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Research Paper

Influence Temperature and Holding Time of Empty Fruit Bunch Slow Pyrolysis to Phenolic in Biocrude Oil

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Abstract

Indonesia has an abundance of biomass from agricultural, plantation, and domestic waste products. Biomass can be converted into fuels and chemicals that are environmentally friendly. Empty fruit bunches (EFB) are biomass from abundant palm oil processing. Pyrolysis was a thermal process with free oxygen at temperatures between 400-600°C. Generally, pyrolysis was carried out under fast pyrolysis to produce a product that leads to bio-crude oil. One of the main components of bio-crude oil was phenol, which had been produced from further processing of crude oil. With the limitations of crude oil, the production of phenol from biomass pyrolysis was an option for the future, especially for fuels and fuel additives. Thus, it is necessary to investigate the effect of heating rate, temperature pyrolysis, and holding time on pyrolysis products including phenols in bio-crude oil. Slow pyrolysis of EFB was performed at various parameters, including temperatures (400, 450, and 500°C) and holding time (5, 10, and 15 min). Slow pyrolysis of oil palm EFB with variations in temperature and holding time has been carried out by producing liquid between (40 - 42 % weight), gas (19 – 21 % weight), and solid products (38 – 39 % weight). Biocrude oil liquid product showed the highest yield compared to biochar and bio pyrolysis gas. Temperature plays an important role in controlling the production of bio-crude oil as a liquid product, including a component in bio-crude oil. Phenol recovery was more affected by temperature instead of holding time.

Keywords: Biomass; Empty fruit bunches (EFB); Slow pyrolysis; Bio-crude oil; Phenol

1. Introduction

Fuels and chemicals are very important needs today along with technological advances. Nowadays, most of the fuel and chemicals used are derived from petroleum, which is a non-renewable material. This condition required alternative raw materials for fuels and chemicals that are more sustainable for a long time. Furthermore, the fossil fuel resources such as petroleum, natural gas, and coal have large impacts on the environment due to gas emission and large waste issues. Hence, the alternative resource should be sustainable and friendly to the environment. Biomass is an alternative raw material for the manufacture of sustainable fuels and chemicals because biomass is a material produced from agricultural or plantation processing waste and its less impact on the environment [1]–[3].

Palm oil processing produces high solid waste around 23 %-wt. for every ton of fresh fruit bunches (FFB) [4]. Indonesia produces around 50 million crude palm oil and 50 million empty palm fruit bunches (EFB) tons every year [5]. The EFB was used for fuel in boilers of palm oil plants or returned to oil palm land. The high effort required for returning the EFB to the land of palm oil plantation. It is also expensive for transporting and unloading the EFB. Thus, it is necessary to optimize the use of EFB either as fuel or chemicals at the palm oil processing plant location.

Biomass can be converted to fuels or chemicals through a thermochemical or biochemical process [6]–[8]. Thermochemical of biomass produces fuels and chemicals in a shorter time than biochemical and more favorable to be commercialized for replacing fossil-based resources [3] [9]. There are various thermochemical routes to convert biomass into chemicals and fuels such as pyrolysis, gasification, and combustion [10]–[13]. The promising thermochemical to convert biomass and produce more products was pyrolysis [12][14][15]. Pyrolysis is the thermochemical of hydrocarbon of solid in absence of oxygen and it can take place from temperature 200 to 850°C. In the pyrolysis of biomass with a temperature range between 200-300°C, the aim was to remove some volatile matter so that the product was mostly in a solid state [16]. At low temperature, pyrolysis was often called torrefaction to change the character of the biomass from hydrophilic to hydrophobic [17]. Then at temperatures between 300-650°C, biomass pyrolysis aims to produce liquid, solid, and gas products. Then the temperature is 650 to 850°C, the resulting product is more towards gas. Generally, the pyrolysis of biomass was performed at temperatures 350-600°C [12].

During pyrolysis, the long and complex structure of carbon-hydrogen-oxygen molecules in the biomass decomposed into smaller molecules in the gas, liquid, and solid products [14]. The main constituent components of biomass are hemicellulose, cellulose, and lignin. Hemicellulose was the first component that undergoes decomposition in pyrolysis at temperatures of 200-300°C. Then, the second component to be converted in pyrolysis was cellulose around temperature 300 – 400°C. The last component was lignin to be converted around temperature 400 -700°C [18].

The composition of the gas, liquid, and solid products produced by biomass pyrolysis is very dependent on the mode and conditions of pyrolysis as shown in **Table 1**. From this table, it can be seen that the slow pyrolysis process can produce almost even product distribution between liquid, liquid, and gas products. Liquid products from biomass pyrolysis can be used for chemicals, while solid products and gases can be used for fuel in the pyrolysis process as auto-fuel. The liquid products derived from rapid pyrolysis that are used for chemicals generally contain up to 87% phenol [19]. Palm biomass was able to produce phenol products higher than wood species because of the high lignin content in palm biomass [20].

Phenol is a chemical product that has many benefits, among others, for fine chemical and resin manufacturing which was called phenolic resin. The phenolic resin was a combination of phenol components with formaldehyde to create large networks of permanently bonded molecules. The phenolic resin was widely used in the plywood industry because it has strong mechanical properties and highly resistant to fire [20]. Phenol is also one of the alternative materials for fuels and fuel additives.

Phenol is commercially produced via the reaction of benzene to cumene through three stages. By using benzene produced from crude oil processing, phenol will face obstacles in its supply. In connection with this, it is necessary to find alternative raw materials that are more sustainable and environmentally friendly, which one of the potential route is slow pyrolysis of EFB biomass. The products of slow pyrolysis was influenced by pyrolysis temperature and holding time [21]. Temperature and holding time have a a strong relationship for slow pyrolysis so that the volatile matter (VM) in biomass can be escaped

Table 1. Typical conditions and product of biomass pyrolysis [22].

Method	Condition	Products %-Weight		
		Liquid	**Solid**	**Gas**
Torrefaction	~300°C, solid, 10 -60 min	0	80	20
Carbonization (slow pyrolysis)	~400°C, vapour, 15 - 60 min	30	35	35
Intermediate pyrolysis	~500°C, hot vapour, 10 -30 s	50	25	25
Fast pyrolysis	~500°C, shot hot vapour, ~ 1 s	75	12	13

from the pores to produce phenol. The aims of this study are to investigate the effect of temperature and holding time on phenol products of EFB biomass pyrolysis in bio-crude liquids. Knowing the effect of temperature and holding time will be the basis for designing bio-crude oil production equipment from EFB pyrolysis to produce phenol products as a disinfectant.

2. Material and Method

2.1. *Materials*

In this research, the material was empty palm fruit bunches (EFB) with the proximate analysis presented in **Table 2.** The volatile matter of the EFB was high and this condition was suitable for the pyrolysis route. EFB was obtained from a palm oil mill in Lebak - Banten. Then, the EFB was crushed to reduce the size to 32 mesh.

2.2. *Methods*

An amount of 200 g EFB was weighted ($m_{initial}$) and feed into the pyrolysis reactor as shown on **Figure 1**. During slow pyrolysis, the heating rate was controlled around 0.120 – 0.265°C/s. Then, the EFB was heated until reached pyrolysis temperature (400, 450, and 500°C). At those temperatures, the heater was controlled for 5, 10, and 15 min as holding time. In this study, the pressure in the pyrolysis reactor was assumed to be atmospheric because, during the EFB pyrolysis process, the gas produced was directly cooled in the condenser without being held. The temperature in the pyrolysis reactor was recorded every 60s during the pyrolysis reactor heating process to determine the pyrolysis heating rate at different holding times. Later, the liquid product container was prepared so that when the gas pyrolysis condensation process takes place, the liquid product can be obtained and weighted (m_{bco}). At the end of the slow pyrolysis, the solid product inside of the reactor was taken to be weighed ($m_{biochar}$). The composition of the liquid product of bio-crude oil was analyzed by GC-MS. The type of GC-MS used was Shimadzu Type QP2010 with the DB5-MS column from Agilent. The correlation of the relationship between the percent yield of products can be seen in equations (1) to (4).

Table 2. Proximate analysis of Empty Palm Fruit Bunches (EFB)

Analysis parameters proximate	Sample EFB	
	% wt	Method
Moisture in air dried	10.68	ASTM D 7582 -15
Ash	6.73	ASTM D 7582 -15
Volatile matter	64.05	ASTM D 7582 -15
Fixed carbon	18.54	ASTM D 3172 - 13

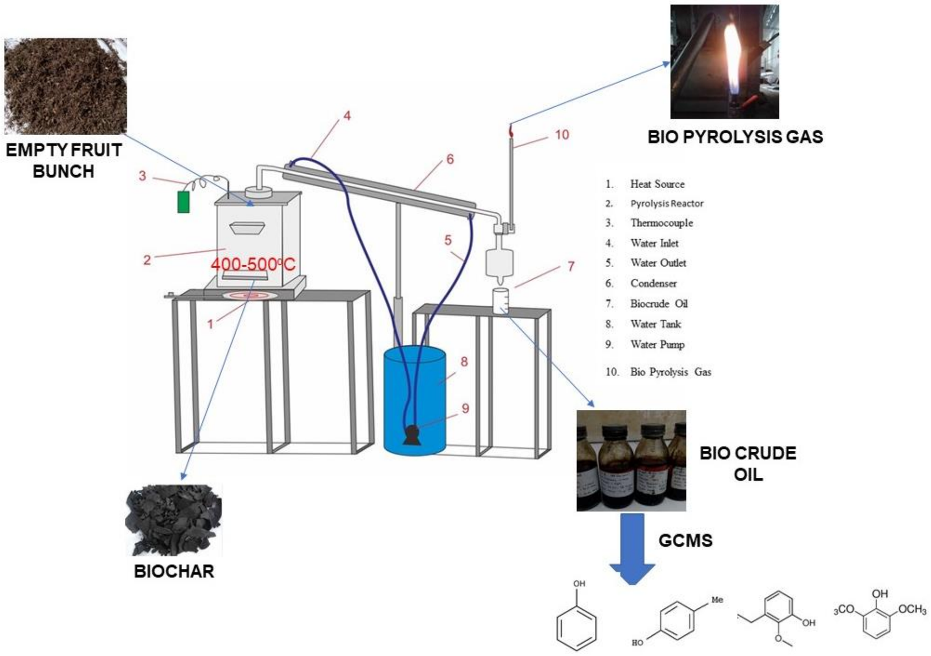


Figure 1. Pyrolysis Empty Fruit Bunch (EFB) experimental setup

$$m_{EFB} = m_{pygas} + m_{bco} + m_{biochar} \tag{1}$$

$$\% \, x_{bco} = \frac{m_{bco}}{m_{EFB}} x \; 100\% \tag{2}$$

$$\% \, x_{biochar} = \frac{m_{biochar}}{m_{EFB}} x \; 100\% \tag{3}$$

$$\% \, x_{pygas} = 100\% - \% \, x_{bco} - \% \, x_{biochar} \tag{4}$$

3. Result and Discussion

3.1. *Empty Fruit Bunch (EFB) pyrolysis*

Figure 2 showed the operation process of EFB pyrolysis with several stages. The initial stages were removing the water content from the biomass EFB and heating the EFB from atmospheric temperature to pyrolysis temperature (400, 450, 500°C). Furthermore, at the pyrolysis temperature (400, 450, 500°C) the holding temperature was called the holding time (5, 10, 15 min). After that the process of decreasing the temperature until it reaches the atmospheric temperature. During the EFB pyrolysis process, the pressure of the pyrolysis reactor was estimated to be slightly above atmospheric pressure because the product gas produced flows directly through the pipe. With the product gas flowing out of the pyrolysis reactor, the reactor pressure does not increase too high so that the product composition was more influenced by temperature.

Slow pyrolysis was pyrolysis with temperature rise slowly over a long time and heating rate. Under these conditions, the liquid product was produced from slow pyrolysis tends to produce a low carbon chain so it is necessary to adjust the heating rate so that the resulting product can lead to liquids, especially phenol components. In this experiment, the heating rate was controlled around slow pyrolysis between 0.126 – 0.160°C/s as represented by holding time (**Figure 2**). Low heating rate (0.125°C/s) was controlled by holding time 15 min and high heating rate (0.16°C/s) was controlled by holding time 5 min. At a lower heating rate than the above conditions, it produced more biochar products than the components of bio-crude oil or bio-pyrolysis gas [23].

At short holding time (5 min) in this slow pyrolysis, the operation time was longer than holding time 10 and 15 min so the heating rate (°C/s) at short holding time higher than 10 and 15 min. Thus, the holding time can be used to control the heating rate in the pyrolysis process [24]. Due to the slow heating rate at high temperature (500°C), the product of EFB pyrolysis can produce bio pyrolysis gas (BPG), bio-crude oil (BCO), and biochar. Biochar has the benefit of being used directly as fuel in slow pyrolysis because biochar had a calorie content of between 5500-5800 kcal/kg [25].

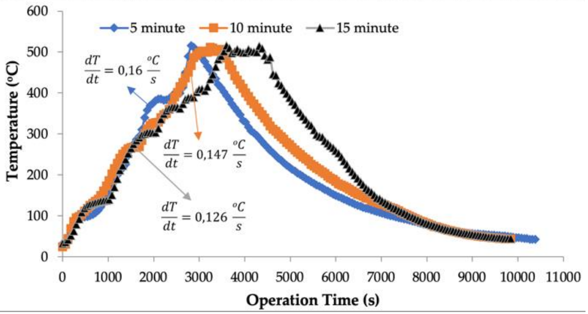
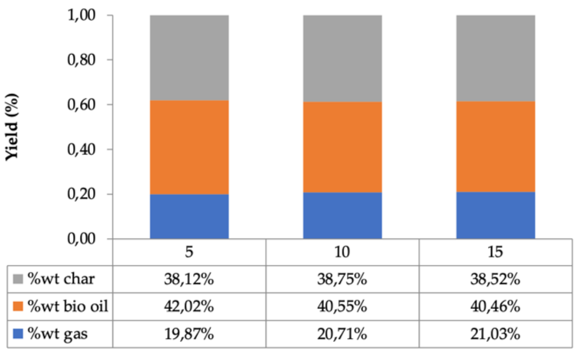


Figure 2. Temperature profile throughout the operating time of EFB Slow pyrolysis at various holding times at temperature 500°C

In this investigation, the slow pyrolysis of EFB produced more liquid products than biochar and bio-pyrolysis gas due to a high heating rate of more than 6°C/min (**Figure 3**). At short holding time (5 min) and high temperature (500°C) had the highest yield of bio-crude oil products like fast pyrolysis. The gasses were difficult to condense in atmospheric condition so that the longest holding time (15 min) produce more pyrolysis gas at temperature 500°C (Figure 3) [26].



	5	10	15
%wt char	38,12%	38,75%	38,52%
%wt bio oil	42,02%	40,55%	40,46%
%wt gas	19,87%	20,71%	21,03%

Figure 3. Effect of holding time to distribution of yield (solid, liquid and gas) of slow pyrolysis EFB at temperature 500°C

In all pyrolysis temperature and holding, time produced more bio-crude oil (BCO) products than gas and biochar products. This is because the temperature of pyrolysis occurred above 400°C which the lignin component experienced depolymerization into smaller components such as guaiacol, phenol, syringol and others [27]. At a temperature of 400°C, only a small of the lignin component occurred depolymerization and an increase in temperature will further increase the rate of BCO formation in the biomass pyrolysis process because more lignin was depolymerized. The short holding time and low temperature (400°C) produced a low yield of bio-crude oil around 34%-wt (**Figure 4**). Increasing pyrolysis temperature to 450 and 500°C resulted in a high bio-crude oil product yield because the high temperature caused a greater amount of depolymerized lignin.

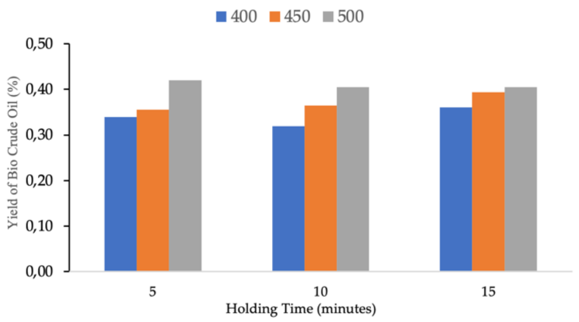


Figure 4. Effect of Holding Time and Temperature to the Yield of Biocrude Oil in Slow Pyrolysis of EFB

Holding time was carried out to maintain the pyrolysis operating conditions so that more biomass was converted at that temperature to BCO or BPG [28]. An increase in the holding time above 30 minutes at temperatures above 400°C will cause a decrease in the amount of BCO because most of the product leads to BPG [29]. In this experiment, increasing holding time at the highest temperature would decrease the yield of bio-crude oil products (**Figure 3**) due to more volatile matter decomposed to the smaller pyrolysis gas. BCO products increase at temperatures of 400 and 450°C along with the increase in holding time because the de-polymerization process of lignin is still not high and does not lead to BPG components. Thus, pyrolysis temperature was more dominant in producing more liquid products than holding time.

3.2. Bio Crude Oil Components Analysis

Biocrude oil products produced from the EFB biomass pyrolysis process can reach 42% which occurred at a temperature of 500°C and a holding time of 5 minutes. The reaction pathway of the EFB pyrolysis process was shown in **Figure 5** that biomass composed of hemicellulose, cellulose, and lignin components were thermally decomposed.

In this study, pyrolysis was carried out at temperatures between 400 to 500°C so that more lignin would be decomposed into smaller components. In some literature, it is said that the depolymerization process of the components that make up biomass was more influenced by temperature [30]–[32]. The pyrolysis temperature will affect heat transfer,polymerization reactions, mass transfer, and phase changes. The length of the process is very dependent on the holding time

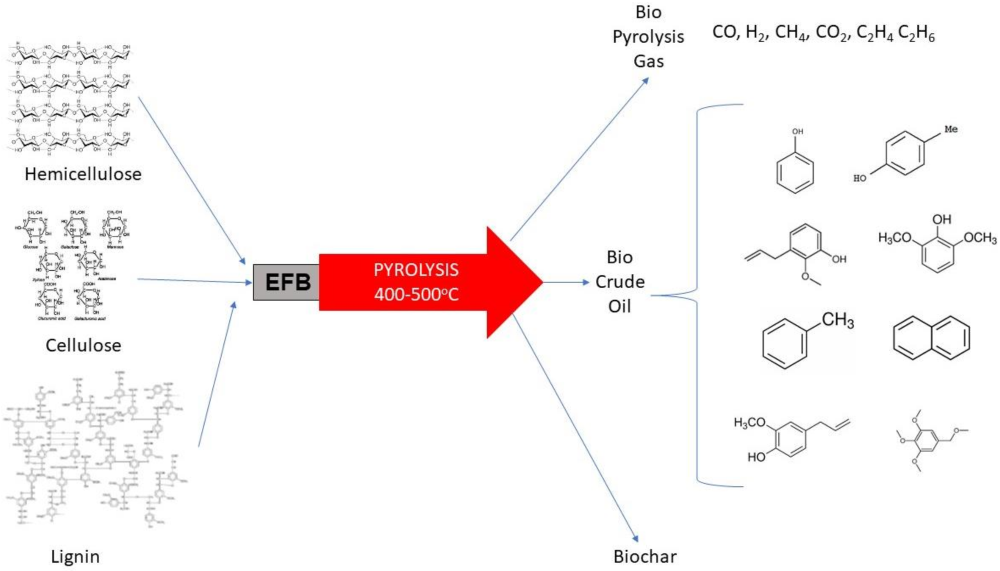


Figure 5. Reaction pathway for EFB pyrolysis at 400, 450 500°C

of the pyrolysis process to decompose the constituents of the biomass. Slow pyrolysis of EFB at temperature 400-500°C produced BPG, BCO, and biochar products. Bio Pyrolysis gas is a light gas containing, among others, CO, H_2, CH_4, CO_2, C_2H_4, C_2H_6, and other gas components which are small in quantity [33]. Bio Pyrolysis gas can be used as fuel for the pyrolysis process which requires heat so that fuel consumption in the pyrolysis process can be reduced.

Then, BCO was further analyzed using GC-MS with a chromatographic shown in **Figure 8**, **Figure 7**, and **Figure 8**, respectively. In this figures, the peaks of the chromatographic showed certain components identified by the GC-MS. The number of peaks that can be detected for low pyrolysis temperature (400°C) was 23 peaks while at medium pyrolysis temperature (450°C) was 25 peaks and high pyrolysis temperature (500°C) was 15 peaks. It can be seen that high-temperature pyrolysis has lower components than medium and low temperature. Then, Components composition of biocrude oil from EFB pyrolysis is presented in **Table 3**.

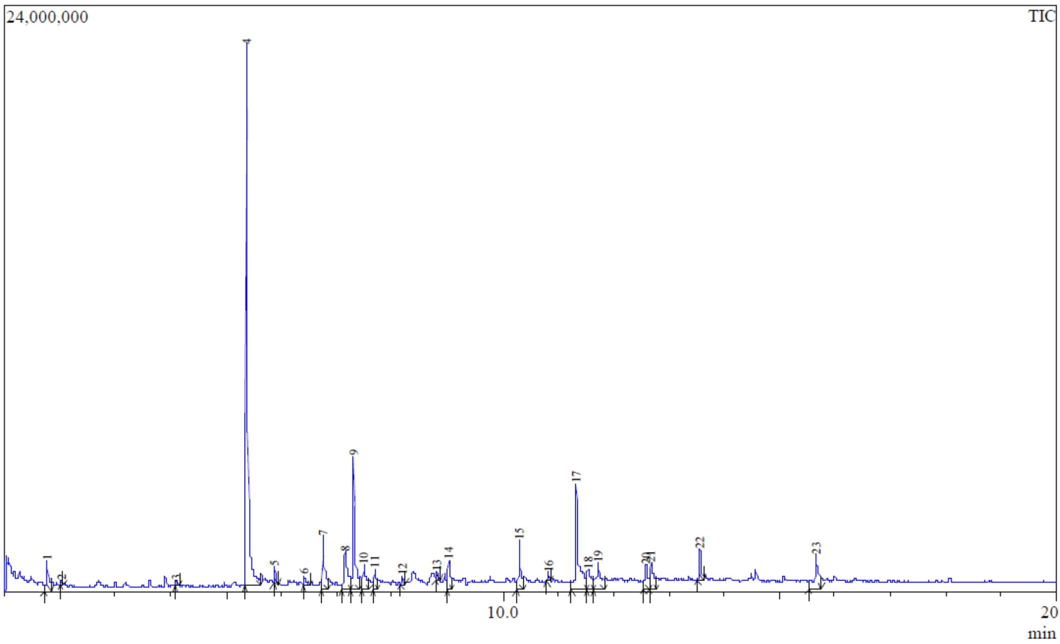


Figure 6. Chromatographic peak identification of EFB pyrolysis by G-CMS: T=400°C and Δt=10 min

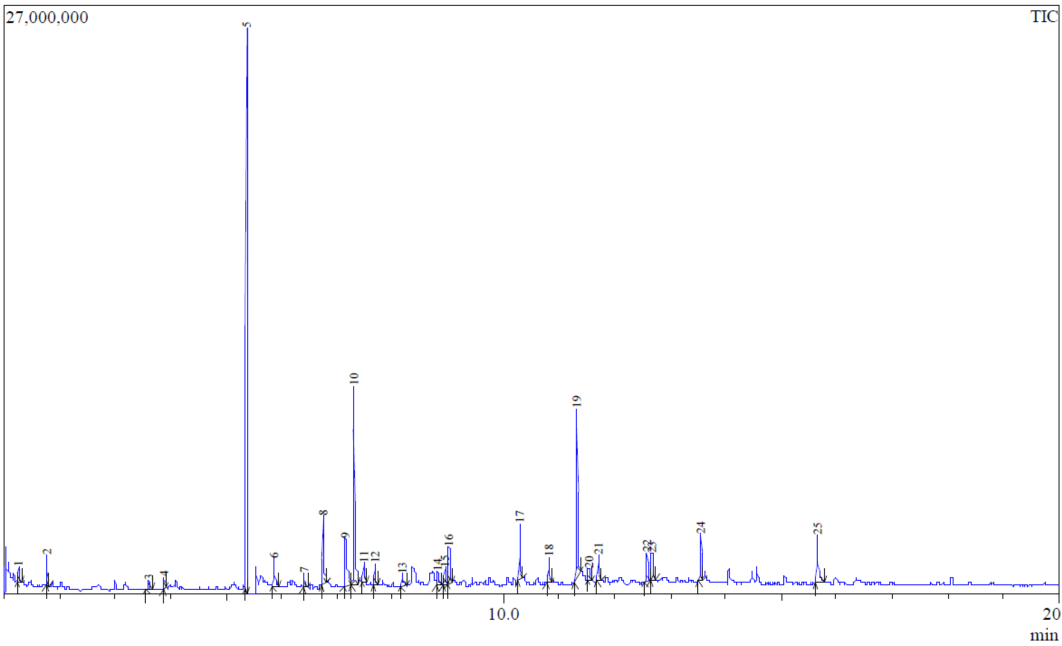


Figure 7. Chromatographic peak identification of EFB pyrolysis by G-CMS: T=450°C and Δt=10 min

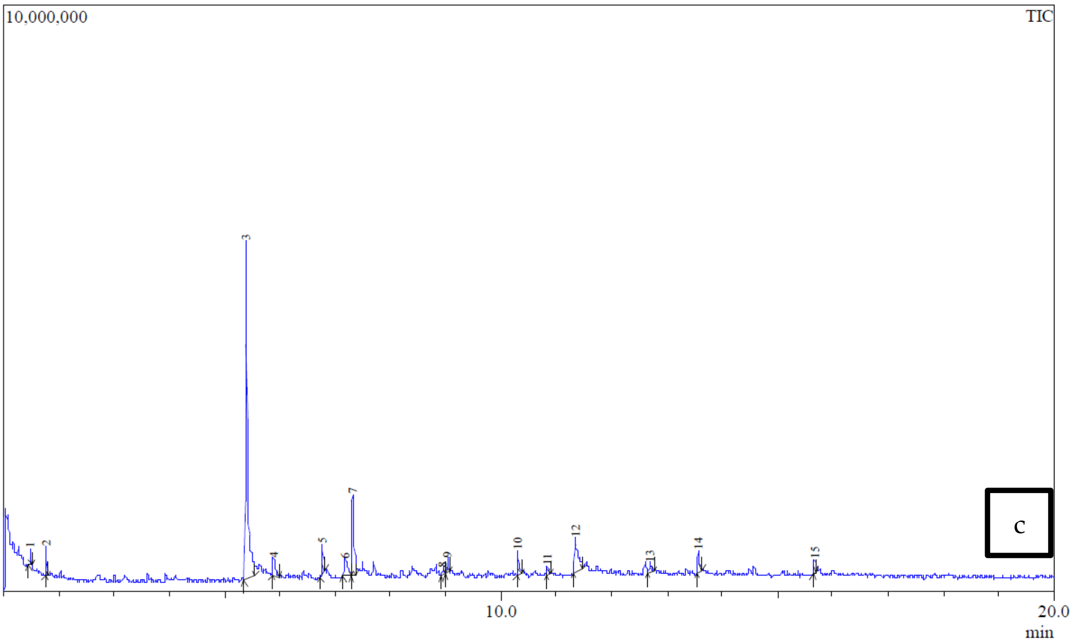


Figure 8. Chromatographic peak identification of EFB pyrolysis by G-CMS: T=500°C and Δt=10 min

Table 3. Components composition of biocrude oil from EFB pyrolysis

No	Components	Composition (%)		
		Pyrolysis EFB at 400°C and holding time 10 minutes	Pyrolysis EFB at 450°C and holding time 10 minutes	Pyrolysis EFB at 500°C and holding time 10 minutes
1	Ethane, 1,1-diethoxy-	0	0	1.22
2	Toluene	2.56	1.94	2.35
3	Benzene, 1,3-dimethyl-	0	0.85	0.00
4	2-Cyclopenten-1-one, 2-methyl-	0	1.04	0.00
5	Benzene, methoxy-	0.32	0	0.00
6	Phenol	30.99	18.16	51.04
7	Butanoic acid, 2-propenyl ester	0	2.51	2.69
8	2-Cyclopenten-1-one, 2,3-dimethyl-	0	1.10	0.00
9	Phenol, 2-methyl-	4.08	5.12	3.82
10	Phenol, 4-methyl-	5.21	6.85	5.09
11	Phenol, 2-methoxy-	9.58	15.23	11.41
12	Benzoic acid, methyl ester	2.94	1.31	0.00
13	2-Propenal, 3-phenyl-	1.96	1.60	0.00
14	Phenol, 2-ethyl-	0.57	1.21	0.00
15	Naphthalene	0	0	1.27
16	Phenol, 2-methoxy-4-methyl-	2.53	0	0.00
17	Phenol, 4-ethyl-2-methoxy-	4.20	4.38	3.10
18	2-Methoxy-4-methylphenol	0	0	1.42
19	2-Methoxy-4-vinylphenol	0.53	0	1.20
20	Phenol, 2,6-dimethoxy-	11.25	12.82	9.21
21	Phenol, 2-methoxy-4-propyl-	3.01	0.89	0.00
22	Benzoic acid, 4-methoxy-, methyl ester	4.35	2.15	0.00
23	Phenol, 4-methoxy-3-(methoxymethyl)-	2.52	2.29	0.00
24	Eugenol	3.53	2.59	1.80
25	Benzene, 1,2,3-trimethoxy-5-methyl-	1.95	3.67	2.97
26	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	5.21	4.90	1.43

Table 3 shown phenolic components are the main compounds found in bio-crude oil (BCO) components. These phenolic compounds are formed from the breakdown of lignin found at

process temperatures above 400°C. Then at temperatures higher than 500°C, the phenolic compounds will decrease due to thermal cracking into lower single components [34]. From this table, it can be seen that there is an increase in the phenol content at the pyrolysis temperature of 500°C compared to the pyrolysis temperature of 400°C (Figure 9a). Phenolic compounds are categorized into 3 types, namely H-phenol, G-phenol, and S-phenol. At temperatures above 450°C, the hydroxylation of the benzene process can occur to form phenol components which are included in the H-phenol category (Figure 9b-7d) [35].

At a longer holding time (15 min), the phenol content was lower than the 10 min holding time which had a higher temperature. It can be seen in **Table 3** that the pyrolysis temperature is more dominant than the holding time of the product composition in bio-crude oil. Phenol products are maximally produced at a temperature of 500°C with a residence time of 10 min at 51% (**Figure 9**). This condition shows that the increase in temperature will cause an increase in the low carbon product of phenolics [36]. An increase in residence time of up to 15 min causes the phenol content to decrease at temperatures of 500°C [37]. The low pyrolysis temperature (400°C) causes low recovery of phenol (**Figure 9**a).

The observation of temperature and residence time on bio-crude components showed that temperature was very influential in producing phenol products [24]. Then the phenolic product in the form of methoxy was produced higher at temperatures of 450°**C** for almost the entire temperature holding time (**Figure 9b-7c**). The increase in temperature to 500°C causes a decrease in the acquisition of phenol methoxy due to the demethoxylation reactions [19].

4. Conclusion

Slow pyrolysis of oil palm empty fruit bunches (EFB) with variations in temperature and holding time has been carried out by producing liquid, gas, and solid products. Pyrolysis temperature played an important role in directing the product to bio-crude oil, including its components phenolic. The longer holding time at higher temperatures makes the phenol component decrease. Temperature played an important role in heat transfer, reaction, and mass transfer during pyrolysis of EFB to decompose the cellulose, hemicellulose, and lignin. In the future, it is necessary to investigate the influence of the reactor pressure on the product composition by holding the gas flow rate before condensing into liquid and gas products.

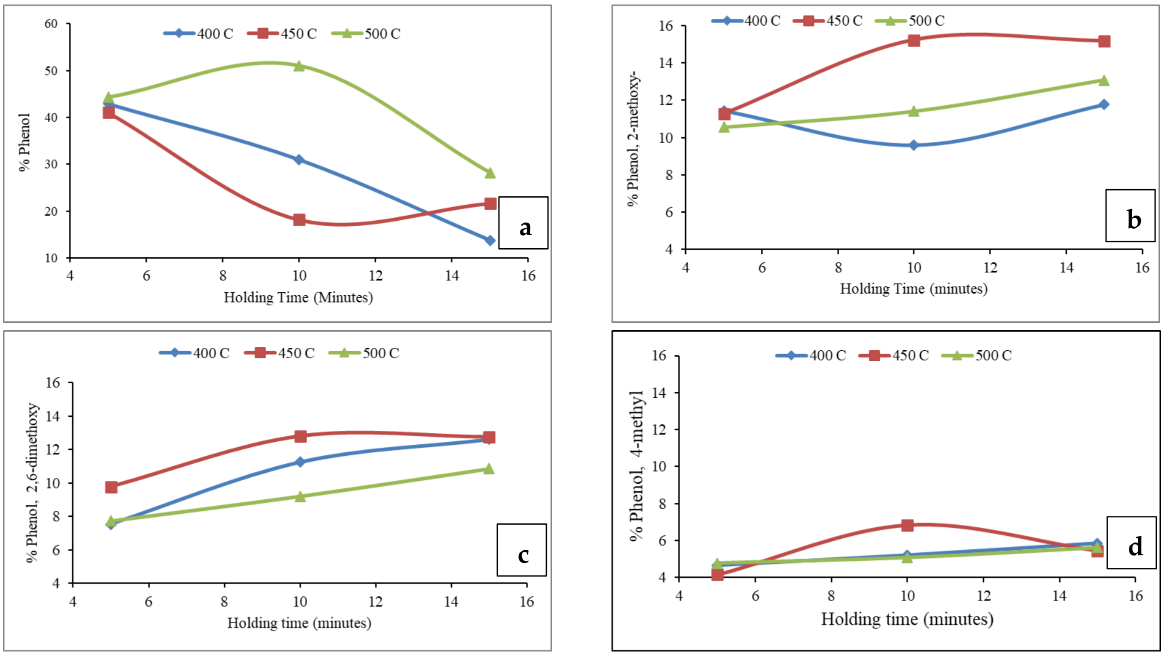


Figure 9. Effect of holding time and temperature of slow pyrolysis EFB in yield of biocrude oil for (a) phenol (b) phenol-2 methoxy (c) phenol 2,6-dimethoxy, and (d) phenol- 4 methyl

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Author's Declaration

Authors' contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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Availability of data and materials

All data are available from the authors.

Competing interests

The authors declare no competing interest.

Additional information

No additional information from the authors.

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