Oil palm empty fruit bunch ash valorization through potassium extraction

Tjokorde W. Samadhi¹, Winny Wulandari¹ and Kezia R. Tirtabudi¹

¹Chemical Engineering Department, Faculty of Industrial Technology, Bandung Institute of Technology, Jl. Ganesha 10, Bandung, Indonesia

E-mail: winny@che.itb.ac.id

Abstract. Oil palm empty fruit bunch (OPEFB) is a by-product of palm oil processing that is considered solid waste. It is produced in a large amount, counting up to 23% of the fresh fruit bunch (FFB). The ash content in OPEFB comprises a potassium compound. Potassium can be potentially recovered as potassium carbonate by extracting it with water. This study aims to investigate a method to recover potassium from OPEFB ash as potassium carbonate for further processing into potassium-based fertilizer. This research consists of pyrolysis process of OPEFB into char, then the char is analyzed by TGA in order to determine the ashing temperature. The temperature of 250°C, 400°C and 550°C are chosen for the ashing (combustion) process. The resulted ash is then extracted by water with the Feed to Solvent ratio of 1:4, 1:5, and 1:6, respectively. From the AAS analysis result, the highest potassium concentration is obtained at temperature of 400°C with F:S ratio = 1:6, with the potassium concentration of 49.94 %-w/w. This value is suitable for liquid fertilizer.

1. Introduction

Indonesia is listed as the country with the largest of palm oil production in the world [1] and it is estimated that the amount of production will continue to increase. The area of oil palm plantations in Indonesia is estimated at 12.3 million Ha in 2017 [2], while the increase of production (crude palm oil) reaches 35.4 million tons [2].

The processing of fresh fruit bunch (FFB) into crude palm oil (CPO) produces several types of waste, including oil palm empty fruit bunch (OPEFB), mesocarp fiber (MF), palm kernel shell (PKS), palm kernel meal (PKM), and palm oil mills effluent (POME) [3]. There has been some usage of PKS and MF to be the boiler fuel used in the palm oil processing plant, and it produces biomass waste as oil palm ash. Other oil palm wastes have established downstream use. Fronds and trunks are used for animal feedstock, while kernel shells are used as fuel for the steam boiler in palm oil mills [4].

It has been reported that oil palm ash has been used as crude fertilizer, novel adsorbent, concrete pozzolanic cement material [5] and blend cement paste [6]. However, OPEFB alone has not been used as fuel to the boiler in oil plant processing plant due to its alkali content that promotes slagging and fouling [7,8]. Alkali-induced slagging in biomass-fired furnaces is the unwanted combustion side effect caused by alkali metal aerosols released from biomass [7]. Typically, OPEFB is burned and partially spread over empty land as a mulch.
Among the several solid wastes from oil palm plantation, OPEFB waste has the highest number proportion with a total of 23% for each FFB [9]. OPEFB is also known to contain potassium, and it has potential to serve as the sources of potassium, including a potential source for fertilizer. From the several works of literature, it is reported that OPEFB contains 30–46 % of K₂O [10], [11], [12] mainly in the form of carbonate.

Potassium extraction from wood ash has been studied, for example, is a study regarding potash production from bamboo ash [13]. From this study, is it known that extraction from bamboo ash produced 0.7 %-mass of K₂O in solution and it is suggested that bamboo ash extract has a potential to be used as the intermediate for fertilizer product [13]. Therefore, OPEFB’s ash is also expected to be used as a source for potassium fertilizer which can be used for oil palm plantations themselves. This study aims to investigate a method to recover potassium from OPEFB ash as potassium carbonate for further processing into potassium-based fertilizer.

2. Materials and Method
The materials used in this study were oil palm empty fruit bunch (OPEFB) demineralized water. OPEFB was obtained from East Kalimantan.

![Figure 1. Block diagram of OPEFB extraction process.](image)

Figure 1 shows the block diagram of OPEFB extraction process. This study consisted of several stages, which are as follows:

1. Pyrolysis process of OPEFB. Pyrolysis of OPEFB was carried out in a 40 cm diameter pyrolysis reactor. The char was then characterized using TGA (Thermogravimetry Analysis/Linseis) in order to determine the melting point and temperature range of the OPEFB ash.
2. Ashing/re-combustion process. The ashing is carried out in order to convert char into ash. The temperature chosen for the ashing process was determined from the TGA result. The ashing process was carried out in a muffle furnace (Nabertherm). This further combustion process aims to remove substances as the volatile matter and fixed carbon contained in the OPEFB char. Then the ash is crushed into 100 mesh. The ash was then analyzed using SEM/EDS (SU3500).
3. Solid-liquid extraction process of ash. Ash was extracted with demineralized water. The extraction process is carried out in a water-bath with a temperature of 80 °C. The extraction is a single-stage solid-liquid extraction. Firstly, 50 g of each ash sample was weighed and
thoroughly mixed with required volume (200 ml, 250 ml, and 300 ml) of demineralized water. Then extraction process is carried out for 4 hours at temperature of 80 °C. Subsequently, filtration is carried out by using vacuum filtration to separate the extract solution from raffinate. The extract solution obtained is then analyzed for its potassium content using Atomic Absorption Spectrophotometry (AAS, Perkin-Elmer).

(4) Evaporation of extract solution. Subsequently, the extract solution is evaporated by heating the solution above a hotplate until it formed solid phase.

(5) Characterization of OPEFB ash and potassium salt. The phase characterization of the ash and the resulted salt was carried out by XRD analysis (Bruker).

The parameters conducted in this study include ashing temperature in muffle furnace and the ratio of feed (ash) to solvent (demineralized water) (F:S). The parameter that is investigated the concentration of potassium in the solution. The variable parameters are as follows:
- ashing temperature: 250 °C, 400 °C, and 550 °C
- Ratio of ash to demineralized water (F:S): 1:4, 1:5 and 1:6

3. Result and Discussions

3.1. OPEFB pyrolysis
Pyrolysis of OPEFB is carried out by pyrolysis using the furnace in the open area. This process aims to convert the biomass of OPEFB into char. The average yield of char to the mass OPEFB biomass (db) is 11.6 %. The char of OPEFB is then ground using ball mill to reduce its size and refine its texture to become powder. Subsequently, the char of OPEFB was analyzed using TGA. The TGA and DSC curves of OPEFB can be seen in Figure 2.

![Figure 2. TGA and DTG analysis result of OPEFB’s char.](image)

The TGA curve in Figure 2 it is stated in black while the DSC stated in blue. The first peak in DSC curve shows the mass loss of 11 % seen in TGA curve. This loss of mass shows the loss of moisture content in OPEFB’s char. Then the second peak is seen at a temperature of 435 °C and is the maximum rate of around 0.054 %-mass /°C. The loss of mass at this peak (230 °C – 500 °C) shows the loss of volatile matters and fixed carbon contained in the OPEFB’s char. Then the pyrolysis process suddenly decreased at temperature of 500 °C to 800 °C, the process continued at a very slow rate.
OPEFB char was subsequently processed into char by ashing. Figure 3 shows the photograph of OPEFB ash in different ashing temperature: 250 °C, 400 °C, and 550 °C. The ash resulted from 250 °C is darker compared to 400 and 550 °C due to its carbon or tar content.

The ash then analyzed by using XRD to determine the potassium mineral phase that found in the ash of OPEFB. Figure 4 shows a graph of XRD analysis result from the three ashing temperature. This is similar to ash from boiler (Oil Palm Ash /OPA), which contains KCl, sylvite [14]. For OPA, however, it also contains a metal-based substance of potassium molybdenum selenium (K₂Mo₃Se₁₈).

![Figure 3. The OPEFB ash in different ashing temperature.](image1)

![Figure 4. XRD analysis of OPEFB ash at different ashing temperature](image2)
Figure 5. The XRD pattern of OPEFB’s ash at ashing temperature of 400 °C and the solid to liquid ratio of 1:4.

Table 1. The XRD analysis of OPEFB’s ash at ashing temperature 400 °C and the solid to liquid ratio of 1:4.

| Phase name       | Formula                  | Figure of merit | Phase reg. detail | DB card number       |
|------------------|--------------------------|-----------------|-------------------|----------------------|
| Potassium Carbonate Hydrate | K₂CO₃ (H₂O)1.5          | 0.655           | ICDD              | 01-073-0470          |
|                  |                          |                 | (PDF2.DAT)        |                      |
| Sylvite, syn     | KCl                      | 0.790           | ICDD              | 00-041-1476          |
|                  |                          |                 | (PDF2.DAT)        |                      |
| Arcanite, syn    | K₂SO₄                    | 1.601           | ICDD              | 00-044-1414          |
|                  |                          |                 | (PDF2.DAT)        |                      |

Figure 5 gives additional information on XRD results, where potassium carbonate, sylvite (KCl) and arcanite (K₂SO₄) are the major phase in the OPEFB ash. Based on Figure 4, it is seen that the three types of ash with different ashing temperatures show a similar configuration. Based on the XRD result, the mineral phases found in OPEFB’s ash are K₂CO₃·xH₂O, KCl, KClO₃, KIO₃, and K₂Ca(CO₃)₂.

Then the three ashes with each ashing temperature were analyzed by SEM/EDS to analyze its alkali content semi-quantitatively. Potassium (K) and K₂O compounds from the result of EDS analysis for each temperature are shown in Figure 6.

The overall result of EDS analysis of OPEFB’s ash showed that the ash contained high potassium. At the ashing temperature of 250°C, the potassium content in OPEFB ash is approximately 58 % as K₂O. It increased to 67% as K₂O at ashing temperature of 400°C; and lowered to 57% as K₂O at higher ashing temperature, i.e., 550°C. This shows that extraction of OPEFB’s ash has the potential to produce extracts with high potassium content.
Figure 6. The EDS analysis of Potash (K) and K$_2$O compound in OPEFB’s ash.

3.2. Extraction process of OPEFB’s ash

Figure 7. Potassium (K) and K$_2$O compound in OPEFB’s ash after extraction with solid to liquid ratio of 1:4; 1:5, and 1:6.

Figure 8. Photographs of OPEFB ash leaching solution

Figure 7 shows potassium yield resulted from solid-liquid extraction at different ashing temperature, while Figure 8 shows the photographs of OPEFB ash leaching solution. The temperature of extraction is at 80°C. Based on AAS analysis, extracts with the highest potassium concentrations (ppm) were
obtained on conditions at ashing temperature variation of 400 °C and variation ratio F:S = 1:4. It can be seen in Figure 7 that the highest potassium yield was produced at temperature variation of 400 °C and variation of F:S = 1:6. From the result, it can also be seen that the more volume of solvent used with the same amount of ash feed, the more amount of potassium is extracted.

One of the raffinates from extraction result was analyzed by XRD for its content. In this study, the raffinate samples that been analyzed were raffinate from variation temperature 550 °C with ratio F:S = 1:5. The result of this analysis can be seen in Figure 9. From this result, its shown that raffinate in the form of OPEFB ash is no longer contained crystalline phase from potassium metal. This shows that most of the potassium has been extracted. The dominant phase in the raffinate is amorphous, which contains quartz, lautite, maghemite, forsterite, and monticellite. The amorphous structure of the raffinates is caused by the leaching process, as the leaching process dilutes all the major crystalline phases in the OPEFB such as potassium carbonate, KCl and K2SO4.

3.3. Crystallization of leaching solution
The process of evaporation of leaching solution is carried out by evaporating the extract solution in beaker glass which is heated on a hotplate. In this study, the evaporation temperature used was maintained at 85 °C. The solid then analyzed using XRD to determine the potassium mineral phase found in the solid phase after evaporation from extract solution. From the XRD result in Figure 10, the solids resulting from the evaporation of extract solution has similar phase to the original ash. The additional information of phase analysis from XRD is shown in Table 2. The mineral phase found in the evaporation solids is KCl, K2SO4, and K2CO3. However, K2CO3 is formed in the hydrate phase (K2CO3.xH2O).

![Figure 9. XRD analysis result from example raffinate.](image-url)

---

Table 2: Additional information of phase analysis from XRD.
Figure 10. The XRD pattern of the potash salt.

Table 2. The XRD analysis of potash salt.

| Phase name       | Formula               | Figure of merit | Phase reg. detail     | DB card number |
|------------------|-----------------------|-----------------|-----------------------|----------------|
| Potassium Carbonate Hydrate | K$_2$CO$_3$·(H$_2$O)$_{1.5}$ | 0.777           | ICDD (PDF2.DAT)       | 01-073-0470    |
| Sylvite, syn     | KCl                   | 0.895           | ICDD (PDF2.DAT)       | 00-041-1476    |
| Arcanite, syn    | K$_2$SO$_4$           | 1.074           | ICDD (PDF2.DAT)       | 00-044-1414    |

From Figure 11, it is also obtained that from the evaporation result, it can be seen that the highest solid mass is obtained at the varying temperature of 400 °C and variation of F:S = 1:4.
4. Conclusion

Potassium as a raw material for fertilizer can be obtained from OPEFB’s ash through an extraction process. The optimum ashing temperature to get the highest amount of potassium is at a temperature of 400 °C. The optimum F:S to obtain the highest yield is at F:S = 1:6 with a yield of 49.94 %. The mass of the most solids is obtained under the temperature conditions of 400 °C filling with F:S = 1:4 with the potassium concentration of 49.94 %-w/w. This value is suitable for liquid fertilizer. Potassium salt resulted from the evaporation of its leaching solution is majorly contains K₂CO₃, KCl, and K₂SO₄.

Acknowledgments

This research is funded by the P3MI grant program 2017 for the Chemical Engineering Product Design and Development Expertise Group at the Faculty of Industrial Technology, Bandung Institute of Technology.

References

[1] Varqa S 2017 Essential palm oil statistics Palm Oil Analytics Available from: www.palmoilanalytics.com/files/epos-final-59.pdf (accessed 18.07.2019)
[2] Direktorat Jendral Perkebunan 2017 Statistik Perkebunan Indonesia 2015-2017 (Jakarta: Kelapa Sawit (Oil Palm))
[3] Hambali E and Rivai M 2017 IOP Conf. Ser.: Earth Environ. Sci. 65 012050
[4] Faizi M K et al 2016 Matec Web of Conferences 90 01064
[5] Foo K Y and Hameed B H 2009 J. Hazard. Mater. 172 523-31
[6] Sinsiri T, Kroehong W, Jaturapitakkul C and Chindaprasirt P 2012 Mater. and Design 42 424-33
[7] Niu Y, Zhu Y, Tan H, Wang X, Hui S and Du W 2015 Proc. Combust Inst. 35 2405-13
[8] Teixeira P, Lopes H, Gulyurtlu I, Lapa N and Abelha P 2012 Biomass and Bioenergy 39 192-203
[9] Sadi S 1992 Proc. 1st Soehadi Reksowardjo Chemical Engineering Seminar (Bandung, Indonesia)
[10] Bassam N El 1998 Energy Plant Species (London: James & James Sci. Publ) p 194
[11] Giorgi C D V 1941 Malay. Agr. J. 29 426-36
[12] Suwandi P P 1991 Bull. Puslitbun Marhat 11(3) 43-6 (in Indonesian)
[13] Samadhi T W, Narcia F and Amril H 2018 MATEC Web Conferences 156 03027
[14] Yin C Y, Kadir S A S A, Lim Y P, Syed-Ariffin S N and Zamzuri Z 2008 Fuel Processing Technol. 89 693-6