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Mineral washing from rice straw to improve its combustion properties

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Abstract. Indonesia has abundant potential for rice straw which can be developed as an alternative fuel. However, rice straw has an ash content with high mineral content which can cause problems in applications involving high temperatures. This study aims to determine the effect of washing rice straw on the fuel quality improvement of rice straw. Sun-dry rice straw that has been cut into 1-2 cm was soaked in tofu industrial wastewater at a ratio of 0.5 kg in 10 L. Sampling for the measurement of ash and mineral content was carried out at 0 (without treatment), 3.75, 7.5, 15, 30, 60, 120, and 720 min. Ashing was carried out using a furnace at a temperature of 550 °C for 2 h. The ash was then analysed using XRF Spectrometry to determine its mineral content. Measurement of the calorific value of rice straw was carried out using a bomb calorimeter. Results showed that soaking straw in tofu wastewater decreased the ash content from 16.0 to 13.67 (% DS) and increased the calorific value from 13.60 MJ/kg (without soaking) to 15.77 MJ/kg (soaking by 720 min.). Soaking was also able to reduce important minerals such as K (17.94% to 9.69%), S (3.40 to 2.06%), Cl (0.91% to 0.3%).

1. Introduction

As the third largest rice producing country in the world [1], Indonesia is a country rich in rice straw waste. The rice harvesting process produces a by-product in the form of straw. Rice straw is the largest component of wastes resulted from harvest and post-harvest activities of rice. This is because rice straw makes up about half of the rice plant [2]. Straw covers the part (stem) that is left during harvesting and straw after the grain is shed. Dry straw production ranges from 2.3 t/ha [3] to 3.86 t/ha [4]. In 2019, Indonesia's rice harvest area reached 10.68 million ha [5], so that with an average straw production rate of 3.0 t/ha, the total potential for Indonesian rice straw is 30.04 million ton of dry matter. Rice straw has an average calorific value of 14.32 GJ/t, so the energy potential of rice straw is 459 PJ/year, equivalent to 12.4 million kiloliters of diesel fuel. Therefore, rice straw can be an alternative renewable energy source to replace fossil energy in order to reduce greenhouse gas emissions and avoid local pollution due to open burning.

However, rice straw has intrinsic properties that are detrimental as a fuel. Haryanto et al. (2019) mentioned that one of the striking disadvantages of rice straw compared to other biomass is the high ash content (up to 22.1%) which reduces the calorific value [6]. In addition, rice straw is a poor fuel, especially for systems operating at high temperatures due to its intrinsic characteristics such high minerals content, especially Si and K [7]. These minerals in ash are responsible for various undesired reactions in the combustion system. The concentration of ash and the high content of silica and alkali

metals in rice straw results in agglomeration, fouling, and slagging of boiler components which results in decreased system efficiency [8] and failure of most furnaces and a boiler. This problem has hampered the utilization of straw for large-scale boilers, even in areas where the straw sources are close to a boiler. The high silica content in rice straw causes the chopping machine components to wear out quickly. Rice straw is also very difficult to burn, especially in furnaces designed for power generation due to the formation of deposits. Si and K are transformed into K_2SiO_3 or other types of silicates at elevated temperatures, while silicates are also formed with other alkali and alkaline metals. Alkaline silicates have melting point temperatures as low as 800 °C [9] and therefore cause problems in gasification operations in form of channelling and defluidization [10]. These deposits inhibit the rate of heat transfer, triggering scale formation in the furnace and in the nests, making fuel feed and ash removal difficult. Thus, removal of alkali metals in particular, potassium, is an important treatment before rice straw is used for combustion fuel.

One way to reduce the mineral content in straw is through the washing or leaching process. Washing is able to significantly decrease minerals content. For example, it was reported that washing oil palm empty fruit bunch have reduced ash content by 81% from 5.43% to 1.03% (db) [11]. This study aims to evaluate washing of rice straw using wastewater from tofu industry. Due to its high organic content [12], tofu wastewater is acidic and is expected to have good mineral leaching.

2. Materials and methods

2.1. Materials

Rice straw was obtained from harvested rice fields, then dried under the sun to dry. The dried straw was then chopped about 1-2 cm and stored in a tightly zipped plastic bag until use. Tofu waste water was obtained from the household tofu industry areas in Gunung Sula, Bandar Lampung. Wastewater samples were taken before the wastewater was discharged into the sewage. The wastewater was acidic because acidic washing effectively removes water-soluble elements from the biomass [13].

2.2. Leaching Process

Rice straw was soaked in tofu wastewater with a ratio of one part by weight of straw into 20 parts by volume of tofu wastewater. In this study 500 g of straw was soaked in 10 L of tofu wastewater. The measured parameters were the straw moisture content, pH of tofu waste, ash content, ash composition and calorific value of straw. Measurements were made at various soaking times, namely 0 (without soaking), 3.75, 7.5, 15, 30, 60, 120, and 720 min. The calorific value of straw is compared between the beginning (without soaking) and after 720 min of soaking time.

2.3. Analysis and Measurement

The measurement of the parameters are conducted as the following:

- Water content (*MC*) of rice straw was measured gravimetrically by drying in an oven (Memert UM 500) for 24 h at 105 °C. Moisture content of rice straw is calculated from:

$$MC = 100\% \times (WS - DS) / WS \quad (1)$$

where *WS* is wet mass of rice straw (before drying) and *DS* is dry solid of rice straw (after drying).

- Acidity (pH) of tofu wastewater was measured by using a pH-meter. Measurement was conducted at various soaking time as previously mentioned.
- Ash content was measured at various soaking time during the leaching process. Before the ash content was measured, the sample was dried in an oven for 24 h at 105 °C. Then the dried sample (*Mk*) was put into the furnace (Banstead Thermolyne 1300) for 2 h at 550 °C. After cooling in a desiccator, the sample was weighed (*Mt*). Ash content is calculated by the formula:

$$\text{Ash} = (Mt/Mk) \times 100\% \quad (2)$$

- Ash composition was measured at various time soaking during the leaching process. In this case rice straw ash samples was sent to Universitas Negeri Padang (West Sumatera) for further analysis using XRF (X-Ray Fluorescence) Spectrometry.

- e. Calorific value of rice straw, was measured using a bomb calorimeter (Cal2k ECO). The measurement was carried out for initial straw and that of after soaking time of 720 min.
- f. The change of important parameters such as pH, ash content, and some minerals as a function of soaking time (t) is modelled as long as possible by exploring power function available in the Excel application as suggested by Pinchuk and Kuzmin [14] with general form of $y = A + B \cdot (t - C)^N$.

3. Results and Discussion

The rice straw used in this experiment had a moisture content of 13% (wet basis). Table 1 compares the properties of untreated (zero soaking time) rice straw along with changes in the acidity (pH) of tofu industrial wastewater used during the washing process of rice straw, the ash content of rice straw, and the mineral composition of the straw ash.

Table 1. The change of wastewater pH, ash content, and mineral composition of ash

Soaking time (min)	pH waste water	Ash content (% DS)	Ash composition (% Ash)								
			Si	K	P	S	Ca	Mn	Mg	CL	Fe
0	2.70	16.00	66.39	17.94	4.30	3.40	3.58	1.43	1.14	0.91	0.15
3.75	3.30	14.80	69.43	14.46	4.37	3.55	4.00	1.21	1.43	0.59	0.17
7.5	3.30	14.16	71.61	13.40	4.92	2.86	3.65	1.14	1.14	0.47	0.16
15	3.40	14.97	70.15	14.50	4.45	2.96	4.17	1.22	1.23	0.48	0.16
30	3.40	14.51	71.05	11.32	NA	2.63	4.35	1.01	1.74	0.30	0.17
60	3.50	13.67	75.18	11.60	3.61	2.68	3.74	1.01	1.05	0.42	0.12
120	3.50	13.74	74.69	10.73	4.64	1.97	4.23	0.96	1.00	0.49	0.18
720	3.50	14.82	78.14	9.69	3.92	2.06	3.83	0.54	0.81	0.30	0.10

Note: NA not available

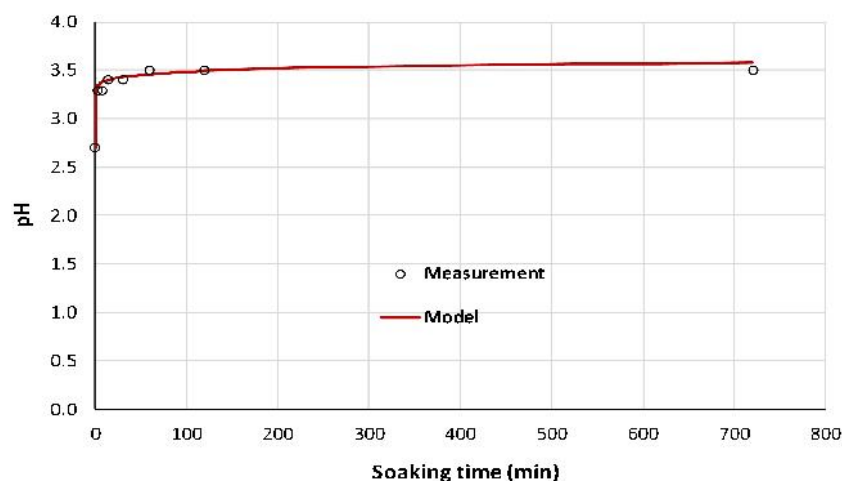


Figure 1. Effect of rice straw soaking time on the pH value of tofu wastewater

3.1. pH of tofu wastewater

Tofu wastewater is acidic with a fairly low pH value, which is 2.70. This condition is expected to result in an effective mineral leaching as stated by Wu et al. that water-soluble elements in biomass such as K, Cl, Na, can be washed through acidic leaching [13]. Mineral depletion of 82.4% can be achieved from empty fruit bunches immersed in 1% nitric acid for an hour duration [15]. During the

leaching process, the pH of wastewater rose sharply for the first 15 min until it reached a pH value of 3.40 (Figure 1). This means that the pH increase is 26% of its initial value. After that, the change in pH value is not significant. The increase in the pH value of tofu waste water during the rice straw leaching process relates to the dissolution of some alkaline metals from rice straw. Figure 1 shows that the decrease in the pH of tofu wastewater can be presented very satisfactorily in the form of a mathematical equation as follows:

$$\text{pH} = 2.7 + 0.597(t)^{0.059} \quad (R^2 = 0.9765) \quad (3)$$

3.2. Ash content

As any other biomass, rice straw is composed by organic components (C, N, H, O) and inorganic minerals (Si, K, Ca, S, Mg, Na, P, and Cl). After combustion, the inorganic components are left as ashes. Ash content in biomass is an important parameter related to fuel quality. Ash content relates contrariwisely to the biomass combustion efficiency, higher ash content in biomass lower the calorific value [13]. For biomass conversion systems working at high temperature such as ash boilers and gasifiers, there are some ash-related problems including sintering, agglomeration, and corrosion [13]. High ash content also reduces calorific value of biomass fuels. Haryanto et al. [6] showed a relationship that calorific value decrease with increase in ash content of the biomass. Rice straw used in this current work has high initial ash content up to 16% of dry solid (DS). These value is very close to Egyptian rice straw ash of 16.81% reported by Said et al. [16], but lower than other data such as 19.6 [7], 20.87 (fresh straw) and 18.28% (windrowed straw) [17]. By soaking in the tofu wastewater, our work shows that ash content of rice straw decrease up to 14.56% from the 16 (%DS, initial value) to 13.67 (%DS, with 60 min soaking) as presented in Figure 2. Ash reduction of 17.06% and 15.80% due to leaching has been reported by Said *et al.* for rice straws originating from Egypt and Valencia, respectively [16]. Rice straw ash was reported with mineral composition 75% SiO₂, 10% K₂O, 3% P₂O₅, 3% Fe₂O₃, 1.3% CaO, and small amounts of Mg and S [18]. The decrease in ash content, therefore, also related with the decrease of some minerals dissolved during soaking treatment. As can be observed from Figure 2, the decreasing of ash content as a function of soaking time can be presented satisfactory by using the following equation with sufficient value R^2 .

$$\text{Ash} = 13.341 + \frac{2.0}{(t + 0.30)^{0.21}} \quad (R^2 = 0.8132) \quad (4)$$

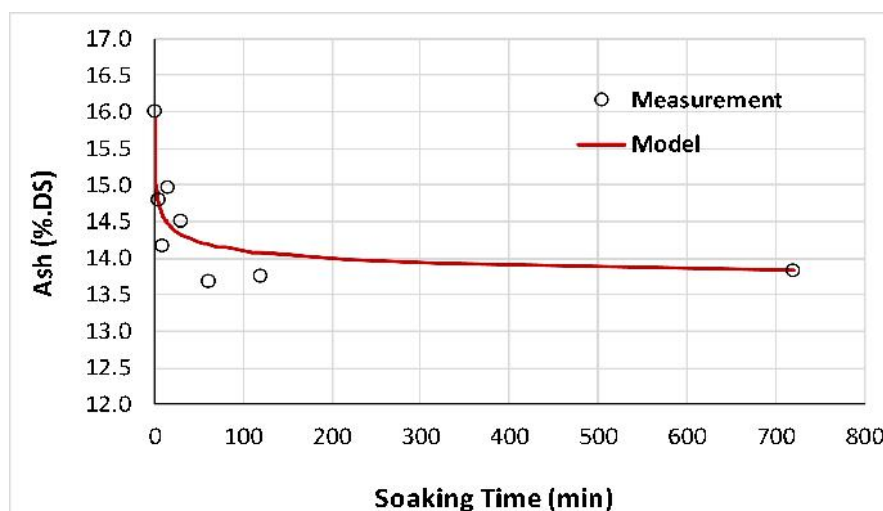


Figure 2. The relation of soaking time and the ash content of rice straw

3.3. Potassium (K) content

Rice straw in our study contained potassium oxide (K_2O) 17.94 (% Ash). This value is higher than that reported by Wu *et al.* [19] as much as 9.10%, but not really different from those of other studies, such as 17.21% [20], 20.87% [21], and 20.87% [22]. Potassium is an alkaline mineral that dissolves easily in water [23]. Potassium content in our study was reduced through soaking in tofu wastewater. Overall, potassium content can be reduced by 46% from initial value 17.94 (% Ash) to 9.69 (% Ash) for soaking time of 720 min. The highest reduction occurred during the first 3.75 minutes as revealed by Figure 3. A sharp decrease in K levels continued until the first 60 min. Our results are still less effective than those of other researchers such as Jenkins *et al.* [7] with a decrease in potassium reaching 77.3% for windrowed straw, or Dayton *et al.* [22] with a decrease in K_2O 88% from baseline. The decrease in potassium can be modelled with high R^2 value as the following:

$$K = 3.90 + \frac{12.858}{(t + 0.479)^{0.12}} \quad (R^2 = 0.9322) \quad (5)$$

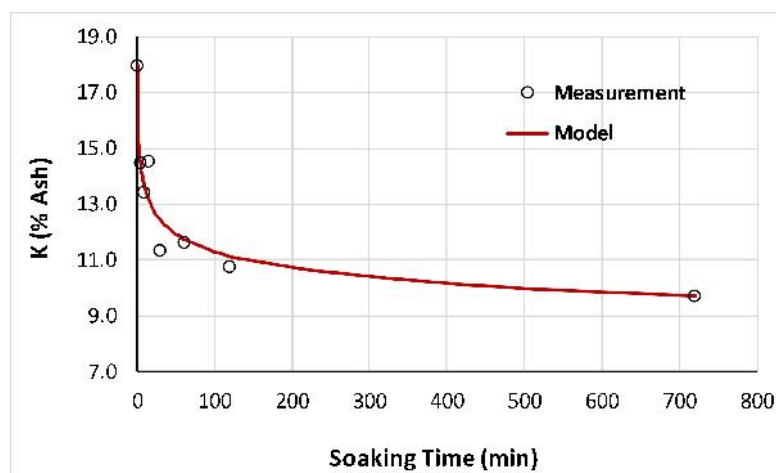


Figure 3. The relation of soaking time and content of potassium (K)

Potassium is an important metal in relation to plant nutrition as well as its effect on the high temperature combustion systems. Reduction of potassium gives triple implications. The decrease in potassium can improve fuel quality of rice straw and avoid the effects of fouling on high-temperature combustion systems. Leached straw also has higher calorific value as compared to the unleached one. Last, the dissolved potassium in wastewater can be used as a source of fertilizer for plants.

3.4. Sulphur (S) and Chlorine (Cl)

Sulfur (SO_3) and chlorine (ClO_2) in biomass ash usually exist in low amounts. However, both compounds have important effects. Chlorine in biomass ash causes corrosion problems [24]. This chlorine-induced corrosion can harm boilers at temperatures above 450 °C. High concentrations of Cl can combine with sodium and potassium to form alkaline chlorides, a troublesome sediment [13]. Meanwhile, alkaline sulfates, which also cause sediments, are produced from sulfur which reacts with sodium and potassium [25]. In our study, the sulfur content in rice straws was effectively reduced from 3.40% to 1.97% within 120 min (Figure 4). In comparison, a depletion of sulfur in rice straw due to leaching from 2.59% to 0.32% was reported by Deng *et al.* [20] and a decrease from 1.11% to 0.41 was noted by Jenkins *et al.* [7]. The reduction in sulfur during the leaching process can be presented by the following equation:

$$S = 2.01 + \frac{12.293}{(t + 17.975)^{0.7533}} \quad (R^2 = 0.8663) \quad (6)$$

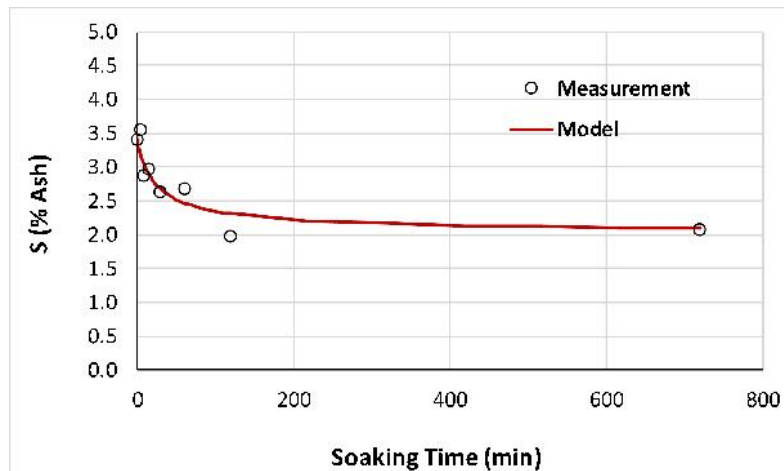


Figure 4. The relation of soaking time and content of sulfur (S)

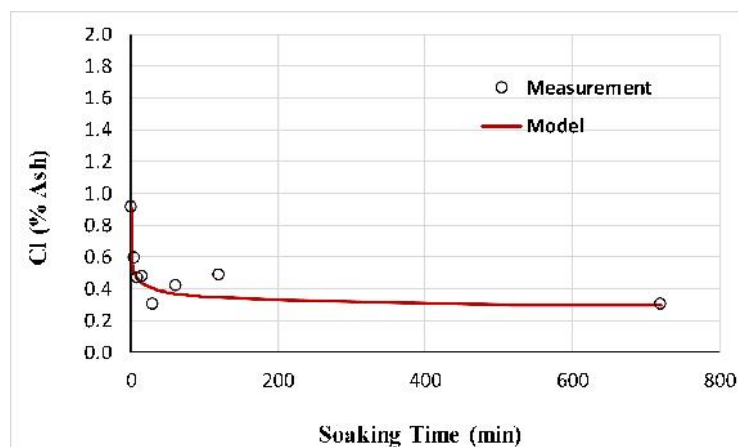


Figure 5. The relation of soaking time and content of chlorine (Cl)

Meanwhile, the Cl content could be reduced from 0.91% to 0.3% in a shorter time, 30 min (Figure 5). Deng *et al.* [20] reported a reduction in chlorine from 0.612% to 0.180%. The reduction in chlorine during the leaching process can be presented by the following equation:

$$Cl = 0.196 + \frac{0.4505}{(t + 0.135)^{0.231}} \quad (R^2 = 0.8711) \quad (7)$$

3.5. Silica (S)

Silica (SiO₂) is the highest mineral that makes up ash with proportion up to 66.39 (% Ash). This value is in the range of other research data such as 72.23% [7], 61.63% [19], 66.47% [20], 72.28% [21], and 77.20% [26]. Silica is a mineral that does not dissolve easily in water. Wu *et al.* [13] reported that the SiO₂ content in wheat straw slightly decreased from 16.64% to 15.93% through leaching with water. In our study, the SiO₂ content in rice straw increased with soaking time as shown in Figure 6. Overall,

silica content increased by 17.7% from an initial value of 66.39% to 78.14% after soaking for 720 min. This result, however, is in line with Jenkins' report of a 17% increase (from 72.23 to 84.47) [7] and Dayton *et al.* [21] with an increase of 23% (from 72.28% to 89.12%). Leaching studies using olive residue also resulted in an increase of silica content from 32.60% to 43.57% [25]. The relative increase in SiO₂ is caused by the relative decrease of other elements such as K, Cl, S, and Mn. As shown in Figure 6, the increase in Si content during leaching can be presented in a good way through equation (6) with the R² value of 0.9055.

$$Si = 66.39 + 2.44^{0.2556} \quad (R^2 = 0.9122) \quad (8)$$

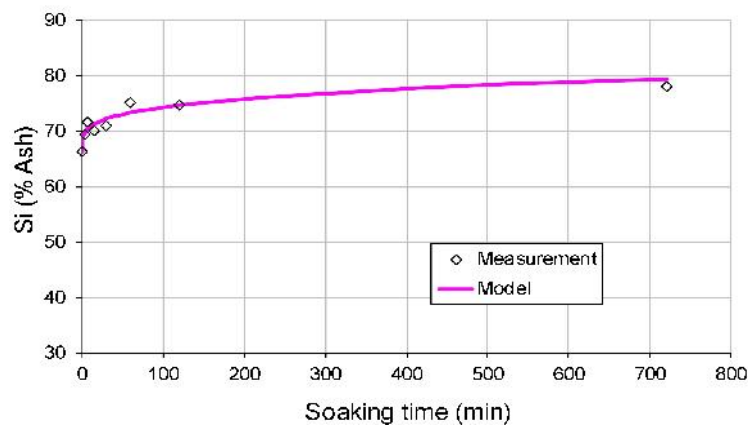


Figure 6. The relation of soaking time and content of Si

3.6. Other Inorganic Elements

Table 1 shows that Manganese (Mn) mineral decreased due to leaching from 1.43% to 0.54% (Figure 7). Meanwhile, other inorganic elements such as P, Ca, Mg, and Fe did not show a clear decrease or increase. These elements tend not to change. Soaking rice straw with tofu wastewater for 720 min did not have a significant effect on the composition of these components in rice straw ash. Similar observation was reported by Jenkins *et al.* [7] and Deng *et al.* [20].

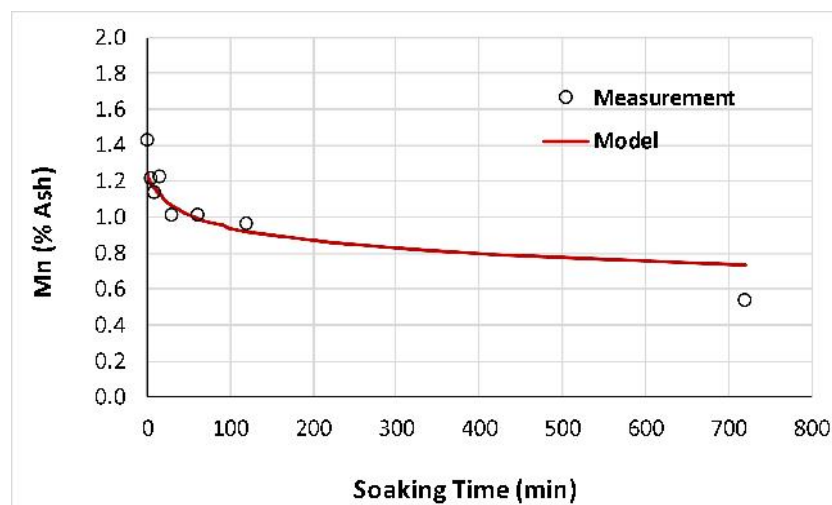


Figure 7. The relation of soaking time and content of Manganese (Mn)

3.7. Calorific value

Another important characteristic of biomass as fuel is its calorific value. High heating value is a good indicator of biomass fuel. Rice straw is a bad fuel because it has a low calorific value. Rice straw used in this work had a calorific value of 13.60 MJ/kg, which comparable to the value of 14.75 MJ/kg reported by Jenkins *et al.* [17]. Soaking straw in tofu wastewater can remove alkali metals such as potassium so as to increase its heating value. The calorific value increases from 13.60 MJ/kg (without soaking) to 15.77 MJ/kg (increasing of 15.96%). This significant increase can occur due to a decrease in ash content in rice straw.

4. Conclusion

Soaking is an effective way to wash some alkali metals in an effort to improve the quality of rice straw for fuel. Soaking rice straw using tofu wastewater for 720 min can reduce ash content from 16% to 14.82%, potassium from 17.94 % to 9.69% and increase silica (Si) content from 66.39% to 78.14%. Other elements such as sulfur (S), Manganese (Mn), Magnesium (Mg) and Chlorine (Cl) were also reduced. In addition, soaking was able to increase the calorific value of rice straw from 13.6 MJ/kg to 15.77 MJ/kg. Soaking rice straw by using tofu wastewater, however, did not significantly influence the content of phosphorus (P), calcium (Ca), and Ferrum (Fe).

5. Acknowledgements

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