Potassium enrichment of treated palm oil mill effluent in a fixed-bed contactor

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Abstract. Treated Palm Oil Mill Effluent (POME) is the effluent of POME-based biogas production process. This liquid is potential as a raw material of liquid organic fertilizer, but the potassium content should be upgraded. Ash of empty palm fruit bunches (EPFB-a) which is locally available in huge amount is an attractive source of potassium. Potassium enrichment of treated POME was performed by contacting this liquid with EPFB-a in a fixed bed contactor. This research studied the effects of treated POME flow rate and height of EPFB-a bed on potassium mass transfer coefficient from solid to liquid phase in the contactor. Treated POME and EPFB-a were obtained from a crude palm oil mill in Rantau Sakti Village, Tambusair Utara Sub-district, Rokan Hulu Regency of Riau Province. The treated POME flow rates were set at 3.72; 3.36; and 2.52 L/min. EPFB-a bed height were fixed at 0.03, 0.06, and 0.09 m. The performance of this fixed bed contactor was evaluated based on extracted potassium content.

1. Introduction
In recent years, Indonesia was the top producer of worldwide crude palm oil (CPO). It is also predicted that the country may provide 39% - 60% of the international CPO demand. This demand would be supplied from 565 to 880 Mton fresh fruit bunch [1]. Water specific consumption of CPO production is about 5.0 - 7.5 tons/ton and more than 50% of water ends up as POME. It means that every ton of CPO production generates 2.5 - 3.75 ton of POME. This abundant quantity of POME is a potential pollutant to the water sources in the nearby of palm oil mills as its elevated content of BOD and COD [2]. However, its content depends on the production process and fresh fruit bunch (FFB) utilized from as low as 16 g O2/mL when using advanced technology process at capacity 150 MT of FFB/hour and as high as 100 g O2/mL when using more primitive one at capacity 2.5 MT of FFB/hour. Many studies focused on treatment of converting POME to biogas in an anaerobic digester using both traditional and advance methods. Microbiological approach [3]–[5], photocatalytic degradation [6], photo-oxidation method [7], adsorption using several types of bio-adsorbents [8], [9], , and electrocoagulation method [10] successfully demonstrated COD removal.

Beside POME, crude palm oil mills also generate a large amount of solid waste which is dominated by empty palm fruit bunch (EPFB) of about 23% for every ton of FFB. Moisture content was reported as high as 60% - 70%. The chemical characteristics of EFB was reported as 43.3% of cellulose, 26.2% of hemicellulose, and 30.5% of lignin[11]. Recently, this enormous amount of empty fruit bunch appears as problematic solution to its utilization. Traditionally, EPFB is dumped in palm oil plantation where

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decomposes naturally which releases methane gas to the atmosphere. This action may contribute greenhouse gas significantly while more environmentally friendly methods are now available. The EPFB is possible to be a feedstock for bio-oil production[12], converted to syngas via gasification[13], pelleted for pyrolysis process[14], and source of cellulose and nanocrystalline cellulose for heavy metal sorption[15], [16]. Production of methane by anaerobic co-digestion of POME and EPFB mixture was also studied. Co-digestion has positively affected to methane production at proper ratio and size of EFB [11].

In this mean time, effluent of anaerobic biodigester based on POME is scarcely reused and is not an area of interest for research among environmentalists, industrialists and scientists. Reusing the effluent for composting and cleaning process of EPFB was proposed in order to save the operating costs of a palm oil mill. But, most of this biodigester effluent is just discharged to the waterbody though its COD and BOD values are sometimes not low enough to comply with the regulation limit. It is advisable to be combined with subsequent aerobic treatment or for other application such as composting [2].

Based on mass transfer phenomena, potassium in EPFB-a can be extracted with the effluent of biodigester to enrich the effluent with potassium. A solid-liquid mass transfer can be processed in several types of contactors, such as fixed beds reactor [17], [18], fluidized beds reactor [17], [19], trickle bed reactor [20], rotating tubular packed bed of spheres reactor [21], and agitated vessel [22]. Most studies showed that the mass transfer operation depends on solid-liquid mass transfer coefficient ($k_{L,a}$) which is affected by liquid flow characteristic and easiness of inter phase contact. The flow characteristic is represented with Reynolds number, and the contact easiness is described with Schmidt number.

Construction of contactor especially fixed bed contactor were observed affecting the solid-liquid mass transfer coefficient. This is represented as the ratio of bed thickness and particle diameter [21] or the ratio of particle diameter and reactor diameter [18].

This research is intended for reusing both effluent of biodigester based on POME and EPFB-a as raw material of liquid organic fertilizer. As a fertilizer, potassium content of the effluent is low enough about 2270 mg/L [6] that addition of potassium from other sources is necessary. While, EPFB ash content may attain 13.65% [12]. Typically, biomass ash contains about 24.2% - 27.7% of potassium [23]-[25]. Thus, EPFB-a is potential source of potassium for producing liquid organic fertilizer from the effluent. In this research, extracting potassium of EPFB-a with treated POME was processed in a fixed bed contactor.

2. Experimental technique

2.1. Calculation method

A model of potassium balance of EPFB-a in a fixed bed contactor is written as equation (1) with $X_A$ is potassium mass fraction in EPFB-a, $\rho_B$ is density of EPFB-a (g/cm$^3$), $C_A$ is potassium concentration in treated POME (g/cm$^3$), and $C_A^*$ is saturated potassium in treated POME. The saturated potassium is approximated with equilibrium concentration of potassium in the water at 25°C (0.6274 g/cm$^3$) as treated POME was an aqueous solution (Haynes, 2011). The analysis showed that at initial condition, mass fraction of potassium in EPFB-a was 1.07% and potassium in treated POME was 3.37x10$^{-4}$ g/cm$^3$. By analyzing the treated POME after extracting for potassium content, equation (1) was solved numerically for calculating the $k_{L,a}$ values of every experiment run.

$$\frac{dX_A}{dt} = \frac{k_{L,a}}{\rho_B} (C_A - C_A^*)$$

The variables that affected solid-liquid mass transfer coefficient ($k_{L,a}$) in the contactor are density ($\rho$), viscosity ($\mu$) and flow rate ($v$) of treated POME, column diameter ($D$), and EPFB-a bed height ($z$). A mathematical correlation among solid-liquid mass transfer coefficient and the related variables was developed according to equation (2) with using dimensional analysis. A quantitative model should be formulated as equation (3) with $C_i$, $C_j$ and $C_k$ are constant parameters which are specific to this case.

$$k_{L,a} = f(\rho, \mu, v, D, z)$$
Matrices technique was applied to calculate those parameters which were applied to predict the solid-liquid mass transfer using equation (3). The relative difference between prediction and experimental values of the coefficient was expressed as average error.

2.2. Experimental setup

A fixed bed contactor experimental set consists of a fixed bed column 0.15 m in inner diameter and 2.50 m in height, 5 L effluent tank made from stainless steel, 5 L treated POME plastic storage tank, 0.25" valves, 3/8" of inner pipe diameter and 25 W electric pump (see figure 1). Treated POME and EPFB-a were collected from a palm oil mill in Rantau Sakti Village, Tambusai Utara Sub-district, Rokan Hulu Regency of Riau Province.

Before extracting, EPFB-a was stacked in the column using 300 mesh filter sheets at a certain height for each experiment: 0.03, 0.06, and 0.09 m. The EPFB-a bed was installed in the distance of 1.50 m from the bottom to avoid inlet flow effect to the bed. Treated POME from the tank was introduced to the column by pumping it to the bottom inlet at various flow rates (2.52, 3.36, and 3.72 L/min) for each EPFB-a stack height by adjusting the valves. The contact between treated POME and EPFB-a took place when the liquid passed through the bed. After contacting, the liquid flowed out from the top of the column to product tank. The first sample of outlet liquid was taken from the tank after 10 seconds of processed for potassium analysis.

The following samples were taken every 5 seconds after that. Potassium content in the samples were analyzed according to Indonesian National Standard (SNI 19-7030-2005) using AA-6200 Atomic Absorption Flame Emission Spectrophotometer (AAS) from Shimadzu. Prior to the use, the instrument
was standardized with potassium solution 1000 ppm in 2% HNO₃ then a standard curve was constructed. The AAS analysis showed potassium content in a sample as absorbance and by using the standard curve potassium concentration was expressed as mass fraction.

3. Results and discussion
3.1. Sample analysis
Figure 2 describes an increasing of potassium in treated POME after flowing through the EPFB-a bed in the column at different bed height. The x-axis of Figure 1 indicates relative difference between potassium content in outlet treated POME and potassium content of fresh treated POME. Obviously, the potassium content in EPFB-a is the highest at the beginning of the process which causes more potassium transferred to the treated POME. It conforms with mass transfer law (Fick’s law) and previous studies [19], [20], [22] that the concentration driving force would be the highest at the initial condition and this encourages more potassium to move from the solid to liquid phase.
Table 1 shows all the experimental results when one liter of treated POME extracts potassium of EPFB-a bed in one second. According to the results the highest the EPFB-a bed the more potassium in the bed, thus the more potassium would be extracted from the EPFB-a bed. The results also indicated that the longer the treated POME residence time the more potassium extracted. In this study, the residence time was less and after 30 seconds of process it achieved 74.09%. This was equivalent to 0.0516 gram of potassium extracted with one liter of treated POME every second. Only 14.21% increasing of potassium was obtained when a bed height of 0.03 m and treated POME flow rate of 3.72 L/min were applied to the process. At this condition, treated POME was capable to extract potassium from EPFB-a bed at a rate of 0.0105 gram/(L sec).

| Volumetric Rate of treated POME (L/min) | EPFB-a bed height (m) |
|----------------------------------------|-----------------------|
|                                        | 0.03      | 0.06       | 0.09       |
| 2.52                                   | 0.0269    | 0.0334     | 0.0516     |
| 3.35                                   | 0.0241    | 0.0297     | 0.0443     |
| 3.72                                   | 0.0105    | 0.0270     | 0.0409     |

3.2. Solid-liquid mass transfer coefficient
Based on sample analysis results, potassium content in EPFB-a and treated POME, solid-liquid mass transfer coefficient of potassium from EPFB-a to treated POME was predicted at every single experiment. Firstly, the $k_{L,a}$ was calculated with equation (1) numerically. Figure 3 and figure 4 present the effect of flow characteristic of treated POME which is expressed as Reynolds Number ($Re$) and geometrical factor which is expressed as ratio of EPFB-a bed height and inner column diameter ($z/D$) on solid-liquid mass transfer coefficient which is expressed as a non-dimensional number of $(k_{L,a} D^2 \rho)/\mu$. It is found that effect of flow characteristic on solid-liquid mass transfer coefficient is inversely proportional to the ratio of EPFB-a bed height and inner column diameter. Some previous studies also presented similar effect of Reynolds number on the coefficient, although the studies used...
different solid-liquid phase and contacting method. The geometrical factor was also expressed with different ways [19].

Figure 3. Effect of Reynolds Number on $\frac{k_L a D^2 \rho}{\mu}$

Figure 4. Effect of geometrical factor $z/D$ on $\frac{k_L a D^2 \rho}{\mu}$

The value of solid-liquid mass transfer coefficient ($k_L a$) varies with Reynolds Number and geometrical factor ranges in this study. It was calculated using equation (1) and the sample analysis results. Liquid flows of all the experiments were in the range of laminar regime, and the geometrical factor were set at 2.00, 4.00 and 6.00. Calculation the parameters on equation (2) needs a set of three equation (2) which relate $\frac{(k_L a D^2 \rho)}{\mu}$ with Reynolds Number and geometrical value as formulated with equation (2). Every equation in the set should consist different Reynolds Number and geometrical value. By using matrices method, the parameters were calculated. The results were applied on equation (2) for calculating the solid-liquid mass transfer equation ($k_L a$). Table 2 shows all the calculated coefficients in the unit of 1/second. It is found that the coefficient decreases with the increasing of Reynolds Number, but increasing with the increasing of geometrical factor. It is formulated in a mathematical model of dimensionless numbers as:

$$\frac{k_L a D^2 \rho}{\mu} = 0.3969 \cdot Re^{-0.7549} \left(\frac{z}{D}\right)^{1.2515}$$  \hspace{1cm} (4)

Table 2. Calculated solid-liquid mass transfer coefficient ($k_L a$) at various Reynolds Numbers and geometrical factors using equation (2).

| Reynolds Number | Geometrical Factor $(z/D)$ |
|----------------|---------------------------|
| 1001           | 2.00  4.00  6.00          |
| 1335           | 2.03 x 10^-3  4.83 x 10^-5  8.02 x 10^-5 |
| 1479           | 1.63 x 10^-3  3.89 x 10^-5  6.46 x 10^-5 |

The parameter values of $C_1$, $C_2$ and $C_3$ of equation (3) are 0.3969, -0.7549, and 1.2515 respectively. The average error was determined as ratio of the absolute difference between experimental value and calculated value of $k_L a$ to experimental value of $k_L a$. Thus, the correlation of three non-dimensional numbers as in (2.3) can be implemented to predict the solid-liquid mass transfer coefficient of potassium from EPFB-a and treated POME in a fixed bed column. The correlation should be applied in laminar flow regime and geometrical factor 2.00 – 6.00.
4. Conclusion

The potassium content in treated POME as raw material of liquid organic fertilizer is potentially to be upgraded by extracting potassium content of EPFB-a in a fixed bed column. This process is represented with solid-liquid mass transfer coefficient which depends on chemical and physical characteristics of treated POME, and ratio of bed height and bed diameter of EPFB-a in the column. The formulated mathematical model of dimensionless numbers is applicable to laminar flow and range of $\left( \frac{z}{D} \right)$ from 2.00 to 6.00 with an average error of about 14.55%.

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