Potential valorisation of agro-industrial wastewater for bioenergy production

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Abstract. Agro-industries generate a high amount of solid waste, wastewater and emissions. In Indonesia's case, many small and medium-scale agro-industries have problems in treating or in valorising their wastes. Specific to wastewater, due to lack of waste treatment facilities or financial support, as well as lack of policies enforcement, many agro-industries directly disposed of the wastewater to the river bodies. Such practices can have a detrimental effect on the environment due to the accumulation of both organic and an-organic pollutants. This study aimed to investigate the potential of various agro-industrial wastewater (i.e. batik wastewater, tofu-processing wastewater and tempeh-processing wastewater) from Malang City as single feedstock for biogas production. The biochemical methane potential (BMP) test was employed under a mesophilic condition and operated for 28 days. The results indicated that anaerobic digestion (AD) of tempeh-processing wastewater produced more biogas and methane potential compared to other wastewater samples. The specific methane potential (SMP) from the AD of tempeh-processing wastewater was 0.027 m³/kgVSadded. However, the energy potential calculation indicated that using these wastewater samples was not feasible as a single feedstock for an anaerobic digestion system. Therefore, combining with other potential biomass feedstock as co-substrates is recommended for further in-depth investigation.

1. Introduction
Small- and medium scale enterprise (SME) or agroindustry, either in food and non-food sectors, plays a key role in the Indonesian economy [1]. However, many agro-industries in Indonesia still have problems of low environmental performance due to a lack of responsiveness in treating their solid waste or wastewater [2]. For example, according to Tegarwati et al. [3], cheese agro-industries often directly disposed of their wastewater (also known as whey) to the environment, which may lead to water pollution. In the case of tapioca agro-industries, their wastewater remained a big problem [4]. Similarly, tofu and tempeh industries, producing popular and favoured products (i.e. tofu and tempeh), generated a large amount of wastewater, yet have inadequate wastewater treatment facilities [5, 6]. In non-food agroindustry sectors, batik industry may pose an example of small-scale industries which struggle to treat the dyes-containing wastewater due to lack of support from the financial, facilities, technology, and awareness aspects [7, 8]. Many of these agro-industries discharge their wastewater, which contains organic and chemical pollutants, to a nearby water body, thus causing a harmful effect to the surrounding
environment. Therefore, treating and valorising agro-industrial wastewater remained critical to improve the effluent quality or to transform into high-value products.

Various treatment options have been investigated for batik wastewater, such as anaerobic baffled reactor, rotating biological contactor [9]; chemicals coagulants [10]; biofilter [11]; and trickling filter [12]. Several studies have highlighted the use of the following treatments such as biological filtration unit [13, 14]; chemical and natural coagulants [15, 16]; phyto remediation [17, 18]; or microbial fuel cell [19, 20], for treating tofu- and tempeh-processing wastewater.

Nowadays, wastewater to energy is a more favourable option as the resulted energy can be reused for processing on-site, thus saving the energy used and reducing the operational costs [7, 21]. Therefore, this study aimed to investigate whether batik wastewater, tofu- and tempeh-processing wastewater have the potential for bioenergy generation, such as biogas.

2. Materials and Methods

2.1. Agro-industrial wastewater and inoculum

Three types of agro-industrial wastewater collected from Malang City, include batik, tofu-processing and tempe-processing wastewater, were used in this study. Batik wastewater (BW) was freshly collected from Batik Blimming Malang SME. Tofu-processing wastewater (ToW) was collected from the tofu industry centre in Kendalsari. Tempe-processing wastewater (TeW) was collected from tempeh industrial centre in Sanan. No pre-treatment was subjected to all agro-industrial wastewater samples. All samples were directly used and analysed upon arrival at Laboratory of Bioindustry, Department of Agro-industrial Technology, Faculty of Agricultural Technology, Universitas Brawijaya. Parameters analysed for batik wastewater samples include pH, biochemical methane potential (BOD), chemical oxygen demand (COD), total suspended solids (TSS), ammonia, sulphide, phenol, oil and grease, and total Cr. While, for tofu- and tempeh-processing wastewater include pH, BOD, COD, TSS, and amonia.

Inoculum was collected from a mesophilic digester treating cattle slurry at Balai Besar Pelatihan Peternakan in Batu City. The procedure and preparation of inoculum for biochemical methane potential (BMP) test was previously described in our studies [7, 8, 22, 23].

2.2. BMP test

The procedure for the BMP test was according to Suhartini et al. [7, 8, 22, 23]. The ratio of inoculum to the substrate (R\textsubscript{I/S}) was 6:1, with the following samples: inoculum only, positive control with α-cellulose, BW 100%, ToW 100% and TeW 100% (as seen in Table 1), and prepared in triplicate. The BMP test was carried out for 28 day at 37°C using a controlled water bath. Changes in the internal pressure were measured using a digital manometer on daily basis.

| Sample ID                  | Substrat added (g) | Inoculum added (g) | R\textsubscript{I/S} |
|----------------------------|--------------------|--------------------|---------------------|
| Blank sample (inoculum only) | 0                  | 40                 | 6:1                 |
| Positive control sample (α-cellulose) | 0.05               | 39.95              | 6:1                 |
| BW 100%                    | 21.08              | 18.92              | 6:1                 |
| ToW 100%                   | 2.71               | 34.57              | 6:1                 |
| TeW 100%                   | 2.82               | 34.37              | 6:1                 |

2.3. Analysis

The proximate analysis includes total solids (TS), volatile solids (VS), moisture content (MC) and Ash content were analysed using the Standard Method 2540 G [25]. The pH value was measured, at the beginning and end of the BMP test, using a digital pH meter and previously calibrated in buffer solution at pH 7 and 9.2 [25]. Theoretical methane concentration was calculated using the Buswell formula [26]. The biogas volume was calculated by converting the pressure readings to gas volume following the
formula described in Suhartini et al. [24] at standard temperature and pressure (STP) of 273.15 K and 101.325 kPa. Specific methane production (SMP) calculated using the formula described in Strömberg et al. [27].

3. Results and Discussion

3.1. Characteristics of agro-industrial wastewater
Selected agro-industrial wastewater samples were found to contain high organic pollutants, as indicated by the COD and BOD values (Table 2). For BW, it can be seen that the values for pH, sulfide, and total chromium (Cr) parameters were well within and below the standard effluent discharge for industrial wastewater. This result was in accordance with other studies reported in Aryani et al. [28] and Hardyanti [29]. Table 1 also shows that BW has a higher concentration of phenol, as well as fat, oil and grease (FOG). All agro-industrial wastewater samples have high BOD, COD, and TSS concentrations exceeded that of the standard effluent discharge. Sinha et al. [30] stated that high BOD and COD values are proportional to the high amount of organic matter (pollutants) in wastewater. If the wastewater is directly discharged into the environment, it may cause the rapid depletion of dissolved oxygen in water and may present toxic constituents. These results demonstrated that BW, ToW and TeW contained high available organic material, thus the potential for transforming into bioenergy, for example. Furthermore, both ToW and TeW have low pH values of < 4.50, indicating that disposed of directly into the environment needs to be avoided and further treatments are advised.

Table 2. Characteristics of BW, ToW and TeW.

| Parameters          | Unit  | BW     | ToW    | TeW    | Standard effluent discharge [28] |
|---------------------|-------|--------|--------|--------|----------------------------------|
| pH                  | -     | 7.6    | 4.13   | 4.41   | 6 – 9                            |
| BOD                 | mg/L  | 8,651  | 6,730  | 9,900  | 60                               |
| COD                 | mg/L  | 54,700 | 17,300 | 22,100 | 150                              |
| TSS                 | mg/L  | 1,483  | 73.40  | 83.00  | 50                               |
| Ammonia (NH₃-N)     | mg/L  | 1.44   | -      | -      | 8                                |
| Sulphide (H₂S)      | mg/L  | 0.062  | -      | -      | 0.3                              |
| Phenol              | mg/L  | 0.616  | -      | -      | 0.5                              |
| Fat oil             | mg/L  | 4.2    | -      | -      | 3.0                              |
| Chromium total      | mg/L  | <0.02  | -      | -      | 1.0                              |

3.2. BMP test results

3.2.1. Characteristics of digestate after BMP test
At the end of the BMP test, the digestate (or organic residue) after anaerobic digestion (AD) was measured for the following parameters: TS, VS, MC, and ash concentration, respectively. The results indicated that the digestate still contains a high amount of remained organic matters, as shown by the VS concentration (Table 3). The organic matters in the digestate can be further reused for composting or for soil conditioners, as well as for bio-fertilizer. This is consistent with a previous study which highlighted that digestate from AD is potential sources for soil amendment due to its organic fraction can contribute to the turnover of soil organic matter (SOM) [31].
Table 3. Characteristics of digestate after the BMP test.

| Sample ID              | MC (%ww) | TS (%ww) | VS (%ww) | VS (%TS) | Ash (%ww) |
|------------------------|-----------|-----------|-----------|-----------|------------|
| Blank sample           | 97.99     | 2.01      | 1.59      | 79.13     | 0.42       |
| Positive control sample| 97.98     | 2.01      | 1.61      | 79.83     | 0.40       |
| BW 100%                | 98.73     | 1.27      | 1.02      | 80.72     | 0.24       |
| ToW 100%               | 99.28     | 0.72      | 0.44      | 61.52     | 0.28       |
| TeW 100%               | 99.20     | 0.84      | 0.47      | 55.62     | 0.37       |

Note: ww= wet weight

3.2.2. Specific methane production

The SMP was calculated by comparing the net methane volume divided by the organic fraction (VS) of the substrate, as shown in Figure 1. The concentration of methane used in the calculation was assumed as 50%. The SMP value for the control sample i.e. blank sample was 0.005 m³ CH₄/kg VS. This value was much lower than our previous study reported [7, 8, 22, 23], which possibly due to the characteristics and poor handling of the inoculum. The positive control has SMP of m³ CH₄/kg VS. The positive control sample with the addition of pure standard α-cellulose (i.e. 100% organic material) was used to investigate the microbial activity contained in the inoculum. A study by Wang et al. [32] showed that α-cellulose substrates can produce methane with a value of 0.34 m³ CH₄/kg VS.

![Figure 1. The SMP of agro-industrial wastewater: BW, ToW and TeW.](image-url)

The figure shows that digesting BW and ToW alone result in a small amount of both cumulative biogas and methane volume, causing a negative SMP value, with the average values of -0.06 m³ CH₄/kg VS and -0.008 m³ CH₄/kg VS. This was because the cumulative biogas and methane volume from these samples was lower than that of the inoculum. Furthermore, a high concentration of COD in BW and ToW may limit the microorganism ability in the AD system to breakdown COD into biogas or methane [8]. However, using TeW as the main feedstock in the AD system did give slightly better biogas and methane production; with the average SMP value of 0.027 m³ CH₄/kg VS. The difference in SMP could also be influenced by the organic matter and the presence or absence of substances that are toxic to consortia of microorganisms in the AD system [33]. The findings from this study demonstrated that agro-industrial wastewater samples, when used as a single-feedstock for AD processes, show
constraints, especially BW and ToW. Therefore, other alternative approaches are recommended, such as co-digestion with other biomass [7] or a combination of AD systems with adsorption technology [34].

From the SMP values, the calculation of energy potential revealed that digesting BW or ToW alone did not provide a great electrical energy potential. While for TeW, it is estimated that the theoretical potential for electrical energy was slightly higher at a value of 0.728 kWh from 1000 L of wastewater.

3.3. Alternatives approach for agro-industrial wastewater valorisation

Various studies have been emphasized valorising BW, ToW and TeW for either bioenergy generation or other high-value products. For example, Fazal et al. [36] and Wu et al. [36] reported that BW can be used as a growth medium for microalgae for biodiesel purposes, as it contains organic matter, phosphorus and nitrogen needed for growth and fat accumulation in microalgae. While Lin et al. [34] found that a combination of mesophilic AD with adsorption technology using granular activated carbon (GAC) was suitable for growing microalgae (i.e. Scenedesmus sp.). Such a combination was effective to remove color, reduce COD content, and improve methane production of 2.07 × 107 kJ/day.

In the case of ToW, several studies have also highlighted its potential for bioenergy production. Lay et al. [21] stated that ToW is greatly feasible to be valorized into ethanol and energy, resulting in additional energy sources for the tofu industry by up to 3.5% of annual energy consumption. Zheng et al. [36] also support the idea of transforming ToW into bio-hydrogen. While a study by Vistanti and Malik [37] found that implementing a multi-stage AD system combined with recirculation can improve biogas production from ToW. Specific to TeW, Zuhri et al. [20] and Utami [38] reported that TeW can be used as a substrate for the production of electric energy using MFC technology. While Nayono and Purwantoro [39] found that implementing up-flow anaerobic fixed-bed reactor (UAFB) combined with natural treatment of constructed wetland (filled with natural filter media) can provide both energy from wastewater (i.e. biogas) and reduce the negative environmental impact from wastewater directly discharge to water bodies. The study also concludes that bioenergy recovered from TeW can generate an annual income of USD 11,951, which clearly evident of economic benefits from the practice.

Such findings, as mentioned above, demonstrated that agro-industrial wastewater can be a great resource for bioenergy production, with further combination with other treatments. Yet, in-depth investigation should be carried out to further evaluate the feasibility of the selected and applied technology.

4. Conclusions

High COD and BOD content in agro-industrial wastewater have inhibited the AD system in producing biogas or methane. This was evident for BW and ToW samples. The energy potential calculation indicated that using these wastewater samples was not feasible as a single feedstock for an anaerobic digestion system. Therefore, using AD of agro-industrial wastewater can potentially be improved by combining other potential biomass feedstock as co-substrates or with other treatments. More investigation on these matters are essential and recommended.

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