Pyrolysis of oil palm fronds in a fixed bed reactor and optimisation of bio-oil using Box-Behnken design

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ARTICLE INFO	ABSTRACT
	A study of the direct pyrolysis of oil palm (Elaeis guineensis) fronds, OPF was conducted in a fixed-bed reactor. The product yields are bio-oil, bio-char and bio-gas. The bio-gas product was analyzed using a portable 5 gas emission analyzer. Effects of pyrolysis parameters such as temperature, heating rate and nitrogen flow rate were studied and optimization was performed using Box-Behnken design. The results from the software suggested the optimal conditions can be attained at temperature of of 600°C, heating rate of 40°C/min and nitrogen flow rate rate at 50 ml/min with the produced yield is expected at 26.80 and the confirmation runs were giving an average of 26.3. The highest oxygen removal was found in between 350-450°C via decarboxylation and decarbonylation. The pyrolysis of oil palm fronds demonstrates a promising route to produce an alternative fuel.

1. Introduction

The exponential rise of energy demand is caused by the uncontrollable expansion of industrialization and population growth. Conventional energy sources involve coal, oil, and gas. This source of energy is finite and non-renewable. As a result, energy management will be a challenging task for the future generations [1].

The rising of awareness on renewable energy has improved the society concerns towards the environment and energy. Biomass is unique among the other renewable sources as it is the only source of carbon that can be converted into convenient carbon, oil, and fuel gas [2].

In Malaysia, oil palm (*Elaeis guineensis*) agriculture occupied the largest land area of planting in year 2014, of 5,392,235 hectare [3]. With the expansion of Malaysia palm oil production, the volume of residue waste produced increased correspondingly. Oil palm fronds (OPF) is reported to have the highest amount of waste from palm oil production, of 24.4 million metric tons annually [3]. However, OPF has a very limited research work and usage. Hence, OPF seen to have a great potential in satisfying the energy demand due to its abundant availability.

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Transformation of biomass into useful form of energy are available through three main thermal conversion processes which include combustion, gasification and pyrolysis. Pyrolysis converts biomass into bio-oil, bio-char and bio-gas through thermal decomposition under inert atmosphere [4]. The quantity and quality of product yield depending on the pyrolysis parameters involved, such as temperature, heating rate, reaction time and biomass composition.

Bio-oil is a type of liquid pyrolyzed from dried biomass and has potential to be a substitute of fuels and chemicals in petroleum refineries. It has a high potential in replacing up to 60% of transport fuels [4]. However, bio-oil consist of high oxygenated compounds that has a major drawbacks on storage instability, high acidity, high viscosity and low heating values [5, 6].

To upgrade the quality of bio-oil yield, pyrolysis with addition of catalyst is introduced. Catalytic pyrolysis is the physical contact of catalyst with biomass for the formation of better quality of bio-oil. For example, reactions involved are the breaking of C-O bond, dehydration, decarboxylation and decarbonylation to minimize the unwanted compounds by selectively increase the desired compounds in the bio-oil yield [5].

In this study, we have performed pyrolysis of OPF at pre-set operating parameters. Like oil and gas, renewable energy sources are also abundant in Malaysia, the most important ones being biomass and solar [7]. Effects of pyrolysis parameters such as temperature, heating rate and nitrogen flow rate were studied and optimization was performed using Box-Behnken design. The effect of temperature on decarboxylation and decarbonylation has also been studied.

2. METHODOLOGY
2.1 Materials preparation

Oil Palm Fronds (OPF) was chosen for the study. Firstly, OPF sample was dried by conventional oven at 110 °C to remove moisture content. Secondly, OPF sample was shredded into smaller chips by plastic shredder in concrete and construction lab. Thirdly, OPF sample was grinded by dry mill and sieved by a 0.6 mm laboratory sieve.

2.2 Direct pyrolysis

The pyrolysis of OPF was conducted using fixed-bed reactor in a vertical tubular reactor with an internal diameter of 1 cm and a length of 37 cm as described in our previous research [2]. This reactor was constructed using 316-stainless steel tube. Approximately 0.5 g of glass wool was inserted into the reactor tube at a depth of 3 in from the mouth and followed by 3.0 g of OPF sample inserted from another mouth entrance. The purpose of using the glass wool was to hold the OPF sample in a specific position for optimum heating without leaking.

Throughout the experiment, the heating rate is pre-set according to the requirement of the experiments. OPF sample is packed inside the pyrolyzer as compact as possible to minimize the presence of air in it. The pyrolysis vapors are condensed in the condensation unit and form bio-oil. In the mean times, the incondensable vapors, also known as bio-gas are analyzed by a Pocket Gas Silver Series Portable 5 Gas Emissions Analyzer before released into the atmosphere. The analyzed data was recorded for every 50°C interval. After pyrolysis process ended, bio-oil and bio-char are collected and weighed after cooled.

The initial heating rate used for the experiment was 10°C/min, and the reaction temperatures were set at 500 and 600°C using the N_2 flow rate of 50 ml/min. For the subsequent optimization process, the operating parameters were according to the Box-Behnken design (section 3.2).

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2.3 Sample and product analysis

In this experiment, the weight of dried raw OPF sample is used in pyrolysis yield calculation. Basically, each yield is averaged at least on three times of experiment. The percentage of bio-char and bio-oil yielded are defined as:

$$\textbf{Product yield } (\%) = \frac{\textbf{weight of OPF char/oil (g)}}{\textbf{weight of dry raw OPF used (g)}} \times \textbf{100}\% \qquad (1)$$

Non-condensable gas is not experimentally measured. Hence, percentage of gas is calculated from the difference between percentage of char and oil yields from the total percentage of 100 %.

3. Results and discussions

3.1 Effect of temperature on product yield

As seen from Figure 1, as temperature was increased from 500°C to 600°C, bio-oil yields from OPF were increased from 21% to 24%. Therefore, the highest bio-oil yields was obtained at 600°C. A similar tendency was found by Aysu [8]. Meanwhile, the yield of bio-char decreased but bio-gas yield increased as temperature increased.

The reason of increasing of the bio-oil yield as pyrolysis temperature rise is due to the cracking of molecular structure of cellulose present in the biomass [9-11]. Meanwhile, the drop of bio-char yield with rising of pyrolysis temperature may be attributed to either higher primary decomposition of the raw material at higher temperature or through secondary decomposition of the bio-char, and hence resulting in the increased of pyrolysis conversion. Besides, the production of non-condensable gas products increases because of the secondary decomposition of the bio-char at greater temperatures, which also contribute to the rise of bio-gas yield as temperature increase [12, 13].
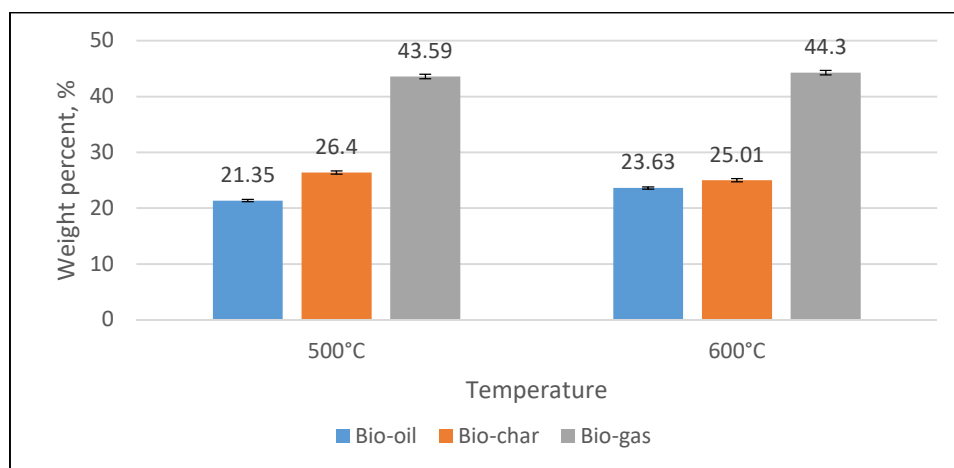

Fig. 1. Product distribution of OPF at different pyrolysis temperature, %

3.2 Optimisation using Box-Behnken design

The factors were investigated by using Box-Behnken design for optimisation and are given in Table 1. Analysis of variance (ANOVA) was performed and the 'prob>F'less than 0.05 indicates factors

of temperature (A) and heating rate (B) are statistically significant (Table 2). Nitrogen flow rate (C) was found insignificant with 'prob>F' value of 0.69. The data are normally distributed and shown in the normal plot of residuals. Residuals vs predicted, residual vs run and predicted vs actual were checked and showed an equal variance and stable. The model was also examined for any transformation that could have been employed but the Box-Cox plot did not suggest any transformation for the response. The equation in terms of coded factors expressed by equation 2:

$$Bio\text{-}oil \ yield = +23.06 + 1.88 * A + 1.75 * B - 0.13 * C \qquad (2)$$

Process optimization was analysed to determine the optimal conditions of the process to obtain high percentage of separation yield. The results from the software suggested the optimal conditions can be attained at temperature of of 600°C, heating rate of 40°C/min and nitrogen flow rate at 50 ml/s with the produced yield is expected at 26.80. We conducted 5 confirmation runs using the suggested condition and obtained an average of 26.5. It was indicated that the experimental values obtained were in good agreement with the values predicted from the models, which recorded small errors between the predicted and the actual values, which was only 1%.

Table 1
Design matrix using Box-Behnken

No	Temperature (°C)	Heating rate (°C/min)	N₂ Flow rate (ml/min)	Bio-oil yield (%)
1	550	10	100	22
2	550	40	50	26
3	550	25	75	23
4	550	10	50	22
5	550	25	75	24
6	600	25	50	24
7	600	10	75	23
8	550	25	75	23
9	500	25	100	21
10	500	40	75	23
11	500	25	50	20
12	550	40	100	24
13	600	25	100	24
14	550	25	75	23
15	600	40	75	28
16	500	10	75	20
17	550	25	75	22

3.3 Effect of temperature on gas compositions

From Fig. 2, the decomposition of OPF begin to generate HC at 350°C and rise sharply until approximately 450°C before started to drop gradually. The formation of HC through pyrolysis of OPF is optimum at temperature range of 450°C to 500°C. However, the alteration in temperature did not show significant effect on the formation of HC.

Table 2
Analysis of variance (ANOVA) for the tested factors using Box-Behnken design

Source	Sum of Squares	df	Mean Square	F Value	P-value Prob > F	
Model	52.75	3	17.58333	22.42953	< 0.0001	significant
A-Temperature	28.125	1	28.125	35.87662	< 0.0001	
B-Heating rate	24.5	1	24.5	31.25253	< 0.0001	
C-N2 Flow Rate	0.125	1	0.125	0.159452	0.6961	
Residual	10.19118	13	0.783937			
Lack of Fit	8.191176	9	0.910131	1.820261	0.2954	not significant
Pure Error	2	4	0.5			
Cor Total	62.94118	16				

As can be seen in Figure 3, during the pyrolysis of OPF at 500°C, the generation of CO started at 250°C, increased sharply and dropped slowly after 400°C. Meanwhile, for pyrolysis of OPF at 600°C, CO began to rise at 300°C, increased steadily until 450°C and remain almost constant or with only slight decrease as temperature further increased. The optimum temperature range for CO formation is approximately at 350°C to 450°C with OPF pyrolyzed at 500°C. In this case, the different setup of pyrolysis temperature showed variation in CO production by shifting the curve to the right at higher temperature set.

As can be seen in Figure 4, CO_2 started to produce at 200°C and rise gradually until 350°C before dropped constantly as temperature further increased. The optimum range of temperature for CO_2 formation is at 350°C to 400°C. However, the difference in pyrolysis temperature set did not show notable effect on the generation of CO_2.

Higher temperature promotes decomposition of bio-oil and thermal cracking of non-condensable gases to increase the proportion of bio-gas significantly [14, 15]. The water present in bio-oil was caused by the cracking of groups containing oxygen, primarily hydroxide OH groups, resulting in increasing of pyrolysis water produced over a wide temperature range. These reactions were the primary factors responsible for the rise of H_2 and CO contents in bio-gas yields. Moreover, the rise of H_2 content in bio-gas yield may be caused by the breaking of HC preferred by higher temperature and the contribution of H_2 from the elemental composition of biomass. Therefore, as the breaking of HC increased at higher temperature, the lower the HC collected in the bio-gas yield.
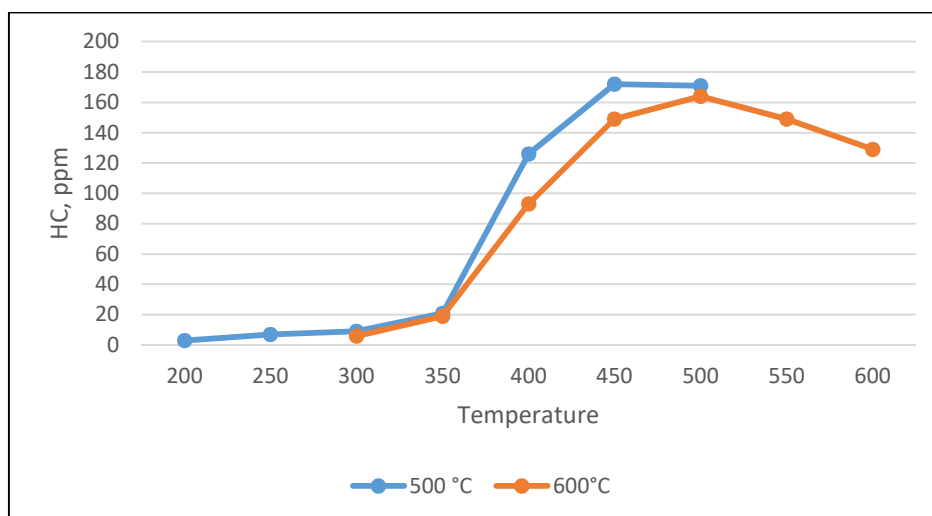

Fig. 2. Effect of temperature on HC

On the other hand, CO may come from the breaking of carbonyl group, the rupture of oxygen heterocycle and the dehydrogenation of hydroxyl group. The sum of CO and CO_2 occupied a large percentage in total bio-gas yield, which reduced as temperature of pyrolysis increased. The decomposition of cellulose and hemicellulose is at 200°C to 380°C, which results in the formation of CO and CO_2 and a small amount of HC [16]. Thus, CO and CO_2 released were optimum at 300°C and dropped as temperature further increased from 350°C to 600°C.
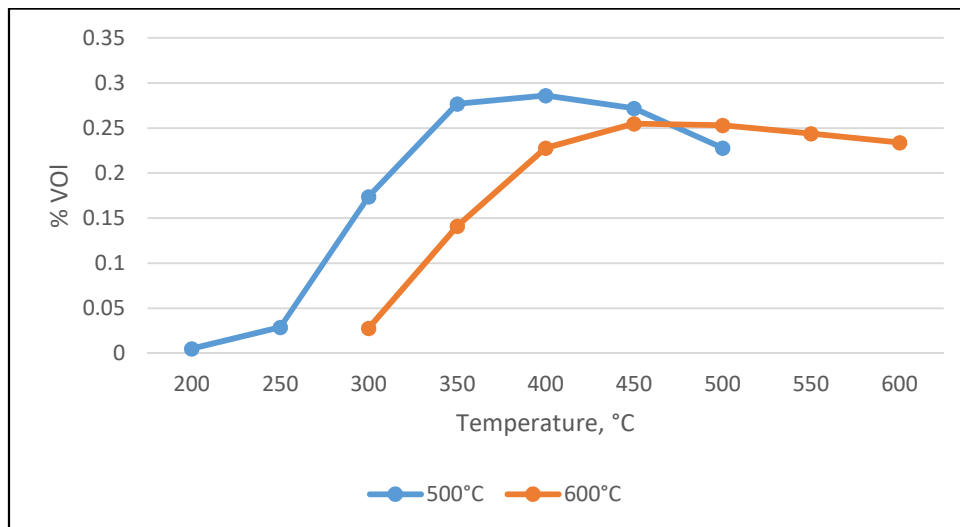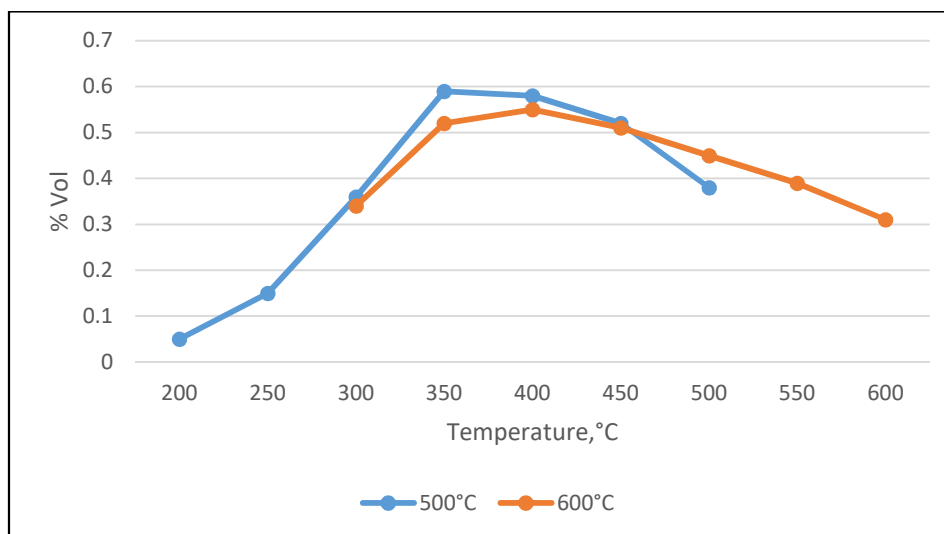

Fig. 3. Effect of temperature on CO

Fig. 4. Effect of temperature on CO_2

4. Conclusion

In this study, pyrolysis of oil palm (*Elaeis guineensis*) fronds, OPF, was carried out in a fixed-bed reactor at 500°C-600°C. The results from the software suggested the optimal conditions can be attained at temperature of 600°C, heating rate of 40°C/min and nitrogen flow rate at 50 ml/min with the produced yield was expected at 26.80 and the confirmation runs were giving an average of 26.3. The highest oxygen removal was found in between 350-450°C via decarboxylation and decarbonylation. The pyrolysis of oil palm fronds demonstrates a promising route to produce an alternative fuel.

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