

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1. Introduction

In Malaysia, oil palm industry generated 40 million tons of biomass in the forms of oil palm frond (OPF), empty fruit bunch (EFB) and oil palm trunk (OPT) annually [1]. It is reported that more than 90% of EFB can be converted into fibrous material while OPT and OPF only convert 25% and 50% into fibrous material respectively. This amount of wastes provide massive resources for the conversion of wastes into value added products. Recently more research has been investigated on utilization of EFB for the production of bio-oil using pyrolysis process [2]. The production of bio oil is one of the alternative way in replacement of fossil fuel which produce environmentally friendly energy source. Several catalyst have been utilized in the catalytic pyrolysis of biomass in order to produce bio-oil with either high yield or with high aliphatic and aromatic content and low oxygenated compounds. Hydrotalcite-like precursor (HT) with different Mg/Al ratios were used in the catalytic pyrolysis process of wheat straw performed in a fixed bed reactor at 550°C. The amount of catalyst used was approximately 0.8 g in 4 g of wheat straw in the bed-mode. It was reported that the Al-mg-mixed mode with reduced Al concentration generated bio-oil with a remarkable reduction of oxygenated compounds [3]. Catalytic pyrolysis of EFB with boric oxide catalyst was conducted in a fixed bed reactor and it was reported that the addition of catalyst has increased char yield, reduced the gas yield and had an overall deoxygenation effect [4]. Sesame stalk and *Euphorbia rigida* were pyrolysed with commercial catalysts namely HCK-1.3Q and DHC-32 respectively. It was stated that both catalyst had positive effect by increasing the bio-oil yield [5]. The catalytic pyrolysis of basic MgO with cotton seed was performed and it was reported that the addition of MgO had also increased the bio-oil yield [6]. Herb residue was pyrolysed with alumina catalyst and it was determined that the bio-oil yield increased as well as the aliphatic content in bio-oil [7]. Hazelnut shell was pyrolysed with several different catalysts such as red mud, HZSM-5, potassium carbonate (K_2CO_3) and tin oxide (SnO_2) nanoparticles. It was reported that with tin oxide (SnO_2) nanoparticles, maximum amount of gas yield was obtained [8]. Zeolites catalysts assisted several reactions such as dehydration, decarboxylation, decarbonylation, isomerization and dehydrogenation during biomass pyrolysis process [9]. It can be seen that there are a lot of reported studies focused on catalytic pyrolysis of biomass. However, there is scarce information regarding catalytic pyrolysis of EFB especially with cobalt doped alumina catalyst. Therefore, this study is aimed to produce conduct catalytic pyrolysis of torrefied EFB using cobalt alumina catalyst. The effect of catalyst to biomass ratio, percentage cobalt to alumina and nitrogen flowrate were investigated towards distribution of pyrolysis products yields.

2. Materials and Methods

2.1 Biomass Pre-treatment

EFB was obtained from palm oil mill North Star Palm Oil Mills which is located in Kuala Ketil, Kedah, Malaysia. The biomass was rinsed with tap water to remove impurities and dried in the oven at 80°C for 24 hours. Then it was cut by using grinder and sieved using the Retsch sieve shaker. The EFB of particle sizes of 780-1000µm was been used in the experiment [10].

2.2 Proximate Analysis of EFB

The proximate analysis was conducted on EFB with particle size in range 125-250 µm in accordance with the American Standard Testing Materials (ASTM). The moisture content was determined following the ASTM E871-82. The volatile matter and ash contents were determined according to ASTM E872-82 and ASTM D1102-84 respectively. The fixed carbon content was estimated by difference.

2.4 Catalyst Preparation

10g of aluminium oxide (Al_2O_3, Acros Organic, Belgium 99% extrapure) was calcined in a furnace at 923K for 5 h at a rising rate of 3 K min^{-1} under stagnant atmosphere and then the catalyst were placed in a desiccators before use. CoO/Al_2O_3 was prepared using wet impregnation method. 10 ml of deionized water was measured and added into a beaker. A pre-weighed respective quantity of nitrate salt of Co with atomic ratio to alumina of 5 % dissolved with deionized water. The solution now held the respective ion was added dropwise into a beaker which contained 10.00g of precalcined alumina until approximately 60% of solution was transferred. Then it was dried at room temperature for 5 hr. The remaining solution was added and dried at 393 K for 2 h. After that, the catalyst precursor was calcined at 873 K for 5h at a ramp rate of 3 K min^{-1}.

2.5 Catalytic Pyrolysis in a Fixed-Bed Reactor

Catalytic pyrolysis of EFB with CoO/Al_2O_3 catalyst was carried out using a vertical fixed-bed reactor placed in an electric furnace (Figure 1). Pyrolysis was performed using approximately 10.00 g of EFB that was mixed with CoO/Al_2O_3 at 5 wt% at in-bed mode. Catalyst to biomass ratio was varied from 5-20 wt%. Reactor was purged with nitrogen at 200 ml min^{-1} for 30 mins to make sure an inert environment for pyrolysis. The final temperature of pyrolysis was set at 500 ^oC with a heating rate of 20 ^oC/min and a holding time of 30 mins. Products of pyrolysis were swept by nitrogen and passed through a condenser and the receiver flask was immersed in ice bath which having cooling and condensing effect. The flask used was weighed before and after the reaction to determine the bio-oil yield by difference. The solid residue left was separated from the reactor tube and its weight was recorded. The experiments were conducted three times to give standard deviation of ±3.0 wt% and the mean values were used for analysis. Based on batch process, the performed calculations are shown in Eqs. 1, 2, 3 and 4 [11].

$$\text{Conversion (\%)} = \frac{mass\ of\ EFB\ (g) - mass\ of\ char\ residue\ (g)}{mass\ of\ EFB\ (g)} \times 100\% \tag{1}$$

$$\text{Bio-oil yield (wt\%)} = \frac{mass\ of\ bio-oil\ (g)}{mass\ of\ EFB\ (g)} \times 100\ \% \tag{2}$$

$$\text{Gas yield (wt\%)} = \frac{mass\ of\ char\ residue\ (g)}{mass\ of\ EFB\ (g)} \times 100\ \% \tag{3}$$

$$\text{Gas yield (wt\%)} = 100\ \text{(wt\%)} - \text{bio-oil yield (wt\%)} - \text{char residue (wt\%)} \tag{4}$$

2.6 Analysis of Bio-oil with Fourier Transform Infra-Red (FTIR) Spectrophotometer

Bio-oil produced was analysed with Fourier Transform Infra-Red (FTIR) spectrophotometer (Perkin Elmer Spectrum 65, Perkin Elmer Inc., USA) to evaluate the presence of functional groups that exist. Small amount of bio-oils obtained after non-catalytic and catalytic pyrolysis of EFB were mounted on a potassium bromide (KBr) disc. Absorbance was measured in the spectral range of 4000 to 650 cm^{-1}.

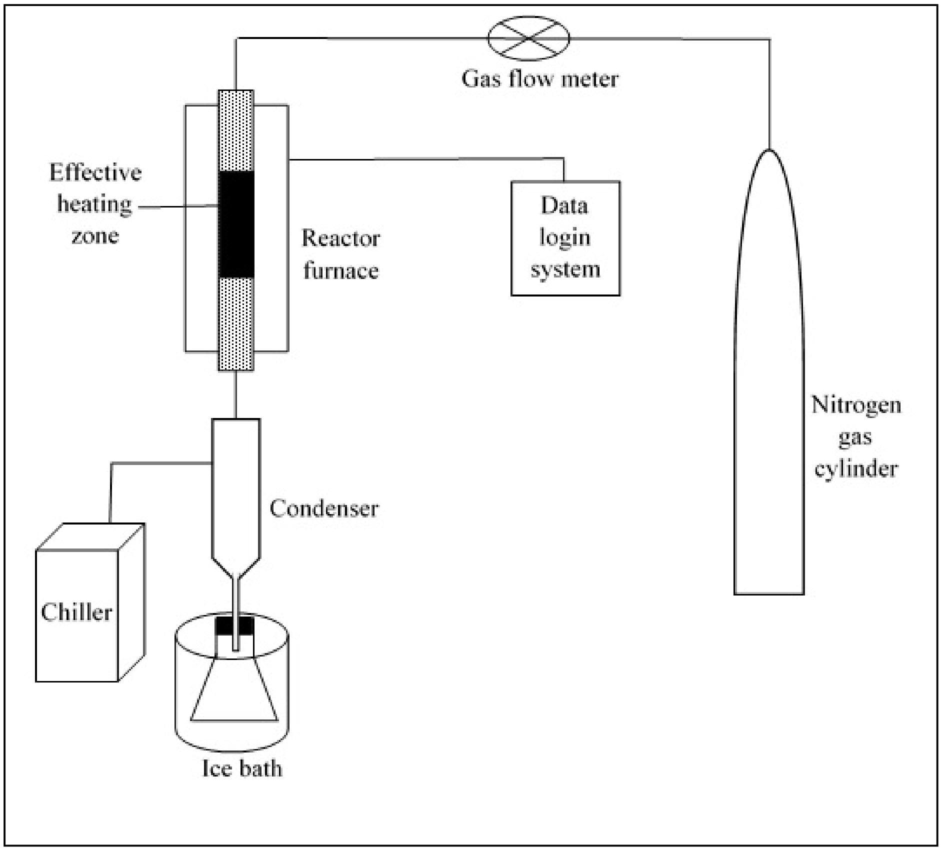

Fig. 1. The vertical fixed-bed reactor furnace

3. Results and Discussions

3.1 Proximate Analysis of EFB

The results for proximate analysis of EFB and comparison with reported studies are as shown in Table 1. The experimental data are in good agreements with the reported studies.

Table 1
The proximate analysis of EFB

Moisture Content (%)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon (%)	Reference
8.20	64.13	8.67	19.00	This study
2.40	81.90	3.10	12.60	[12]
4.10	65.30	6.90	23.70	[3]
7.95	83.86	5.36	10.78	[13]

3.2 Reactor Studies on the Effect of CoO/Al_2O_3 Catalyst to Biomass Ratio towards Pyrolysis Product Yield

In this study, both non-catalytic and catalytic pyrolysis of EFB with CoO/Al_2O_3 were conducted in a fixed-bed reactor to produce bio-oil, bio-char and gas products. The catalyst to biomass ratio varied was in the range of 5-20 wt%. The percentage addition of CoO to Al_2O_3 catalyst was kept constant at 5 wt%. The results are as shown in Table 2.

The bio-oil, char and gas yields for non-catalytic EFB pyrolysis were 32.90, 25.65 and 41.45 wt% respectively with a conversion of 74.35%. When 5% CoO/Al_2O_3 catalyst was mixed with EFB, the bio-oil yield increased to 38.11 % with a lower yield of gas. The bio-oil yield was at its maximum of 44.28 wt% when 10 % CoO/Al_2O_3 catalyst was mixed with EFB. Concurrently, the gas yield was at its minimum yield of 30.73 %. The addition of 10 % CoO/Al_2O_3 catalyst to biomass had promoted the primary reactions that occurred during EFB pyrolysis. This contributed to the highest bio-oil yield. Further increasing the CoO/Al_2O_3 catalyst addition to 20 wt% only resulted in the decreased bio-oil yield of 34.17 wt% (Table 2). Throughout, the changes in CoO/Al_2O_3 catalyst addition in EFB during pyrolysis, the bio-char yield was rather consistent in the range of 23.63-25.42 wt%. The conversion was also consistent in the range of 74.24-76.38 % in catalytic pyrolysis process. Generally, the addition of Co/Al_2O_3 catalyst during catalytic pyrolysis of EFB showed an increase in bio-oil yield.

Table 2
The effect of catalyst to biomass ratio over the pyrolysis products yields

Catalyst to biomass ratio (%)	Bio-oil (wt %)	Bio-char (wt %)	Gas (wt %)	Conversion (%)
0	32.90	25.65	41.45	74.35
5	38.11	25.42	36.48	74.58
10	44.28	25.00	30.73	75.00
15	36.71	25.76	37.54	74.24
20	34.17	23.63	42.21	76.38

3.3 Reactor Studies on the Effect of Different Percentage Composition of Co in CoO/Al_2O_3 Catalyst Towards Pyrolysis Products Yields

From previous study, it was determined that when catalyst to biomass ratio was set at 10 wt%, the maximum bio-oil yield was obtained. Therefore, in this subsequent study, the catalyst to biomass ratio was kept constant at 10 wt% in the catalytic pyrolysis process. However, the percentage composition of Co in the CoO/Al_2O_3 catalyst was varied in the range of 5-25 wt%. The evaluation towards catalytic pyrolysis process of EFB with CoO/Al_2O_3 catalyst in a fixed bed reactor was performed by monitoring the distribution of pyrolysis product yields such as bio-oil, bio-char and gas. The experimental data are as shown in Table 3.

Table 3
The effect percentage compositional addition of Co into CoO/Al_2O_3 catalyst towards pyrolysis products yields

Co: Al % catalyst				
Co:Al (wt%)	Bio-oil (wt%)	Bio-char (wt%)	Gas (wt%)	Conversion (%)
0	32.90	25.65	41.45	74.35
5	44.28	25.00	30.73	75.00
10	41.89	24.00	34.12	76.00
15	41.72	24.39	33.90	75.62
20	41.83	23.89	34.28	76.11
25	41.89	24.84	33.28	75.17

According to Table 3, the bio-oil, char and gas yields for non-catalytic EFB pyrolysis were 32.90, 25.65 and 41.45 wt% respectively with a conversion of 74.35%. In catalytic pyrolysis process, when the percentage composition addition of Co into CoO/Al_2O_3 catalyst was increased to 44.28 wt%. This was the highest bio-oil yield with bio-char and gas yields of 25.65 wt% and 41.45 wt% respectively. Further increasing the percentage composition of Co into CoO/Al_2O_3 catalyst from 10 -25 wt% had resulted in decreased bio-oil yield ranging from 41.72-41.89 wt%. The gas yield showed an increased amount in the range of 30.73-34.28 wt%. The addition of Co into CoO/Al_2O_3 catalyst had actually inhibited primary reactions during catalytic pyrolysis process of EFB. Simultaneously, it promoted the deoxygenation reactions or removal of oxygenated compounds via decarboxylation and decarbonylation reactions . In decarboxylation reaction, two oxygen atoms from EFB combined with one carbon atom and being removed as CO_2 while in decarbonylation reaction, one oxygen atom combined with one carbon atom and underwent expulsion as CO [14]. These processes were entropically favored because the products released were gases.

3.4 FTIR Analysis of Bio-oil

The FTIR spectra of bio-oil from pyrolysis of EFB from non-catalytic and catalytic pyrolysis optimum bio-oil yield are shown in Figures 2 and 3 respectively. From the non-catalytic and catalytic pyrolysis bio-oil, the O–H stretching vibrations between 3400-3200 cm^{-1} show the presence of free hydroxyl bonds phenol and alcohols [15]. An absorbance peak of C-H stretching vibrations in between 2930-2850 cm^{-1} with another C-H deformation vibrations between wavenumber of 1460-1380 cm^{-1} suggested the presence of alkanes [16]. On top of that, the C=O stretching vibrations between 2400-2300 cm^{-1} and 1720-1700 cm^{-1} showed the existence of ketones, aldehydes and carboxylic acids. The peak at 2350 cm^{-1} that existed in the non-catalytic bio-oil was absent in the catalytic bio-oil. Therefore, it is suggested that the CoO/Al_2O_3 catalyst possessed decarboylation activity that able to assist the expulsion of CO_2 group. The sharp peak at the wavenumber range of 1640-1510 cm^{-1} indicated the presence of C=C stretching vibrations originated from the presence of alkenes and aromatics. C-O vibrations are absorbed from carbonyl components such as alcohols, esters, carboxylic acids or ether which happens in between 1060 cm^{-1} and 1240 cm^{-1} of the bio-oil.

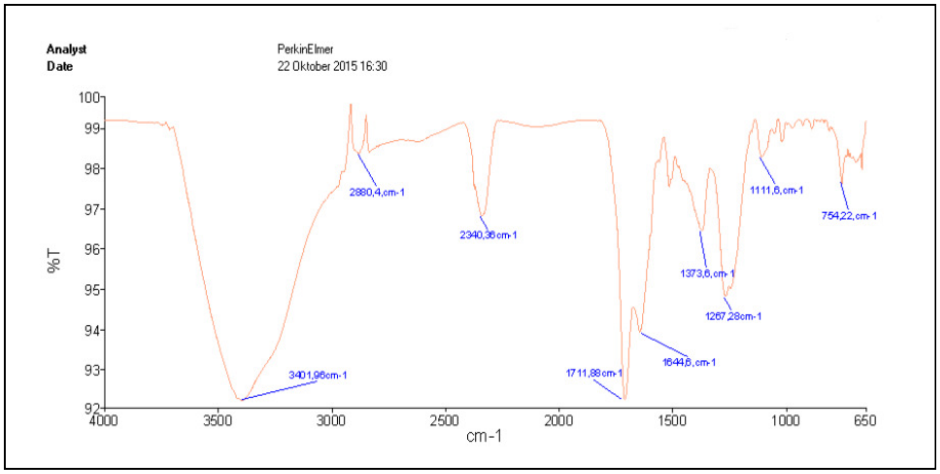

Fig. 2. FTIR spectrum of bio-oil from non-catalytic pyrolysis of EFB

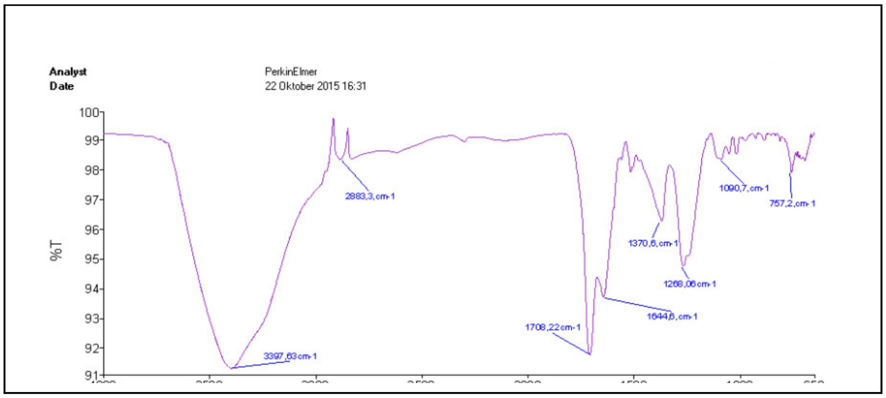

Fig. 3. FTIR spectrum of bio-oil from catalytic pyrolysis of EFB

4. Conclusion

Catalytic pyrolysis of EFB and CoO/Al_2O_3 was performed in a fixed-bed reactor at 500 ^oC under nitrogen atmosphere at a ramp rate of 20 $^oC/min$. It was identified that the addition of 10 wt% CoO/Al_2O_3 catalyst with 5 wt% Co had increased the bio-oil yield. The bio-oil analysis using FTIR spectroscopy showed that the presence of catalyst has deoxygenating effect since the presence of carboxyl group that initially present in the non-catalytic bio-oil had been removed in catalytic bio-oil.

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