Separation of Potassium from The Model Solution

Ratna Puspita¹ and Herri Susanto¹,*

¹ Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132 Indonesia
*herri@che.itb.ac.id

Abstract. Potassium content in biomass ashes, especially empty fruit bunches was quite high and had not been utilized maximally. This research dealt with the development of a technique for recovering potassium salt from a solution of ash extraction. Experiments were carried out using a solution model containing KCl, NaCl, MgCl₂, and CaCl₂ with concentrations of 164.19, 8.39, 7.44, dan 39.60 mg/L respectively. Results of a preliminary experiment indicated that the solubilities of KCl and NaCl were reversed: 280.4 and 280.4 (g/L in water) to 6.9 and 14.2 (g/L in absolute ethanol), while the solubilities of MgCl₂ and CaCl₂ were still high (68.7 and 383.5 g/L in ethanol). Using these values of solubility, a combined evaporation and adding ethanol was trialed firstly to increase the precipitation of KCl. Evaporation of KCl solution 164.19 g/L until an evaporation level of 15% did not give any precipitation yet, while adding ethanol to the remaining solution (at solution ratios of 4/1 and 3/2 ethanol) yielded precipitations with the potassium recoveries of 60% and 48% respectively. At an evaporation level of 30%, the evaporation yielded a 5% potassium recovery, while the combined technique gave 60% and 50% recoveries for adding ethanol with ratios of 4/1 and 3/2 respectively. The application of the combined technique on the mixed salts solution was modified slightly. The precipitate from the evaporation (containing KCl and NaCl) was redissolved into water and followed by adding ethanol to precipitate only KCl. Thus, two precipitates were finally obtained: (i) precipitate from adding ethanol to filtrate of evaporation, and (ii) precipitate from dissolving precipitate from evaporation. At an evaporation level of 30%, the evaporation only gave a precipitate recovery of about 10%, while the application of combined technique gave about 80% and 60% recoveries by adding ethanol with ratios of 4/1 and 3/2 respectively. Hopefully this technique could separate KCl from its mixture with NaCl, MgCl₂, and CaCl₂.

Keywords: selective precipitation of potassium salt, combined evaporation and adding ethanol, solubilities of salt in water-ethanol

1. Introduction
Palm oil is a commodity produced in large quantities in Indonesia, which used in the food and renewable energy industries. Production of crude palm oil (CPO) is accompanied with generation of biomass approximately 58% palm oil mill effluent (POME), 21% oil palm empty fruit bunches (EFB), 5% palm kernel shell (PKS) and 14% fiber [1]. These by-products can be used as energy resources through a thermal conversion process. Combustion of fiber and PKS in the boiler of CPO
mills produces ash containing various mineral such as the sufficiently high content of K2O, Na2O, Al2O3, Fe2O3, CaO, and SiO2 [2]. Many researches also indicate that the ash of EFB has a high potassium content [3]. However, this potential potassium for fertilizer has not been utilized maximally.

Besides potassium, ash from EFB, PKS, and fiber contain various salts of sodium, magnesium, and calcium in the form of carbonate, chloride, phosphate, and sulfate [4]. Extraction of salts from ash is a well-known separation of those minerals from ash or event directly from biomass. A problem in separating potassium from the solution is due to the close solubilities of potassium and sodium salts in water. Evaporation of salts solution and followed addition of organic compounds to the solution has been proposed in the literature. Organic compounds may reduce and change the order of solubility of sodium and potassium, as well as other salts from ash [5, 6]. Evaporation followed by ethanol addition has been investigated to separate potassium from fly ash of municipal waste incineration [7].

Results of our preliminary experiment are reported in this paper. The objective of the research is to find a procedure for precipitating KCl from its solution. In the preliminary step of research, a model solution containing KCl, NaCl, MgCl, and CaCl2 was used with a composition based on our experiments on the hydrothermal process of EFB (oil palm empty fruit bunches).

2. Materials and Methods

2.1. Materials

All reagents used in this research were of analytical reagent grade, i.e.: KCl, NaCl, MgCl2, and CaCl2. Distilled water was used as the solvent. Analytical ethanol p.a. was used for precipitating salts from its aqueous solution.

2.2. Methods

The first series of experiments was the precipitation of KCl from its solution with a concentration of 164.19 g/L, below its solubility of about 280 g/L (measured at 30 oC). Solution of KCl (80 mL) was firstly evaporated at a temperature of 50 oC to evaporation levels of 15%, up to 80%. The precipitate obtained from this stage was filtered, dried and weighed (as precipitate-1, in Figure 1a). Each filtrate was treated further by adding ethanol:

(a) 4 mL ethanol to 1 mL filtrate-1, designated as evaporation and ethanol 80%
(b) 3 mL ethanol to 2 mL filtrate-1, designated as evaporation and ethanol 60%.

These additions of ethanol might give more precipitation (as precipitate-2).
In the second series of experiments, the feed was the model solution containing (mg/L): KCl 164.19, NaCl 8.39, MgCl₂ 7.44 and CaCl₂ 39.60. The proportion of these concentrations were about the same as those in the filtrate obtained from the hydrothermal treatment of EFB.

The experimental procedure (Figure 1b) was slightly different from that in the first series of experiments. Since the feed was the solution of four salts, precipitate-1 might contain all salts. Therefore, in order to get purer of KCl, the precipitate-3 was redissolved in water and followed by adding ethanol to precipitate KCl (precipitate-5). Meanwhile, ethanol was added to filtrate-1 to get precipitate-4. As in the first series of experiments, the ratio of ethanol to filtrate were 4/1 and 3/2 by volume. This method was based on [7].

Performance of precipitation was expressed as potassium recovery:

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recovery = \frac{mass\ of\ potassium\ in\ precipitates}{mass\ of\ potassium\ in\ the\ initial\ solution}\]

(1)

3. Results and Discussion
Evaporations were carried out up to the evaporation levels of 15% up to 80%. Theoretically, if the evaporation level achieved 40%, the solution with the initial KCl concentration of 164.19 g/L would become a saturated solution with a concentration of 280 g/L (see Table 1). So the precipitation became more and more with increasing the evaporation level as presented visually in Figure 2.

Table 1. Solubility of salts, g/L (measured at 30°C).

|        | KCl | NaCl | MgCl₂ | CaCl₂ |
|--------|-----|------|-------|-------|
| in water, 30°C | 280.4 | 258.6 | 336.2 | 484.2 |
| in ethanol, 30°C | 6.9 | 14.2 | 68.7 | 383.5 |
Figure 2. Precipitation due to addition of ethanol to filtrate after evaporation and filtration evaporation levels.

Figure 3. Potassium precipitation by evaporation and adding ethanol.

| KCl     | Potassium recovery from evaporation only, precipitate-1 (see Figure 1a) |
|---------|-----------------------------------------------------------------------|
| KCl + 80% ethanol | evaporation and adding 4 mL ethanol to 1 mL filtrate-1 \(\rightarrow\) precipitate-1 and -2 |
| KCl + 60% ethanol | evaporation and adding 3 mL ethanol to 2 mL filtrate-1 \(\rightarrow\) precipitate-1 and -2 |

By evaporation only, the precipitation was not obtained at evaporation levels of 15%, 20%, and 30% (see Figures 2 and 3). Precipitate-1 (see diagram in Figure 1a) was obtained at the evaporation...
levels of 40% and more. Since the evaporations were conducted at a fixed temperature, the results of the experiment indicated that the potassium recoveries increased more or less linear with the evaporation level. The potassium recovery as a function of evaporation level is presented as the blue curve in Figure 3.

By adding ethanol, more precipitate could be obtained from filtrate-1 (see diagram in Figure 1a). Even the adding ethanol to filtrate-1 from the evaporation levels of 15%, significant precipitations were obtained, i.e. 50%, and 60% from adding of 60%, and 80% ethanol (as presented respectively with green and red dots in Figure 3). More precipitates were obtained by adding ethanol, since the solubility of KCl in ethanol was much lower than that in water (measured at 30°C, see Table 1).

Unlike the results from evaporation only, the combined effects of evaporation and adding ethanol to the potassium recovery were clearly in the form of S-curves for both adding ethanol of 60% and 80%. This phenomenon is challenging for further study with respect to the solubility of salts in an ethanol-water mixture.

From the second series of experiments, the precipitation started already at the evaporation level of about 15% (Figure 4). This is understandable because the feed solution was a solution of KCl with the concentration similar to that in the first series of experiments, plus three other salts (see Figure 1). In this solution, the solubility product of [K⁺] and [Cl⁻] became very high that caused precipitation.

Based on their solubilities (Table 1), the precipitate-3 might contain KCl, NaCl, MgCl₂, and CaCl₂. Therefore, the precipitate-3 was further treated by dissolving into water and then adding ethanol, so the precipitate-4 might contain mainly KCl, a small amount of NaCl, and expectantly
no-MgCl₂ and no-CaCl₂. Again, adding ethanol to the filtrate gave more precipitates. The curves green and red in Figure 4 are the sum of precipitate-4 and precipitate-5. Although the concentration of KCl in these precipitates were not measured yet, potassium content in these precipitates presumably very high based on the different solubilities of salts in ethanol.

The evaporation gave a higher potassium recovery from the mixed salts solution than that from the KCl solution (compare blue curves in Figure 4 and Figure 3). This phenomenon is understandable because of the effect of solubility product in the mixed salts solution in water. However, the potassium recoveries using evaporation and adding ethanol were the other way around. More significant precipitates were observed in the precipitation from the single salt solution than those from the mixed salt solutions. This was probably due to the solubilities of CaCl₂ and MgCl₂ in ethanol were still relatively high, while those of KCl dan NaCl dropped. These values of solubility were advantageous in keeping CaCl₂ and MgCl₂ in the water-ethanol solution instead of precipitation together with KCl and NaCl.

4. Conclusions
The solubilities of KCl, NaCl, MgCl₂, and CaCl₂ in ethanol were much lower than those in water. The solubility of NaCl in water was higher than that of KCl, but it changed in reverse in ethanol. This behavior was used for separating KCl from the solution of mixed chloride salts.

Compared to the method of evaporation only, the method of combined evaporation and adding ethanol could increase the recovery of KCl and advancing the incipient precipitation from the single KCl solution. Application of this combined method also indicated the increase in the precipitate recovery assuming that the precipitate contained mainly potassium.

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