Palm Oil Mill Effluent Biochar as An Alternative Potassium Source: Effect of Pyrolysis Time and Its Kinetic Release
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(Received 11 September 2023; Revised 06 May 2024; Accepted 29 May 2024; Published 31 May 2024)

Abstract

Palm Oil Mill Effluent (POME) is one of the waste products of palm oil processing that can be processed into a biochar. POME biochar contains high levels of nutrient, such as NPK which can be used as an alternative potassium source material. This study aims to produced biochar from POME and the influence of pyrolysis time on the characteristics and its kinetic release. Biochar production from POME was conducted at 300°C with pyrolysis time variation of 1 hour, 3 hours and 5 hours. Biochar characterization was conducted using Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX), Surface Area Analysis (SAA). Study of potassium release was conducted by mixing one gram amount of biochar with 0.01 M CaCl2 as a function of time. The used kinetics modelling in this study are first-order, second-order, pseudo-first order, pseudo-second order. The results showed that the biochar yield decreased, while the biochar pH value, exchangeable potassium, non-exchangeable potassium and surface area increased with the increasing of pyrolysis time. The pseudo-second order model is the most fitted model to describe the potassium release. The pseudo-second order kinetics model gave K release rates of 0.018; 0.024; 0.020; 0.014 (mg g⁻¹ min⁻¹), the qₑ values are 0.814; 0.839; 0.927; 1.111 (mg g⁻¹), respectively.

Keywords: biochar, kinetics release, POME sludge, potassium, pyrolysis

1. Background

The use of palm oil in various industries to meet market demand will generate large amounts of palm biomass. Palm biomass is an agricultural by-product generated from the palm oil industry during replanting, logging, and milling activities, which in most cases is discharged into the environment [1].

POME is the liquid waste generated from the oil extraction process from palm fruit bunches in palm oil mills. For every ton of crude palm oil (CPO) produced, an estimated 5-7.5 tons of water is used in the process and more than 50% of the water ends up as POME. This means that about 2.5-3.75 tons of POME will be generated per ton of CPO production. POME sludge is a liquid waste with high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values, besides that the acidic nature of POME can cause environmental and ecosystem problems and if discharged into waters without prior treatment [2]. POME has been utilized as a renewable energy source, including as a source of biogas [2], polyhydroxyalkanoate (PHA) [3], organic fertilizer [4,5] or adsorbent in the form of biochar [6-8]. In recent years, there has been an increasing amount of literature on the conversion of oil palm biomass into biochar [9].

Biochar can be obtained through thermochemical processing of biomass, known as pyrolysis or gasification at temperatures between 300°C and 1000°C [9]. Pyrolysis temperature plays an important role in changing the characteristics of biochar [10]. The increase in pyrolysis temperature will cause a decrease in volatile matters, namely nitrogen, hydrogen, oxygen components which then cause loss of functional groups in biochar [8]. Loss of functional groups will facilitate the formation of pore structures in the biochar structure thereby increasing the surface area and pore structure of biochar [11]. In addition to pyrolysis temperature, other factors such as pyrolysis time can also affect the physicochemical properties of biochar. Pyrolysis time affects the surface area of biochar [12], biochar yield [13,14] and nutritional traits [15].

The utilization of biochar for soil has attracted attention in terms of enhancing carbon sequestration and restoring contaminated soil. As a
nutrient source, biochar can supply nutrients such as nitrogen (N), phosphorus (P), potassium (K), and other microelements that are inherently present in the original raw materials used for biochar production [16]. Potassium (K) availability in the soil tends to be low and can be reduced due to K uptake by plants (harvesting), K leaching by water, and soil erosion [17]. The availability of K in the soil is met by providing additional potassium nutrient through fertilizers and potassium-rich materials. Various studies have reported the utilization of biochar from various sources as a potassium source including bamboo biochar [18], biochar from banana peel [19], biochar from rice husk [20].

Influence of temperature and residence time on characteristics of biochars derived from corn stalk, rape straw, wheat stalk and peanut shell as feedstock has been studied. Biochar properties, including the pH, ash content, the ability to retain nutrients, were positively related with increasing temperature and prolonged residence time. However, the water-extractable organic matter and available nutrients were negatively related with temperature and residence time. There was a minimal release of NH$_4^+$-N, NO$_3^-$-N, and PO$_4^{3-}$-P from the generated biochars, and their concentrations were reduced through carbonization. By comparison, the water-soluble K content steadily increased with pyrolysis [15].

Other findings [21] have been reported that that longer pyrolysis times promote the enrichment of potassium during pyrolysis.

Previous studies showed that POME contains high levels of nutrients, such as N-total, P$_2$O$_5$-total, K$_2$O and MgO [5] and element such as Mg, P, S, Cl, K, Ca and Fe were also detected in POME biochar [22]. This shows that POME biochar has potential as an alternative potassium source material. Currently, a lot of research is being carried out regarding making biochar from POME and studying its characteristics.

A little research works were dedicated to the application of POME biochar as an alternative of potassium source material and how its released. The aim of this study was to manage POME waste into an alternative potassium source material by pyrolysis method. The influence of pyrolysis time was conducted to obtain information about the characteristics of the biochar produced. The study of kinetics release was conducted to study the

kineits model and mechanism of potassium release in biochar namely first order kinetics model, second order kinetics model, pseudo-first order kinetics model, pseudo-second order kinetics model. Hence, that it is expected that the released potassium information can be further utilized as a potential alternative potassium source material that can be used for soil remediation and is environmentally friendly.

## 2. Methodology

### Tools and Materials

Tools used in this research include laboratory glassware, OHAUS Pioneer analytical balance, Hanna HI 98107 pH meter, thermolyne muffle furnace, Jenway PFP7 Flame Photometer, Hitachi FlexSEM 1000 SEM-EDX, Quantachrome Novatouch LX-4 surface area analyzer, spectrum two system L160000A FTIR, THERMO SCIENTIFIC Orion AquaMate 8100 UV-Vis Spectrophotometer. Materials used in this research include POME sludge waste from MPS Tebedak plant, Ngabang, filter paper, distilled water, CaCl$_2$, NH$_4$OAc, HCl.

### Sample Preparation

The palm oil POME was dried in the sun for 3 days and then oven dried at 105°C for 24 hours. The dried POME was then allowed to reach room temperature before being stored in dry buckets and sealed.

### POME Pyrolysis

The dried sludge after being dried using an oven is then burned as much as 5 kg at a temperature of 150°C for 3 hours. Then wrapped in aluminum foil, it will be loaded in a crucible porcelain. Pyrolysis was continued by carried out at a temperature of 300°C with time variations of 1 hour, 3 hours and 5 hours using a furnace. The resulting biochar is cooled and then mashed using sieving with a 60-mesh sieve, biochar that passes sieving is taken to produce size uniformity.

### pH Determination

A total of 2 grams of biochar from the preparation of variations in pyrolysis time was added to 20 mL of distilled water (1:10) and then stirred for 30 minutes. After stirring is complete, the mixture is closed for 1 hour then filtered and measured the pH of each biochar [23].
Determination of exchangeable-K ($K_{exch}$) and non-exchangeable K ($K_{nonexch}$)

The determination of exchangeable K ($K_{exch}$) was carried out with 5 grams of biochar at various times mixed with 50 mL of 0.01 M CaCl$_2$ (1:10) for 6 hours [23]. Each mixture was filtered, and the concentration of extracted potassium was measured with a Flame Photometer.

Determination of non-exchangeable K ($K_{nonexch}$) was done with strong acid HCl 2M. A total of 5 grams of biochar at various times was mixed with 50 mL of HCl 2M for 1 hour, then allowed to stand for 48 hours [23]. After standing, the mixture was filtered, and the concentration of extracted potassium was measured with a Flame Photometer.

Potassium release kinetics study

The potassium release kinetics study was conducted by mixing biochar with CaCl$_2$ 0.01 M and measured potassium concentration as a function of time [23]. A total of 5 grams of biochar was mixed with 150 mL of 0.01 M CaCl$_2$ solution.

The first filtrate sample was taken within 30 minutes after the start of contact; subsequent samples were taken every 30 minutes for 6 hours. The concentration of potassium released into the solution was then measured using a Flame Photometer.

The experimental data analyzed in the determination of the kinetics model estimated the correspondence of the experimental data obtained on K release with four kinetics models, namely first order kinetics model, second order kinetics model, pseudo-first order kinetics model, pseudo-second order kinetics model.

First order kinetic model [24]:

$$\ln q_t = \ln q_o - k_1 t$$  \hspace{1cm} (1)

Second order kinetic model [24]:

$$\frac{1}{q_t} = \frac{1}{q_o} - k_2 t$$  \hspace{1cm} (2)

Pseudo-first order kinetic model [25]:

$$\ln(q_e - q_t) = \ln q_e - k_3 t$$  \hspace{1cm} (3)

Pseudo-second order kinetic model [25]:

$$\frac{1}{q_t} = \frac{1}{k_4 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (4)

$q_t$ and $q_o$ are the potassium released (mg g$^{-1}$) at equilibrium, $k_1$ is the first-order release rate constant (min$^{-1}$), $k_2$ is the second-order release rate constant (min$^{-1}$), $k_3$ is the first-order pseudo rate constant (min$^{-1}$), $k_4$ is the second-order pseudo rate constant (mg g$^{-1}$min$^{-1}$).

3. Results and Discussion

Process and product of biochar from POME

The production of biochar from POME sludge began with the initial preparation, where 10 kg of POME sludge was dried in the sun for 3 days and then dried in an oven at 105°C for 24 hours to remove the water contained in the POME sludge. 10 kg of POME sludge resulted in 5.5 kg of dried POME. Then, the dried POME was allowed to reach room temperature before being stored in a dry container and sealed to minimize moisture and mold contamination. The oven-dried POME was then burned for 5.5 kg at 150°C for 3 hours to reduce the water and oil content in the dried sludge. The resulting dried sludge is black in color as shown in Figure 1 (a) with a yield of 81.82%.

The dried sludge was then pyrolyzed in a furnace at 300°C for 1, 3, and 5 hours to see the effect of pyrolysis time on potassium release. The resulting biochar was left to cool down and then pulverized using a blender, the biochar was then sieved with a 60-mesh sieve to homogenize the size. The resulting biochar is a fine black solid as shown in Figure 1 (b). The yield of biochar at temperature variations of 1 hour; 3 hours and 5 hours are 81.24%; 79.51% and 78.14%, respectively. It has been previously reported that the yield of biochar from POME sludge prepared using pyrolysis method was 79.16% [22].

Figure 1. (a) POME dry sludge, (b) synthesized biochar.
The variation of pyrolysis time at the same temperature affects the yield of biochar produced. The longer the pyrolysis lasts, the lower the biochar yield, in line with previous findings [15]. As time increases, the content of volatile matters will decrease, while the carbon content increases in biochar [26]. The decrease in yield is related to the decomposition of biopolymer compounds from the biomass. At lower temperatures of 180°C-250°C the biomass begins to decompose releasing H2O and gases of CO and CO2. At higher temperatures of 250°C-450°C, the heat generated will release more H2O and gases of CO2, CH4, and N2 causing a decrease in yield.

The lignocellulose content in POME sludge is in the form of hemicellulose, cellulose, lignin, and extra-cellulose which can be fat, protein, moisture, and other minerals [22]. Hemicellulose is reported to be decomposed at 220°C to 315°C, cellulose will be decomposed at 315°C to 400°C, and lignin is more difficult to decompose due to its wide decomposition temperature range of 160°C to 900°C [27]. During the pyrolysis reaction, hemicellulose will decompose first at lower temperatures followed by cellulose and finally lignin. Volatile matters consist of CO, CO2, H2, CH4, N2 and carbohydrate gases which are associated with hemicellulose and cellulose content [26]. The longer the pyrolysis time, the longer the contact between heat and energy with the biochar material so that more volatile matter is lost from the lignocellulosic compounds resulting in less mass left behind as biochar.

Cellulose, which has a relatively simple structure, will briefly depolymerize initially at a temperature of about 300°C and further conversion into active cellulose species, such as levoglucosan (LGA), levoglucone (LGO), and other monosaccharides through bond breaking and dehydration (Figure 2a). Hemicellulose has a more complex structure with abundant branched chains and various substituents, consisting of xylan and glucomannan, which in turn contain pyrolytic properties similar to anhydrosugar (leading to pyrolytic characteristics similar to cellulose) (Figure 2b). Lignin, a complex biopolymer with an aromatic structure in the pyrolysis process of lignin, higher temperatures are required for bond breaking to produce large amounts of phenolic compounds along with small amounts of acids.

Table 1. Chemical physics characteristics of biochar at various times.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Biochar on time variation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>81.24%</td>
</tr>
<tr>
<td>pH</td>
<td>8.3</td>
</tr>
<tr>
<td>Exchangeable potassium (mg.g⁻¹)</td>
<td>1.562</td>
</tr>
<tr>
<td>Non-exchangeable potassium (mg.g⁻¹)</td>
<td>3.295</td>
</tr>
<tr>
<td>S BET (m²/g)</td>
<td>0.266</td>
</tr>
<tr>
<td>V tot (cc/g)</td>
<td>0.00588</td>
</tr>
</tbody>
</table>
alcohols, and light aromatic hydrocarbons (Figure 2c) [28].

**Characterization of biochar at various pyrolysis times**

Biochar preparation results on pyrolysis time variations were characterized in the form of pH determination, characterization with FTIR, surface area determination with methylene blue and SAA methods, morphological characterization, and elemental content with SEM-EDX and determination of potassium availability in biochar as exchangeable potassium and non-exchangeable potassium. The characteristics of the biochar produced are presented in Table 1. Biochar preparation results are alkaline which is in line with the findings of previous studies [29]. The alkaline nature of biochar pH can be applied to reduce soil acidity in acidic soils. The results showed that the pH of the biochar increased as the pyrolysis time increased. The pH values of POME sludge pyrolyzed at 1 hour, 3 hours and 5 hours in this study were 8.3; 8.5; 8.7, respectively.

Longer pyrolysis time promotes further pyrolyzation. The pH values of one hour pyrolysis time are lower than those of 3 hours probably because no reaction or partial reaction in some components in biomass occurred [21].

The pH of biochars increased with increasing temperature, which was mainly due to the functional groups such as -COOH and -OH decreased with increasing pyrolysis temperature [21]. The functional groups of the prepared biochar can be seen from the FTIR spectra in Figure 3 and Table 2. The bands of 3425 cm⁻¹ shows the stretching of hydroxyl groups (O-H) experiencing widening at higher pyrolysis times which may indicate the start of loss of hydroxyl groups from biochar. This is reinforced by the absorption of bending O-H at 1410-1415 cm⁻¹ which shifts to higher wave numbers indicating a reduced number of these groups, thus causing an increase in the pH of the biochar produced to be more alkaline. The

Table 2. Functional groups in biochar from POME sludge.

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3424 – 3425</td>
<td>O-H stretching of alcohol and phenol groups</td>
</tr>
<tr>
<td>2920-2922</td>
<td>C-H stretching of alkane groups</td>
</tr>
<tr>
<td>1597 – 1606</td>
<td>C=C and C=O stretching in aromatics</td>
</tr>
<tr>
<td>1410-1415</td>
<td>O-H bending in alcohols and carboxyls</td>
</tr>
<tr>
<td>1316-1318</td>
<td>C-N stretching, aromatic C-O stretching</td>
</tr>
<tr>
<td>1087-1089</td>
<td>C-O stretching of alcohol and phenol groups</td>
</tr>
<tr>
<td>777-874</td>
<td>C-H on aromatics</td>
</tr>
<tr>
<td>600s</td>
<td>C-X stretching on halocarbons</td>
</tr>
<tr>
<td>400s</td>
<td>Vibration of metal oxides Si-O-C, K₂O and FeO₆</td>
</tr>
</tbody>
</table>

Figure 3. FTIR spectra of biochar prepared at (a) 1 hour, (b) 3 hours and (c) 5 hours.
absorptions shown from the FTIR spectra indicate that the biochar produced has an aromatic carbon structure, with functional groups dominated by alcohols, phenols, amines, and halocarbons.

Exchangeable cations such as K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) on the surface will be bound to biochar functional groups or bound through ions on biochar. The metals and minerals contained are likely to be in the pore structure of biochar. Figure 4 shows an assumed depiction of biochar composition in general. Me represents exchangeable cations (K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)), red circles represent ions contained in biochar (ash) and yellow circles represent metals and minerals in biochar.

The results of surface area analysis from characterization with SAA at pyrolysis time variations of 1 hour; 3 hours and 5 hours are 0.266 m\(^2\)/g; 0.724 m\(^2\)/g and 1.231 m\(^2\)/g, respectively. The results of surface area analysis showed an increase in surface area directly proportional to the increase in pyrolysis time. The increase in surface area can be caused by the decomposition of organic matter and the formation of micropores. It can be explained that as the pyrolysis time increases, the basic pore structure in the biochar increases over time due to the increased volatilization of volatile matters [14]. The observed increase in volume with increase in pyrolysis time could be attributed to more pyrolysis time for the carbon–CO\(_2\) reaction at the reaction temperature which brings about evolution of more pore structures [13].

Biochar from POME has a high content of macro elements such as P and K. The results of Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) characterization of biochar samples from POME are presented in Table 3.

Table 3. EDX Biochar from POME

<table>
<thead>
<tr>
<th>Elements</th>
<th>Elemental Weight of Biochar from POME (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 hour</td>
</tr>
<tr>
<td>C</td>
<td>31,06</td>
</tr>
<tr>
<td>O</td>
<td>37,25</td>
</tr>
<tr>
<td>Mg</td>
<td>1,85</td>
</tr>
<tr>
<td>Al</td>
<td>1,19</td>
</tr>
<tr>
<td>Si</td>
<td>6,54</td>
</tr>
<tr>
<td>P</td>
<td>0,95</td>
</tr>
<tr>
<td>S</td>
<td>0,46</td>
</tr>
<tr>
<td>Cl</td>
<td>1,26</td>
</tr>
<tr>
<td>K</td>
<td>3,97</td>
</tr>
<tr>
<td>Ca</td>
<td>10,13</td>
</tr>
<tr>
<td>Fe</td>
<td>2,03</td>
</tr>
</tbody>
</table>

Figure 4. Depiction of biochar composition.

Figure 5. shows SEM micrographs of biochar samples from POME at various pyrolysis times (a) 1 hour, (2) hours, (c) 3 hours at 3000 times magnification. The surface of the biochar sample in Figure 5 (a) the biochar looks polyhedral with pores that are still irregular. The surface of the biochar sample in Figure 5 (b) shows that there is a more clear formation of small pores. The pore structure is formed more clearly in Figure 5 (c), namely biochar preparation results at 5 hours which affects the increase in biochar surface area [7]. This indicates that the pyrolysis process has caused the decomposition of volatile matters and the remaining components are transformed into...
biochar with pores of various shapes and sizes observed on the biochar surface [29]. The pore structure of biochar can improve soil porosity, increase soil surface area, increase the number of potassium bacteria, accelerate mineralization and slow release of available potassium, and increase potassium supply capacity [30].

Determination of exchangeable potassium and non-exchangeable potassium is done to determine the available and exchangeable potassium from biochar to the soil layer to optimize its optimal application. In biochar, potassium may be in its oxidized form, K₂O through FTIR absorption around 470 cm⁻¹ [31] or bound on the surface through biochar functional groups. The exchangeable potassium value of biochar at time variation of 1 hour; 3 hours and 5 hours are 1.562 mg g⁻¹; 1.702 mg g⁻¹ and 1.940 mg g⁻¹, respectively.

The mechanism of potassium release can be explained in two mechanisms. The first mechanism where potassium is rapidly released from the biochar structure and mentions that certain amounts of potassium are still sub-compartmentalized in the biochar. This sub-compartment can be released through the second mechanism where the decomposition of the silica phase controls the diffusion of potassium. The non-exchangeable potassium in biochar from POME sludge was higher than the exchangeable potassium. The non-exchangeable potassium is possible from the sub compartment of biochar with HCl. The data of exchangeable potassium and non-exchangeable potassium are supported by the EDX data in Table 3.

The kinetics study was conducted by mixing a certain amount of biochar with 0.01 M CaCl₂. Determination of the release kinetics in this study was carried out with a variation of the contact time of 0-360 minutes. A total of 10 mL of solution was taken every 30 minutes until 360 minutes to determine the concentration of potassium released as a function of time. Equilibrium model testing was conducted to determine the appropriate equilibrium model used.
Determination of the equilibrium model depends on the value of the correlation coefficient ($R^2$). A suitable equilibrium model is an equilibrium model with a higher $R^2$ value or close to 1. First-order kinetics model, second-order kinetics model, first-order pseudo kinetics model, second-order pseudo kinetics model to explain the potassium release process on biochar. The rate constant value is determined based on the line equation from the graph. The rate constant value is related to the speed of potassium mass transfer from biochar to solution in a certain period. The results of the potassium release kinetics study are presented in Table 4. The best correlation coefficient ($R^2$) was shown with the pseudo-second order kinetic model. The process of potassium release in biochar is described by this kinetic model assuming that the concentration of CaCl$_2$ is much greater than the concentration of potassium in biochar to be exchanged.

The pseudo-second order kinetics model gave release rate constant values of 0.018; 0.024; 0.020; 0.014 (mg g$^{-1}$min$^{-1}$), $q_e$ values of 0.814; 0.839; 0.927; 1.111 mg g$^{-1}$ with correlation coefficient ($R^2$) values of 0.9577; 0.9833; 0.973; 0.982 mg$^{-1}$, respectively. The $q_e$ value increases as the pyrolysis time increases, indicating that more potassium can be released at equilibrium. While the release of potassium under acidic conditions from biochar preparation for 5 hours has the largest $q_e$ value, it is possible that H$^+$ plays a role in the process of releasing potassium into solution because of the continued ion exchange between K$^+$ and H$^+$ ions.

### 4. Conclusion

Based on the results of the research conducted, it can be concluded that the production of biochar from POME can be used as an alternative of potassium source material. Biochar produced from POME using pyrolysis method at a temperature of 300°C provides better characteristics as the increase of pyrolysis time, hence the further research need to study the optimum parameter to produce high potassium characteristics biochar from POME.

Biochar produced for 5 hours in this research pyrolysis time has by the highest surface area, the greatest potassium availability and exchangeable potassium exchangeable potassium value of 1,940 mg g$^{-1}$. The potassium release in this study followed the pseudo-second order kinetics model characterized by the release rate constant (K) values in the pseudo-second order kinetics model are 0.018 (mg g$^{-1}$min$^{-1}$), 0.024 (mg g$^{-1}$min$^{-1}$), 0.02 (mg g$^{-1}$min$^{-1}$) 0.014 (mg g$^{-1}$min$^{-1}$) respectively.

### Bibliography


