

# **Study of Potassium Recovery from Biomass Ash Using Tartaric Acid and Syngenite Method**

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How to cite this paper: Mananda, A.B., Harada, H., Halem, H.I.A., Mitoma, Y. and Keiko, F. (2021) Study of Potassium Recovery from Biomass Ash Using Tartaric Acid and Syngenite Method. *Journal of Materials Science and Chemical Engineering*, **9**, 39-52. https://doi.org/10.4236/msce.2021.95004

**Received:** April 21, 2021 **Accepted:** May 28, 2021 **Published:** May 31, 2021

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## Abstract

Biomass has the potential and benefits of being an alternative energy source to replace fossil fuels that exist today in Indonesia and other tropical countries. In addition, biomass has an abundant stock or supply. By assessing the feasibility of recovering potassium, it is hoped that more potassium resources and in future Indonesia will be dependent on imported fertilizers and increase the agricultural industry, which is the aims of this study. The best extraction result is using CH<sub>3</sub>COOH. Treatment of 1:10 solid-liquid ratio with the help of 1 mol/l CH<sub>3</sub>COOH was chosen as the best treatment because it is more economically efficient. Recovery of K with the help of tartaric acid and acetic acid resulted in a K recovery efficiency of around 94%. The optimal condition for the syngenite method is the addition of a magnesium dose of 5 mmol/l and at pH 11, the Ca: K ratio is 1:2.1 with 42% K. This can be a suggestion which method is more effective and efficient in recovery K.

# **Keywords**

Biomass, Rice Husk Coffee, Potassium Recovery, Tartaric Acid

## **1. Introduction**

The global population is still growing, with an estimated 7.7 billion people worldwide in 2019, the medium-variant projection 1 indicates that the global population could grow to around 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 [1]. This situation will lead to a situation in which the percentage of global energy used in the world is increasing considerably.

During this time, the use of petroleum is very vital because it is the main source of energy in the world, including as a fuel for human transportation. In fact, petroleum is non-renewable fossil energy, so it is feared that in the future it will run out if it is not handled such as finding renewable energy sources. One of the renewable energy sources is biomass. Biomass is any organic matter that is renewable over time. More simply, biomass is stored energy [2]. In addition, biomass is a carbon-neutral energy source, since the biomass during its growth absorption of  $CO_2$  that is then released into the atmosphere during its combustion, with a zero-net balance of  $CO_2$  emissions [3]. Due to the wide availability of biomass worldwide, mainly because it can be obtained as a by-product of many industrial and agricultural processes, biomass represents a growing renewable energy source with high growth potential [4].

In Indonesia, the potential for biomass generation has been recorded in the Ministry of Energy and Mineral Resources (ESDM), which shows that the annual national biomass production volume was 65 tons in 2011, which was generated primarily by the highly developed plantation and agricultural sectors [5]. In addition, the Republic of Indonesia Presidential Regulation Number 22 of 2017 states, that Indonesia's forests of 120 million hectares have a very large potential source of biomass. In the next 30 years, biomass consumption for energy production in Indonesia is projected to reach 150 million BOE [6].

Ash utilization action is deemed necessary to increase the potential volume of biomass ash produced by the biomass-based energy sector. Potassium Recovery from Tropical Biomass Ash [7] and Phosphorus recovery from the biomass ash [8] are studies that utilize biomass ash. After analyzing using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-6300), rice husk coffee has the potential to contain a relatively high potassium content, around 3.48%, and its abundant production in Indonesia around 307,500 tons per year [9], making it an attractive raw material for the recovery of potassium from biomass ash.

Potassium is routinely used as a fertilizer in agriculture and plantations to compensate for losses from the potassium cycle due to harvest and export of crops outside the boundaries of agriculture or plantations, so potassium is considered the main nutrient needed by plants. The ability to recover potassium from biomass ash can economically reduce the volume of imported potassium fertilizers. In 2016, Indonesia imported around 877 million tons of combined types of fertilizers containing potassium, so reducing the volume of imports of potassium fertilizers is very important. While the general trend of total fertilizer imports to Indonesia has decreased in the 2012-2016 period, the annual import quantity is still very substantial [10].

Although the need for recycling of K is high, there have been few studies on potential methods of K recovery. Zhou *et al.* recovered 44.3% K from a dried stem-leaf sample of water hyacinth during the formation of  $\text{KC}_4\text{H}_5\text{O}_6$  by adding tartaric acid [11]. In this study we also found that charcoal from activated sludge and chicken manure has the potential to produce high Ca values, 2.42% for Activated sludge and 2.62% for chicken manure.

Syngenite ( $K_2Ca(SO_4)_2 \cdot H_2O$ ) was synthesised already in 1850 by J.A. Philips as a by-product during the process of vinegar fermentation [12] but it wasn't until 1872 that it was discovered as a naturally occurring mineral. Since then, it has been found as one of the crystalline compounds in salt stains on bricks together with gypsum [13] [14]. Syngenite is described in the research of Kloprogge *et al.*  [15] as a product which is also formed during fertilizer production. Hiroki *et al.* [16] observed that potassium isolates from molasses, using the syngenite method resulted in more than 15% Ca recovery and more than 10% K recovery with a maximum pH below 13, because if it is above pH 13, decay occurs. Other than that only a few studies have found the optimum pH for syngenite processing. So this study used a pH of 11 because in a previous study [17] was the optimum pH for the magnesium potassium phosphorus complex method.

Rice husk coffee is used to supply potassium, while charcoal is used to supply calcium. Calcium, potassium and sulfate complex salts are produced by increasing the dose of magnesium and by adjusting the pH 11. These compounds were easy to solidify. The use of Ca and K together increases the prospects for sygenite production if magnesium dosages from  $MgSO_4$  are also added. The formation of syngenite as an intermediate product in one of the methods developed for the production of mineral fertilizers from natural polyalkite  $K_2Ca_2Mg(SO_4)_4$ ·2H<sub>2</sub>O [18], is expected to provide positive benefits for the agricultural sector.

From the above point of view we set our aim for this study, which is to prepare tartaric acid solution and syngenite formation by adding Mg dosages to the Ca and K rich solutions obtained from K extraction from rice husk coffee with Ca rich extraction fluids. It is hoped that this study will become the basis for the development of a pilot scale potassium recovery process using biomass ash as raw material. Therefore, this research is the first step in efforts to develop a larger process that aims to further reduce Indonesia's dependence on imported fertilizers, and to increase the sustainability of the nation's agricultural industry.

## 2. Materials and Methods

#### 2.1. Materials

Raw materials for coffee husk waste were obtained from the Solok Radjo Cooperative, Solok City, West Sumatra, Indonesia, using Arabica coffee, from 3 varieties namely Kartika, Sigararutang and Andungsari. The material has been examined by the Agricultural Quarantine Agency, Agricultural Quarantine Office, Class 1, Padang, Indonesia.

In addition, activated sludge is obtained from the Sewage Treatment Plant, in Miyoshi City, Hiroshima Prefecture. Activated Sludge is obtained from burning without using oxygen. For charcoal from chicken manure that is already on the market, so we get it by buying.

#### 2.2. Methods

#### 2.2.1. Preparation Materials

Melting point and ashing temperature range of biomass charcoal samples were determined using a Linseis STA Platinum Series (simultaneous TGA-DSC analyzer). Biomass charcoals were burned in a Yamato type FO100 furnace at 450°C - 550°C to convert them to ashes. Care was taken to ensure that the ashing temperature did not exceed 600°C, since biomass combustion at 600°C - 850°C

causes significant volatilization of potassium and fusion reactions between potassium salts and silica [19]. The produced ashes were cooled down and stored in a desiccator.

#### 2.2.2. Potassium Extraction

Types of potassium extracts are hydrochloric acid solution (kanto chemical CO., INC., referred to as HCl), sodium hydroxide solution (kanto chemical CO., INC., referred to as NaOH), acetic acid solution (kanto chemical CO., INC., referred to as CH<sub>3</sub>COOH), and the types of concentrations used are 0.1, 0.5 and 1 mol/l. Than dissolved in 100 ml of distilled water. Mix the solutions using homogenizer (Rotator RT-50) for 24 hours. After the homogenizer was complete, the extract was filtered using quantitative filter paper 5C (As One Corporation). The K concentration in the filtrate was measured using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-6300). The rate of K extraction in rice husk coffee ash is calculated from Equation (1) based on the K content of the rice husk coffee burning residue.

$$E = \frac{C \cdot VE}{w \cdot Ck} \times 100 \tag{1}$$

with the information, *E*: potassium extraction rate (wt%), *C*: potassium extract concentration (mg/L), *VE*: total extract volume (L), *w*: total initial weight of material (g), *Ck*: potassium content in wood burning (g/Kg).

#### 2.2.3. Calcium Extraction

Charcoal from chicken manure and activated sludge weighed as much as 2 grams, is put into the erlenmeyer, then into the erlenmeyer each is added with an acid and alkaline extraction solution. HCl (kanto chemical CO., INC., referred to as HCl) and CH<sub>3</sub>COOH (kanto chemical CO., INC., referred to as CH<sub>3</sub>COOH) were used as an acid extraction solution with a concentration variation of 0.1 mol/l; 0.15 mol/l; and 1 mol/l. As an alkaline extraction solution used NaOH (Kanto Chemical CO., INC., referred to as NaOH) with a concentration variation of 0.1 mol/l; 0.5 mol/l; and 1 mol/l. The mixture is stirred with a magnetic stirrer and shaker (Taitec, Bio Shaker V.BR-36) for 24 hours. After 24 hours and then filtered using quantitative filter paper 5C (As One Corporation), the resulting filtrate is collected and analyzed using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-6300). The rate of calcium extraction in charcoal from chicken manure and activated sludge were calculated from Equation (1) based on the calcium content of the charcoal residue.

#### 2.2.4. Control of Precipitation Condition

Nearly saturated tartaric acid was prepared by adding 20 g of tartaric acid to 15 ml of distilled water. Precipitation is controlled by varying the amount of tartaric acid solution added to potassium containing a clear solution. For 0.1, 0.5 and 1 ml treatments, tartaric acid solution was added to 10 ml of pure acetic acid, then separated using quantitative filter paper 5C. After that, drying at 60°C for 24

hours, the weight is determined by an electronic balance. After the filtrate was formed, it was weighed and dissolved in 1 mol/l  $H_2SO_4$  and the concentration was measured using atomic absorption spectrometry (AAS) (Shimadzu AA-6300). Morphological determinations were also determined using Scanning Electron Microscopy (SEM).

## 2.2.5. Effect of Increasing pH and Mg Dosages in the Syngenite Formation

From the best extraction treatment using rice husk coffee (K) combined with the best extraction treatment using charcoal (Ca). The determination of the variation in the addition of the Mg dosages has been decided: 5 mmol/l, 10 mmol/l, 15 mmol/l. Then from previous research [17] that pH 11 has been selected as the best treatment for increasing pH. After the filtrate is formed, it is weighed and dissolved in 1 mol/L of  $H_2SO_4$  and the concentration is measured using atomic absorption spectrometry (AAS) (Shimadzu AA-6300). The determination of atomic weight and morphology has also been decided using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX).

## 3. Results and Discussion

### 3.1. Type of Extract

Potassium extraction increases with increasing concentrations of  $CH_3COOH$ , HCl and  $H_2SO_4$ . The highest potassium extraction was achieved at 1.0 mol/l using  $CH_3COOH$  then subsequently decreased at a concentration of 0.5 mol/l and 0.1 mol/l (see Figure 1).

The increase in potassium extraction is because of the higher concentration of CH<sub>3</sub>COOH as the extracting media. From these results, it is considered that the optimal type of solution for potassium extraction is CH<sub>3</sub>COOH with a concentration condition of 1.0 moles which results in the highest concentration level.

According to Larsson *et al.* [20] said that Acetic acid, formed by deacetylation of hemicellulosic parts of biomass, is the most common carboxylic acid available in the lignocellulosic hydrolyzates. This statement is reinforced by Pandey *et al.* [21] that Coffee husk contains some amount of caffeine and tannins, which can make it toxic and slow degradation in nature, resulting in the disposal problem. However, the coffee husk is rich in lignocelluloses materials, which makes it an ideal substrate for microbial processes.

#### 3.2. Effect of Dosage CH<sub>3</sub>COOH on Extraction Ratio

The K extraction ratios for solid-liquid ratios of 1:50, 1:10, and 1:5 with 0.1, 0.5, and 1.0 mol/l CH<sub>3</sub>COOH solutions (see **Figure 2**). The smaller ratio, such as 1:50, the higher extraction rate, indicating that K extraction requires a certain amount of solution. However, since the extraction rate is less affected by the solid-liquid ratio as the CH<sub>3</sub>COOH concentration is higher, maintaining the acid concentration higher than the solution volume was considered effective in increasing the extraction rate.



Potassium extraction ratio using CH<sub>3</sub>COOH, HCl and  $H_2SO_4$ solutions of 0.1, 0.5 and 1 mol/l and distilled water. Error bars are standard deviation

**Figure 1.** Potassium extraction ratio using  $CH_3COOH$ , HCl and  $H_2SO_4$  solutions of 0.1, 0.5 and 1 mol/l and distilled water. Error bars are standard deviation.



**Figure 2.** Potassium extraction ratios at solid-liquid ratios of 1:50, 1:10 and 1:5 using CH<sub>3</sub>COOH solutions of 0.1, 0.5 and 1.0 mol/l.

Assuming that extraction is performed batch-wise, the solid-liquid ratio. Examination of potassium recovers from coffee husk combustion residue. The larger value means the greater amount of combustion residue that can be extracted at one time, which is advantageous in terms of cost. However, when the solid-liquid ratio was 1:5, the mixture of the combustion residue and the extract became slurry during stirring, making filtration difficult. Furthermore, since the extract is absorbed by the combustion ash at a high rate, the amount of extract that can be finally recovered is approximately halved, and even if the concentration of extracted K is high, the amount of K that can be recovered is substantially reduced.

Therefore, it is necessary to consider the recovery of the phosphorus extract together with the extracted K concentration in order to determine the optimal extract and solid-liquid ratio. Treatment 1.0 mol/l  $CH_3COOH$  solution with a

high solids ratio and a solid-liquid ratio of 1:10, which is easy to stir and filter, was selected as the optimal extraction condition and was used as the extraction condition for the K recovery test [22].

#### **3.3. Calcium Extraction**

From **Figure 3** it can be seen that calcium extraction using chicken manure with variations in the addition of acids and alkaline shows that the higher the addition of moles, the higher the percentage of calcium extraction ratio, with NaOH as the best chemical.

The same situation is shown in **Figure 4**, it can be seen that calcium extraction using activated sludge with the addition of acids and alkaline shows that the higher the addition of moles, the higher the percentage of calcium extraction ratio, but CH<sub>3</sub>COOH is the best chemical.



Calcium extraction ratio using CH<sub>3</sub>COOH, HCl and NaOH solutions of 0.1, 0.5 and 1 mol/l. Error bars are standard deviation.







■ CH<sub>3</sub>COOH ■ HCl ■ NaOH

**Figure 4.** Phosphate extraction ratio using CH<sub>3</sub>COOH, HCl and NaOH solutions of 0.1, 0.5 and 1 mol/l on charcoal from activated sludge.

Acetic acid still plays a role in the type of chemical for extraction, this is because in the acid medium, the carboxyl, carbonyl, or hydroxyl groups on the extract become protonated and do not attract positively charged metal ions, resulting in the release of metal ions into the solution or the agent. In the acidic medium, protons ( $H^+$ ) in solution replace metal ions on the extract surface. The low percentage of extraction is found in alkaline agents/solutions, possibly due to the fact that these groups become less protonated, so that the metal ions that bind are difficult to escape from the extract [23].

## 3.4. Effect of Tartaric Acid

**Figure 5** shows that the amount of solid is precipitated and recovered by adding tartaric acid. From the figure, it is known that the amount of precipitation increases due to the addition of tartaric acid along with the increasing concentration of tartaric acid. This is due to the potassium tartaric precipitate but is insoluble in acetic acid solutions. However, the potassium content is still low, namely 13.8%. The figure also shows the amount of precipitation. With a concentration of tartaric acid of 10%, the amount of precipitation was about 0.4 grams, and the amount of sediment increased with the increasing concentration of tartaric acid. So it is assumed that the higher the concentration, the more sediment is obtained. The difference between 5% and 10% is not as large as between 1% and 5%, so it is considered that 10% is a sufficient concentration.

#### 3.5. Control of Precipitation Condition

**Figure 6** shows that when the tartaric acid concentration is added, the components in it will split. Some of the organic substances detected were calcium, potassium and sodium, and the rest were inorganic substances caused by tartaric acid and acetic acid.



The ratio by weight of the solids to the amount of K recovered was the highest





Figure 6. The effect of adding tartaric acid to contents of precipitation.

calcium, with calcium about 210 grams in the three treatment additions of tartaric acid, potassium about 35 grams and sodium about 10 grams. From these results there is no significant difference in the proportion of the components deposited under the conditions of adding tartaric acid concentration, but taking into account the amount of K obtained, then 10% is still used as the appropriate concentration. Then the filtrate is heated and concentrated to increase the rate of potassium recovery.

From Figure 7 it can be seen that about 94% K is recovered and Ca is not recovered by a method that combines the addition of tartaric acid and storage of concentration at a hot oven temperature of 60°C. The higher the addition of tartaric acid, it means that the Ca precipitate obtained and the percentage of K recovery is also greater. From these results it can be seen that in K extraction using CH<sub>3</sub>COOH, K can be recovered efficiently by combining the addition of tartaric acid and storage of concentration at a hot oven temperature of 60°C.

# 3.6. Effect of Increasing pH and Mg Dosages in the Syngenite Formation

After obtaining the results that the charcoal from chicken manure has a higher Ca extraction value than chicken manure, it is then combined with the extraction of rice husk coffee which has a high K value, with several additional Mg doses and is set at pH 11 to form precipitate syngenite formation. **Figure 8** shows a SEM image of additional magnesium doses of 5 mmol/l (A), 10 mmol/l (B), 15 mmol/l (C) and compared with pure potassium tartrate (D).

At the addition of a dose of 5 mmol/l magnesium has a poor crystal structure, does not have a crystal surface and has many cracks. Slightly different conditions were seen in the addition of a magnesium dose of 10 mmol/l, where several crystal structures were found although the surface area was wide and the particle structure was still very large. At the addition of the magnesium dose of 15 mmol/l,



**Figure 7.** The effect of heating and concentrating on increasing the rate of potassium recovery.



**Figure 8.** SEM images of the precipitates obtained in the experiment at pH 11. With additional dosage of Mg 5 mmol/l (A), 10 mmol/l (B), 15 mmol/l (C) and pure potassium tartrate (D).

it was seen that many crystal structures were found and the particle structure was smaller and scattered. Whereas in the pure potassium tartaric condition, it can be seen that almost the entire structure is in the form of crystals with small particles that are evenly distributed.

Figure 8(A) and Figure 8(B) indicate that calcium tartaric still has an impact on morphology, so it is mean the sample has a low degree of crystallinity, inversely compared to Figure 8(C) which shows that potassium tartaric is more exsist. This can also be seen from the EDX spectrum in Figure 9 (Mg: 5 mmol/l), Figure 10 (Mg: 10 mmol/l), Figure 11 (Mg: 15 mmol/l) and Figure 12 (pure potassium tartaric acid). As the magnesium dose increases, the atomic weight of



**Figure 9.** EDX analysis of syngenite crystals obtained from the addition of 5 mmol/l Mg dosages.



Figure 10. EDX analysis of syngenite crystals obtained from the addition of 10 mmol/l Mg dosage.







Figure 12. EDX analysis of syngenite crystals obtained from pure potassium tartrate.

Ca decreases. It is also in accordance with the research of Ando *et al.* [16] that the syngenite crystallization process in isolate potassium from molasses containing higher potassium.

However, in the study only Ca and K, the S ion can not identified as crystals formed because these minerals may precipitate in the order of days and are influenced by the pH of the solution and the concentration of magnesium and phosphate [24]. The molar ratio of Ca and K in syngenite based on EDX analysis for additional magnesium doses of 5 mmol/l, 10 mmol/l and 15 mmol/l at pH 11.0 were 1:2.1, 1:2.8 and 1:3.2 respectively with the best %K and %Ca are 42% and 31%. The phosphate value in this study is also quite high, because besides being able to react with syngenite, calcium ions can also actively react with phosphate to form calcium phosphates [24].

This result may be because the magnesium solution used was  $MgSO_4 \cdot 7H_2O$ . The  $SO_4$  ion in solution tends to prevent the smooth process of Ca inhibition against K. Because it has been explained in Harada's research [17] that they concluded that sulfate is not included as a compound containing sulfur in crystals but is inhibited.

The magnitude of the decrease in potassium and magnesium looks very different from the increase in the addition of the magnesium ion solution. Approximately the same ratio is obtained, regardless of the presence of the magnesium ion, thus indicating that the effect of magnesium ion (MgSO<sub>4</sub>·7H<sub>2</sub>O) on the formation of syngenite formation is quite large.

## 4. Conclusion

Potassium recovery is considered very important to do so that in future Indonesia can dependent on imported fertilizers and the agricultural sector can develop more. In this study, two methods were used to recover potassium, namely the addition of tartaric acid and the syngenite method. The best condition in the method of adding tartaric acid is extraction using  $CH_3COOH$  because it is the most effective compared to HCl and  $H_2SO_4$ , with a ratio of 1:10 in increasing the reaction rate. Combining tartaric acid and temperature concentration results in a recovery of 94% K. Extraction of Ca using charcoal from chicken manure was chosen for syngenite formation because it has a higher percentage of Ca extraction than activated sludge. The optimal condition for the syngenite method is the addition of a magnesium dose of 5 mmol/l and a pH of 11, the Ca:K ratio is 1:2.1 with 42% K. So it can be concluded that the recovery of potassium by the method of adding tartaric acid is considered more efficient.

## Acknowledgements

The authors would like to thank the Prefectural University of Hiroshima, Shobara Campus, for financial support to the author while the author is studying.

# **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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