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Process optimization on empty fruit bunch catalytic pyrolysis with copper oxide/alumina and quantitative analysis of bio-oil produced using gas chromatography–mass spectrometry

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ABSTRACT

In this work, a fixed-bed reactor was used to catalytically pyrolyze empty fruit bunches (EFB) using copper oxide-doped aluminum oxide (CuO/Al_2O_3). CuO/Al_2O_3 was analyzed by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The existence of monoclinic CuO and Al_2O_3 phases was identified. The presence of CuO distributed onto spherical and rectangular-shaped Al_2O_3 was observed by SEM analysis. Response surface methodology was employed to optimize the process, with three independent parameters selected within predetermined ranges: catalyst-to-biomass ratio (7.65–30.00 wt%), heating rate (20–60 °C/min), and reaction temperature (300–600 °C). Analysis of variance (ANOVA) shows that the model's p-value of 0.0312 indicated that it is significant. With a p-value of 0.0057, the pyrolysis temperature (Factor A) was identified as a significant factor. The optimal values were determined to be a reaction temperature of 540.69 °C, a heating rate of 58.01 °C/min, and a catalyst-to-biomass ratio of 9.12 wt%, resulting in an average bio-oil yield of 30.87 wt%. Using gas chromatography-mass spectrometry (GC-MS), the bio-oils produced at pyrolysis temperatures of 300 °C, 600 °C, and 540.69 °C were analyzed to examine variations in their chemical compositions. It was found that the bio-oils produced at pyrolysis temperatures of 300 °C, 600°C, and 540.69 °C contained high amounts of ketones of approximately 54.96, 30.35, and 50.44%, respectively. Specifically, the major ketone compounds identified were 2-propanone-1-hydroxy and 1-hydroxy-2-butanone, which are present in all bio-oils but at different proportions, such as 35.53, 26.74, and 40.25% in bio-oils produced at a pyrolysis temperature of 300 °C, 600 °C, and 540.69 °C respectively. The chemical compositions were also grouped into functional groups, including carboxylic acids, alcohols, esters, phenols, aldehydes, aromatics, furans, and hydrocarbons.

Keywords: empty fruit bunch (EFB), catalytic pyrolysis, bio-oil, pyrolysis temperature, response surface methodology.

INTRODUCTION

Currently, global warming is identified as one of the most critical environmental issues, which is caused by the burning of fossil fuels (Rajesh et al., 2025). The harmful environmental impact associated with the burning of fossil fuels has spurred the development of renewable and

sustainable energy resources (Wu et al., 2017). Biomass is widely acknowledged as a promising energy source due to its renewable characteristics and reduced environmental impact compared to fossil fuels. The palm oil industry produced substantial quantities of 16–18 million tons of empty fruit bunches (EFB) during the crude palm oil (CPO) processing (Rosli et al., 2017; Hamdan et al., 2021). EFB refers to the coarse, brown biomass remaining after the sterilized oil palm fruits are detached by a rotary thresher drum in palm oil processing plants (Chang, 2014). Biomass pyrolysis is a thermochemical degradation process of biomass in the absence of oxygen at moderate temperatures, typically in the range of 400–700 °C (Mohan et al., 2006; Özbay et al., 2006). The pyrolysis process produces significant yields by heating the biomass and condensing the resulting vapors either under a nitrogen gas stream or under a reduced oxygen atmosphere. Due to its operational simplicity, pyrolysis has become a preferred technique for thermal degradation (Onay, 2014). The products are pyrolysis liquid, bio-char, and bio-gas (Abdullah et al., 2011). In comparison to biomass conversion processes like combustion and other biological techniques, biomass pyrolysis offers a cheaper cost for liquid fuel production, can process a wider spectrum of feedstock, has a shorter residence time, and requires less feedstock pre-treatment.

Pyrolysis end-product compositions and yields are largely determined by biomass species, structural and chemical composition, heating rates, temperature, reactors, co-reactant, particle size, and other factors. Currently, biomass pyrolysis with the addition of catalyst material is a preferred technique to enhance the pyrolysis liquid, also known as bio-oil, either qualitatively or quantitatively. Under non-catalytic pyrolysis, normally the bio-oil contains a high amount of oxygenated compounds with low yield (Hamdan et al., 2021). Hence, catalytic pyrolysis with the addition of catalyst material could modify the process towards either reducing the oxygenated compounds, increasing the aliphatic and aromatic compounds, or increasing the bio-oil production. The catalyst enhances C-O bond breaking, assists dehydration, decarboxylation, and decarbonylation of lignocellulosic materials, hence promoting the removal of oxygenated compounds and increasing the required components in bio-oil (Chang, 2014). The pyrolysis is affected by the doped and undoped metal oxide with the catalyst. The hydrolysis, decarbonylation, and decarboxylation reactions of the catalyst may assist oxygen removal in pyrolysis. The deoxygenation reaction, such as decarboxylation removes oxygen by releasing carbon dioxide, whereas decarbonylation removes oxygen by removing carbon monoxide. Because of the acidity and porosity, copper oxide-doped alumina (CuO/Al_2O_3) catalyst is chosen in this study. CuO is a transition metal oxide that accepts electrons during the pyrolysis process (Zhang et al., 2019). Al_2O_3 was chosen as the acidic catalyst, which led to the pyrolysis of biomass via decarbonylation reaction (Stefanidis et al., 2011). It was reported that Cu/Al_2O_4 spinel structure and Cu_2O showed good catalytic activity in shifting the cracking temperature slightly in paper pyrolysis (Chattopadhyay et al., 2009). The application of mixed metal oxide in the biomass pyrolysis process has been considered as a technique to improve the bio-oil qualitatively and quantitatively. Ozbay et al. (2018) reported the activity of Cu/Al_2O_3 in the pyrolysis of tomato in a reactor that produced bio-oil of 30.31 wt% (Özbay et al., 2018). Onay (2014) mentioned Ni/Al_2O_3 in the catalytic pyrolysis of Daphne seed (*Laurus nobilis* L.) in a fixed-bed tubular reactor that produced 38.4 wt% bio-oil yield (Onay, 2014). Auta et al. (2014) reported a high bio-oil yield of 42.64 wt% in the presence of $Ca(OH)_2$ catalyst (Auta et al., 2014). Normally, the catalytic pyrolysis process is conducted under one-factor-at-a-time, which requires a higher number of experimentations, is more time-consuming, and uses a high amount of chemicals. By using response surface methodology (RSM), the number of experimentations can be reduced. Thus, save time and chemicals. This study focused on using RSM for the optimization of catalytic pyrolysis of EFB in the presence of CuO/Al_2O_3 catalyst.

Following that, the compositional analysis of bio-oil using gas chromatography-mass spectrometry (GC-MS) and derived from the catalytic process of EFB with CuO/Al_2O_3 catalyst at three types of bio-oils with low yield, high yield and under optimum conditions are scarce. Therefore, this paper aimed to report on the optimization of catalytic pyrolysis of EFB with CuO/Al_2O_3 through validation of the predicted conditions. The complete quantitative analyses using GC-MS were performed on three types of bio-oils with low yield, high yield, and at optimum conditions. These three types of bio-oil were quantified in order to investigate the chemical compounds that exist in these bio-oils.

METHODOLOGY

Materials

In the current study, fibrous empty fruit bunch (EFB) was collected in Kedah, Malaysia. The EFB sample was dried for 24 hours after washing. Next, it underwent shredding and sieving to yield EFB with a particle size lower than 500 µm, which is suitable for the application in the reactor tube.

Methods

Proximate analysis

The values for volatile matter, fixed carbon, moisture, and ash contents were quantified by proximate analysis. The moisture content was analyzed using the moisture analyzer, MX-50. In each run, approximately 2.00–2.05 g of biomass sample was introduced into the analyzer, and these were conducted in triplicate to calculate the average value. The volatile matter was conducted based on ASTM E872-82, and the ash content was performed following the ASTM E1755-01. The value of fixed carbon was obtained from the difference value (Awang et al., 2019).

Catalyst preparation

CuO/Al_2O_3 catalyst was prepared by wet impregnation method. A sample of Al_2O_3 (10.00–10.05 g) was heat-treated at 650 °C for 5 hours in a muffle furnace. A sample of 1.180–1.185 g of copper nitrate trihydrate salt was dissolved in deionized water in a beaker to produce copper salt solution. Next, half of the solution was poured onto precalcined Al_2O_3 followed by drying. Another half portion was added later. Then, it was calcined at 600 °C for 5 hours (Awang et al., 2019).

X-ray diffraction (XRD) analysis

The crystallization phase of CuO/Al_2O_3 was determined using a D8 Bruker Advanced, with Cu Kα in the range of 10–80°, with a step size of 2θ = 0.03° and 38.4 s scan step time. The evaluation of phases exist was determined using XPert Highscore Plus software.

Scanning electron microscopy (SEM) analysis

The morphological properties of the catalyst was evaluated using a scanning electron microscope (SEM). It was carried out by using model JEOL JSM-6010LV with an acceleration voltage of 10 kV. Sticky tape was used to bind the CuO/Al_2O_3 powder to the SEM stubs layer. Then, it was placed in sputter coating for five minutes to coat it with platinum in order to attain high reflectivity during the scanning process.

EFB catalytic pyrolysis with Cuo/Al_2O_3 catalyst in a fixed-bed reactor

Catalytic pyrolysis of EFB with CuO/Al_2O_3 was carried out in a fixed bed reactor. A sample of 5.00–5.05 g EFB was located in a reactor tube. The levels of pyrolysis temperature, heating rate, and catalyst to biomass ratio were set by DOE software as shown in Table 1. Nitrogen gas (N_2) was purged into the reactor prior to the experimental run at 100 ml min^{-1} for 20 minutes to remove oxygen. The holding time for each experiment was set at 30 minutes. During the heating process, the vapor from the reactor tube was quenched into bio-oil. Bio-oil was collected in the receiver flask and then it was immersed in a mixture of water and ice to cool the remaining uncondensed vapor. The gas was discharged into the atmosphere, and the solid product, bio-char, was taken out from the reactor tube (Mohamed et al., 2020). The, bio-oil yield was calculated using Equation 1.

$$Bio-oil\ yield = \frac{Mass\ of\ bio-oil\ (g)}{Mass\ of\ EFB(g)} \times 100\% \quad (1)$$

Design of experiments

The parameters that were investigated with their respective levels are as shown in Table 1. 20 experimental runs were suggested as shown in Table 2. The values of 197.73 °C and 702.27 °C are included in this study because these are the -α and + α values, which are suggested by the software that could capture both linear and interaction effects. A paired t-test was performed on the mean from the experimental runs with the predicted run with the null hypothesis (H_o), which states that there is no significant difference between the mean of the experimental runs and the mean from the predicted run suggested from RSM. Meanwhile, the alternative hypothesis (H_1) states that there is a significant difference between the mean of the experimental runs and the mean from the predicted run suggested by RSM.

Table 1. Parameters followed for the optimal study

Independent variable (Numerical)	Units	Symbol	Low actual	High actual
Pyrolysis temperature	°C	A	300	600
Heating rate	°C/min	B	20	60
Catalyst to biomass ratio	wt %	C	7.65	30

Table 2. Experimental runs as per the DoE analysis

Run	A	B	C
1	450	73.64	18.82
2	450	6.36	18.82
3	450	40	18.82
4	450	40	18.82
5	702.27	40	18.82
6	600	20	30
7	300	60	7.65
8	197.73	40	18.82
9	450	40	18.82
10	300	20	30
11	450	40	0.03
12	450	40	18.82
13	300	20	7.65
14	450	40	18.82
15	300	60	30
16	450	40	18.82
17	600	20	7.65
18	600	60	7.65
19	600	60	30
20	450	40	37.62

Bio-oil pretreatment

Three samples of bio-oil that underwent pretreatment prior to GC-MS analysis were those from the highest and lowest yields, as well as from the optimum condition. 150 µL of bio-oil was added with 5 mL of methanol solvent inside the normal vials and then shaken gently until fully dissolved. Then, the mixture was transferred into the syringe. The syringe was then attached with a 0.45 µm filter membrane. Then, the mixture from the syringe that was attached with a membrane filter was transferred into 2 mL special vials to filter out the impurities. Finally, the diluted sample was ready to be injected into GC-MS (Ferreira et al., 2020).

GC analysis of bio-oil

The oven temperature started from 35 °C for 2 minutes up to 250 °C at a heating rate of 20 °C/min for 20 minutes and helium as a carrier gas with the inlet flow rate at 1.5 mL/min. The injector and detector temperatures were set at 280 °C. Split ratio of injector port was 1:20. Electron impact (EI) mode was at 70 eV with ion source temperature 200 °C. The mass range was 20 to 500 amu (m/z), and the sample injection volume was 1.0 µL (Rajesh et al., 2025).

RESULTS AND DISCUSSION

Catalytic pyrolysis is a thermochemical process that uses heat and a catalyst to break down organic materials, such as biomass, into smaller molecules. This procedure is an improved version of pyrolysis in which a catalyst is added to help reduce the temperature of the reaction, increase the yield of desired products, including syngas, biochar, and bio-oils. EFB offers great promise as a biomass material for a number of uses, such as energy production, composting, and the creation of bio-based materials. In this investigation, the EFB pyrolysis process was assisted by CuO/Al_2O_3 in a fixed-bed reactor. Because of its special physicochemical characteristics, this combination is extensively researched and used in many different applications, especially in catalysis. Al_2O_3 is an efficient catalyst in chemical reactions such as pyrolysis and combustion when CuO is present because it improves the catalytic, adsorptive, and thermal properties of Al_2O_3. Herein, in order to produce bio-oil, from EFB catalytic pyrolysis is performed in a fixed-bed reactor.

XRD analysis of CuO/Al_2O_3 catalyst

Figure 1 illustrates the XRD pattern of CuO/Al_2O_3 catayst prepared by the wet impregnation method. The selected processing method, which is wet impregnation, has successfully produced highly crystalline peaks with different intensities.

The diffraction peaks at 2θ values of 25.572°, 35.16°, 37.778°, 43.354°, 52.534°, 57.498°, 68.208° and 76.844° indicated the existence of the Al_2O_3 phase which is consistent with the literature

reported by Özbay et al. (2018). This phase is abundant since it is the support oxide used, and it is in a pure phase. Additionally, the slightly lower intensity of the characteristic peaks that appear at 2θ values of 38.662°, 61.476° and 66.508° correspond to the CuO monoclinic phase. These lower intensity peaks may be due to the low amount of CuO, which is 5wt% added into the Al_2O_3.

SEM analysis of CuO/Al_2O_3 catalyst

The surface morphological properties such as shape and particle size of CuO/Al_2O_3 were studied through SEM at 10,000X magnification. From Figure 2, it can be observed that the presence of clumps of CuO on the surface of Al_2O_3. It can be identified that CuO was in a non-homogenous state distributed onto Al_2O_3 surfaces. This observation is in good agreement with Nwanna et al. (2021). The shapes of CuO/Al_2O_3 were a combination of round or spherical form and rectangular. The particle sizes of Al_2O_3 are in the range from 0.71–1.79 µm.

EFB proximate analysis & design of experiments

The results of the EFB proximate analysis are shown in Table 3. The EFB sample contains 8.54 % moisture content. Similar results were reported by Azduwin et al. (2014) and Ferreira et al. (2020). The composition of EFB consists of 79.72% volatile matter, 5.36% ash, and 6.38% fixed carbon. The experimental data are in good agreement with reported studies, as shown in Table 3. The data recorded in Table 4 show the design parameters, levels and results of the experiments.

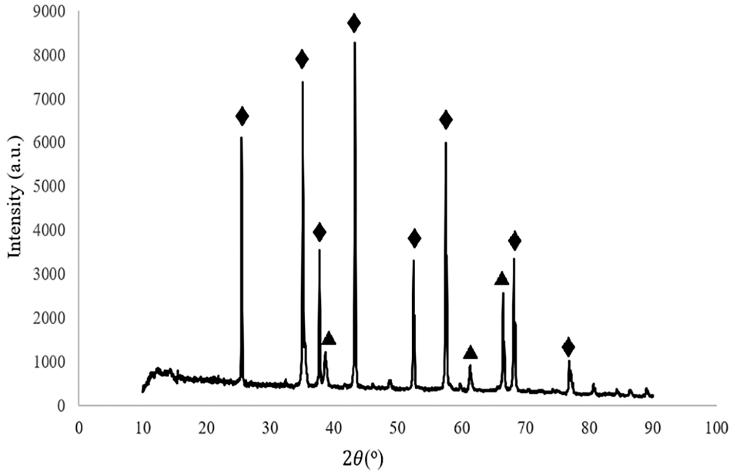


Figure 1. The XRD pattern of CuO/Al_2O_3 catalyst (▲: CuO, ◆: Al_2O_3)

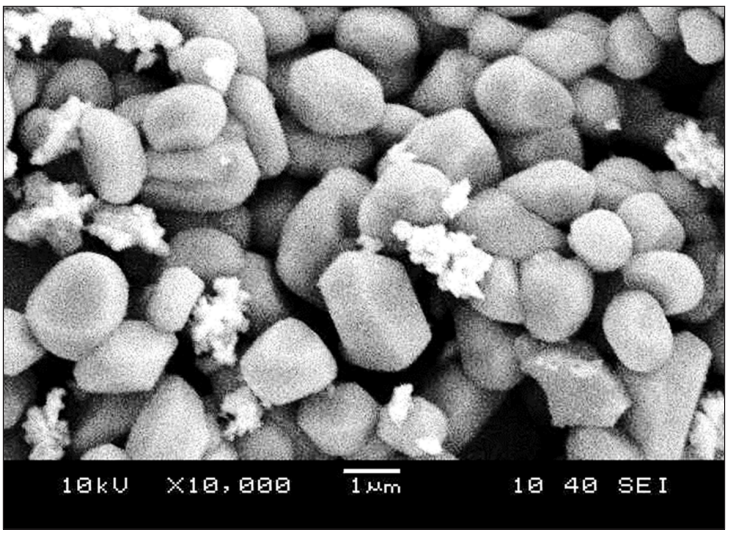


Figure 2. SEM micrograph of CuO/Al_2O_3 catalyst

Table 3. Proximate analysis of EFB and comparison with the current research

Moisture content (%)	Volatile matter (%)	Fixed Carbon (%)	Ash Content (%)	Ref
8.54	79.72	6.38	5.36	This study
7.95	83.86	10.78	5.36	Adzuwin et al. (2014)
3.92	81.49	10.45	4.14	Ferreira et al. (2020)

From Table 4, the pyrolysis temperatures of 197.73 °C and 702.27 °C were represented by the pyrolysis temperature of 198 °C and 703, respectively. It is identified that at low pyrolysis temperature of 197.73 °C, heating rate of 40 °C/min, and catalyst to biomass ratio of 18.82 wt%, there is no bio-oil obtained. It is because the biomass components such as hemicellulose, cellulose, and lignin are stable and not affected by the low temperature. It is because at a low temperature of 197.73 °C, only moisture and light volatiles are released which are insufficient for condensation to occur to produce bio-oil. However, when the pyrolysis temperature is increased to 450 °C at the same heating rate and catalyst to biomass ratio, the bio-oil yield increased in the range of 27.29–31.08 wt%. This is because the higher temperature of 450 °C has affected hemicellulose and cellulosic devolatilization. This resulted in an improved bio-oil yield. When the pyrolysis temperature is increased further to 600 °C, at a heating rate of 20 °C/min and at a lower catalyst to biomass ratio of 7.65 wt%, the bio-oil yield achieved the highest value of 31.87 wt%. This shows that reducing the catalyst to biomass ratio has improved the bio-oil yield, provided that the temperature is maintained at 600 °C.

The statistical analysis

Analysis of variance (ANOVA) of the bio-oil yield model is shown in Table 5. It can be determined that the p-value of the model is 0.0312, which positively indicates that the model is significant. The F-value of 3.53 indicates that the model is significant. The values of p-value less than 0.0500 indicate model terms are significant. In this study, A which is the pyrolysis temperature is a significant model term with a p-value of 0.0057. The "Lack of Fit F-value" of 21.37

Table 4. Experimental results for the catalytic pyrolysis process

Run	A	B	C	D
1	450	73.64	18.82	29.60
2	450	6.36	18.82	26.35
3	450	40	18.82	27.29
4	450	40	18.82	27.69
5	702.27	40	18.82	23.60
6	600	20	30	13.77
7	300	60	7.65	21.12
8	197.73	40	18.82	0.00
9	450	40	18.82	27.74
10	300	20	30	22.91
11	450	40	0.03	27.4
12	450	40	18.82	31.08
13	300	20	7.65	9.18
14	450	40	18.82	31.08
15	300	60	30	11.75
16	450	40	18.82	29.80
17	600	20	7.65	31.87
18	600	60	7.65	24.50
19	600	60	30	31.14
20	450	40	37.62	30.94

implies the lack of fit is significant. The relationship between bio-oil yield and coded factors is represented by the model equation in Equation 2.

$$Bio-oil\ yield = +29.17 + 5.57 \times A + \\ +1.19 \times B - 0.084 \times C + 1.15 \times A \times \\ \times B - 1.98 \times A \times C + 0.21 \times B \times C - \\ - 6.51 \times A^2 - 0.79 \times B^2 - 0.37 \times C^2 \quad (2)$$

Moreover, the adequacy of the model fit is confirmed by estimating the regression coefficient, R^2 which is found to be equal to 0.7604. The value of R^2 is 0.7604, which indicates a moderate correlation between the selected factors in this study, such as the catalyst to biomass ratio, heating rate and pyrolysis temperature, and the response, which is the bio-oil yield. In other words, approximately 76.04 % of the variation in the bio-oil yield can be explained by selected factors and the respective ranges. However, it is also identified that about 24% of variability not accounted by the selected factors. Other factors such as the holding time or residence time, nitrogen flowrate and biomass particle size could contribute to the remaining variability in the bio-oil yield.

Optimal design and validation test

Process optimization was carried out to establish the best conditions for obtaining a high percentage of bio-oil yield. The optimum conditions can be achieved at a pyrolysis temperature of 540.69 ℃, heating rate of 58.01 ℃/min, catalyst to biomass ratio of 9.12 wt% and bio-oil yield of 31.8927 with maximum desirability of 1.000. Then, a validation test was undertaken when optimization was achieved. The parameters were set to "in range," but the bio-oil yield was set to "maximize" to produce the maximum bio-oil production possible. Table 6 lists the set values for each of the variables. From the suggested optimal condition from DOE, the optimization of bio-oil yield was conducted experimentally for five times.

The average bio-oil yield was 30.87% from 5 experimental runs performed at the optimized conditions that agreed with the suggested yield of 31.89%. From the paired t-test performed on the mean from the experimental runs with the predicted run, it was determined that the value for $t_{calculated}$ was 1.35, which is lower than the value of t_{table} of 2.776 at 95% confidence level. Therefore, it was determined that there is no significant difference between the mean of the experimental and the predicted run from RSM.

GC-MS analysis of bio-oil

GC-MS analysis was performed in order to obtain information regarding the organic compounds in the bio-oil. The percentage area of the chromatography peaks was used to determine the chemical compound distributions. In this study, three types of bio-oil were analyzed by GC-MS. These were bio-oils from pyrolysis temperatures of 300, 600, and 540.69 ℃.

Table 5. ANOVA for factorial model

Source	Sum of squares	DoF	Mean square	F value	p-value	Note
Model	1096.52	9	121.84	3.53	0.031	S
A	423.05	1	423.05	12.24	0.005	S
B	19.33	1	19.33	0.56	0.471	NS
C	0.096	1	0.096	2.786E-003	0.958	NS
AB	10.63	1	10.63	0.31	0.591	NS
AC	31.28	1	31.28	0.91	0.363	NS
BC	0.34	1	0.34	9.731E-003	0.923	NS
A^2	610.25	1	610.25	17.66	0.001	S
B^2	8.96	1	8.96	0.26	0.621	NS
C^2	1.93	1	1.93	0.056	0.817	NS
Residual	345.49	10	34.55			
Lack of fit	330.05	5	66.01	21.37	0.002	S
Pure error	15.44	5	3.09	-	-	-
Cor total	1442.01	19				

Note: S – significant, NS – not significant, R^2 value – 0.7604.

Tables 7, 8, and 9 show the major compounds obtained from the quantitative analysis of each type of bio-oil. The complete quantitative analysis of bio-oil is shown in the supplementary file S1. Figure 3 shows the percentage compositions of functional groups for all three types of bio-oils. It was determined that the all three types bio-oils at pyrolysis temperatures of 300, 600, and 540.69 ℃ have high amount of ketones of approximately 54.96, 30.35, and

Table 6. Optimal design for catalytic pyrolysis of EFB

Factor	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
A	In range	450	550	1	1	3
B	In range	40	60	1	1	3
C	In range	7.65	20	1	1	3
Bio-oil yield	Maximize	0	31.87	1	1	5

Table 7. The major compounds obtained from the condition for bio-oil (pyrolysis temperature = 600 ℃, heating rate = 20 ℃/min, catalyst:biomass ratio = 7.65 wt%)

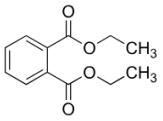
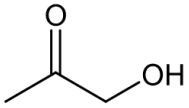
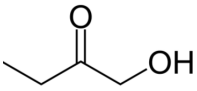
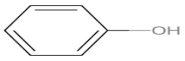
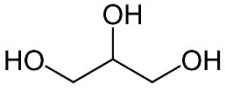
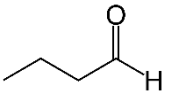
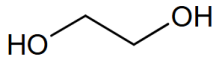
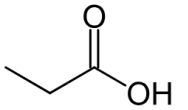
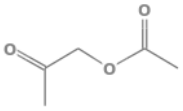
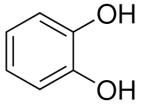
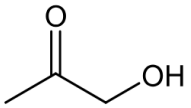
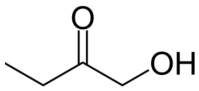
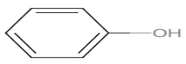
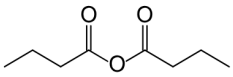
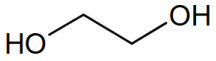
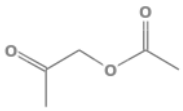
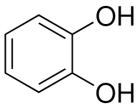
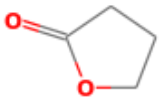
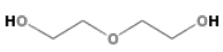
Peak No	RT (mins)	Compound	Formula	Molecular weight (g/mol)	Chemical structure	Group	Area (%)
1	10.822	Diethyl Phthalate	$C_{12}H_{14}O_4$	222.2372		Ester	34.93
2	2.542	2-Propanone, 1-hydroxy-	$C_3H_6O_2$	74.0785		Ketone	18.37
3	3.764	1-Hydroxy-2-butanone	$C_4H_8O_2$	88.1051		Ketone	8.37
4	6.249	Phenol	C_6H_6O	94.1112		Alcohol	6.10
5	6.547	Glycerin	$C_3H_8O_3$	92.0938		Alcohol	4.15
6	7.389	Butanal	C_4H_8O	72.1057		Aldehyde	3.42
7	2.936	1,2-Ethanediol	$C_2H_6O_2$	62.0678		Alcohol	2.60
8	3.095	Propanoic acid	$C_3H_6O_2$	74.0785		Carboxylic acid	2.21
9	4.971	2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	116.1152		Esters	1.39
10	8.246	1,2-Benzenediol	$C_6H_6O_2$	110.1106		Aromatic alcohol	1.23

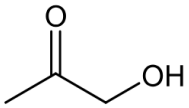
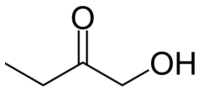
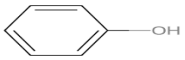
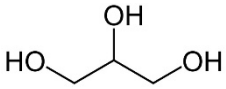
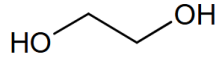
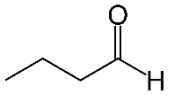
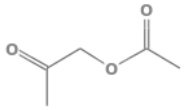
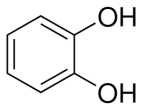
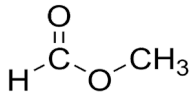
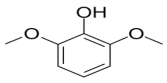
Table 8. The major compounds obtained from the condition for bio-oil (pyrolysis temperature = 300 °C, heating rate = 20 °C/min, catalyst:biomass ratio = 7.65 wt%)

Peak No	RT (mins)	Compound	Formula	Molecular weight (g/mol)	Chemical structure	Group	Area (%)
1	2.54	2-Propanone, 1-hydroxy-	$C_3H_6O_2$	74.0785		Ketone	22.79
2	3.764	1-Hydroxy-2-butanone	$C_4H_8O_2$	88.1051		Ketone	12.73
3	7.389	Pentanal	$C_5H_{10}O$	86.1323		Aldehyde	10.03
4	6.246	Phenol	C_6H_6O	94.1112		Aromatic alcohol	9.39
5	7.085	Butanoic acid, anhydride	$C_8H_{14}O_3$	158.1950		Ester	5.40
6	2.93	1,2-Ethanediol	$C_2H_6O_2$	62.0678		Alcohol	5.39
7	4.974	2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	116.1152		Ketone, Esters	3.25
8	8.244	1,2-Benzenediol	$C_6H_6O_2$	110.1106		Aromatic alcohol	3.00
9	5.487	Butyrolactone	$C_4H_6O_2$	86.0892		Cyclic ester	2.36
10	6.08	Ethanol, 2,2'-oxybis-	$C_4H_{10}O_3$	106.1204		Ether, Alcohol	2.27

50.44 % respectively. This is followed by the ester content, whereby for bio-oil at a pyrolysis temperature of 600 °C, the ester content is 36.59 %. However, for bio-oil at pyrolysis temperatures of 300 and 540.69 °C, the ester contents are low at about 2.38, and 3.58% respectively. It is determined that the major compounds from catalytic pyrolysis of EFB with CuO/Al_2O_3 are ketones because >50% ketones identified in the bio-oil. Therefore, this reaction is an alternative route for producing ketones. Ketones are desirable products from the catalytic pyrolysis process because ketones are stable compounds which can be utilized in the aldol condensation to produce hydrocarbon or as a chemical feedstock. In aldol condensation reaction, an enolate ion reacts with a carbonyl compound to produce β-hydroketone. Then, a water molecule and an aldol are produced. The aldol condensation is an alternative route for upgrading bio-oil since the oxygen atom is removed and the carbon chain is increased to produce heavier carbon compounds.

The next functional group identified in the bio-oils was the alcohol with the amount of approximately 13.31, 19.46 and 7.67% for bio-oil at a pyrolysis temperature of 300 and 540.69 °C. The phenolic compounds were also determined with the amount of 12.51, 12.40 and 8.22% for bio-oils at pyrolysis temperature of 300, 540.69 and 600 °C. Other functional groups such as carboxylic acids, aromatic, aldehydes, furan and

Table 9. The major compounds obtained from the condition for bio-oil (pyrolysis temperature = 540.69 °C, heating rate = 58.01 °C/min, catalyst:biomass ratio = 9.12 wt%)

Peak No	RT (mins)	Compound	Formula	Molecular weight (g/mol)	Chemical structure	Group	Area (%)
1	2.559	2-Propanone, 1-hydroxy-	$C_3H_6O_2$	74.0785		Ketone	28.25
2	3.773	1-Hydroxy-2-butanone	$C_4H_8O_2$	88.1051		Ketone	12.00
3	6.253	Phenol	C_6H_6O	94.1112		Aromatic alcohol	9.23
4	6.562	Glycerin	$C_3H_8O_3$	92.0938		Alcohol	8.52
5	2.941	1,2-Ethanediol	$C_2H_6O_2$	62.0678		Alcohol	4.95
6	7.392	Butanal	C_4H_8O	72.1057		Aldehyde	4.45
7	4.976	2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	116.1152		Ester	2.50
8	8.246	1,2-Benzenediol	$C_6H_6O_2$	110.1106		Aromatic alcohol	2.34
9	3.718	Methyl formate	$C_2H_4O_2$	60.0520		Ester	1.81
10	9.486	Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	154.1632		Aromatic alcohol, Ether	1.80

hydrocarbons are also identified in all bio-oil with the amount lower than 10%.

Generally, bio-oil consists of carboxylic acids, aromatic, aliphatics, aldehydes, and phenolic compounds. Similar observation was reported by Zhang et al. (2019), which showed that the utilization of CuO in poplar wood pyrolysis at 500 °C produced bio-oil with a high amount of acetic acid acetaldehyde and ketone. The decomposition of lignin components of biomass produced phenols and derivatives, while degradation of the cellulose and hemicellulose components of biomass produced esters, aldehydes, alcohols, and ketones (Sutrisno et al., 2018). Aromatics, aliphatics, and oxygenated compounds are the three types of compounds that have been identified. Aromatic compounds include furans, phenols and their derivatives. Alkanes, alkenes, and their derivatives are the most common aliphatic compounds. Aldehydes, ketones, carboxylic acids, and esters are examples of oxygenated compounds. Various organic compounds were also reported by Özbay et al. (2018), who investigated the catalytic pyrolysis of tomato waste using Cu/Al_2O_3 catalyst within a reactor setup. The resulting bio-oil was categorized into several compound groups, including hydrocarbons, aromatic compounds, phenols and their alkylated derivatives, carboxylic acids, carbonyl

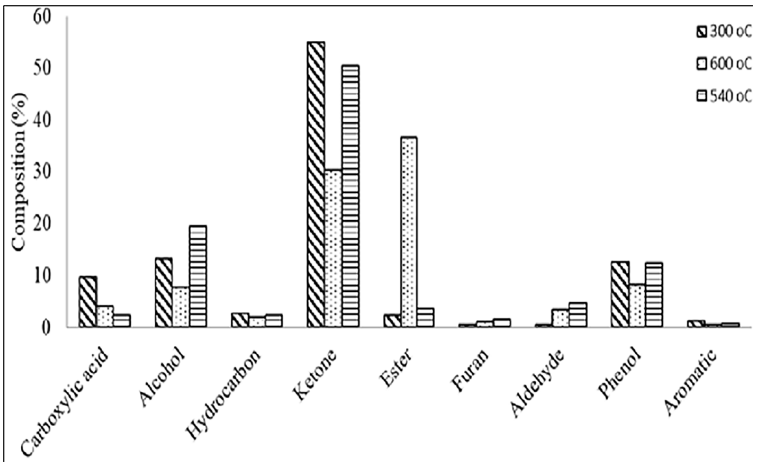


Figure 3. Composition of compounds in the all three types of bio-oil yield

compounds, and polycyclic aromatic hydrocarbons. Chong et al., 2019 reported the catalytic pyrolysis of EFB with three different types of metal oxide catalysts, such as CaO, MgO, and ZnO. The catalytic pyrolysis process was conducted in a horizontal fixed-bed reactor at a reaction temperature of approximately 575 °C. The bio-oils from the catalytic pyrolysis process were quantified using the GC-MS technique. The presence of acetic acid and phenolic compounds were increased in bio-oil with the catalysts from CaO, MgO to ZnO. However, the presence of levoglucosan and furan was determined, but these were produced by all three types of catalyst. Thus, CaO showed the best deoxygenation properties compared to MgO and ZnO. Basically, metal oxide catalyst in EFB pyrolysis showed a certain degree of deoxygenation properties that resulted in different proportions of chemical compounds in the respective bio-oils.

CONCLUSIONS

EFB is a useful biomass resource that can support environmentally friendly practices, material recovery, and sustainable energy generation when utilized in techniques like catalytic pyrolysis. A fixed-bed reactor configuration for producing bio-oil from EFB was desired because of its simplicity, scalability, and flexibility. It can be used for both large-scale biofuel production and small-scale research. Good optimal conditions for bio-oil yields and improved quality were achieved by the process by including appropriate catalysts, CuO/Al_2O_3, which supports sustainable energy and material recovery. The maximum bio-oil yield obtained was 30.87 wt% under optimal conditions. According to ANOVA, pyrolysis temperature was identified as the significant factor. GC-MS analysis of the bio-oil revealed the presence of ketones, carboxylic acids, aldehydes, alcohols, esters, and hydrocarbons, all derived from the catalytic pyrolysis of EFB with CuO/Al_2O_3. In the catalytic pyrolysis of EFB, CuO/Al_2O_3 provides a flexible and efficient catalyst. For the preparation of CuO/Al_2O_3 catalyst, the copper nitrate salt was used with alumina powder, and the rough cost estimation is approximately USD 203.92 for 1 kg of catalyst. Meanwhile, the rough cost estimation for the preparation of the zeolite catalyst is about USD303.61. Thus, CuO/Al_2O_3 is more cost-effective than zeolite catalysts. It is a useful material in sustainable technologies because of its capacity to increase reaction rates, improve selectivity, and function in challenging environments.

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