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EFFECTS OF VINASSE AND SILICA MUD ON THE PERFORMANCE OF THERMOPHILIC FERMENTATION OF BREWERY SLUDGE FROM BREWERY WASTE SUBSTRATES

The anaerobic digestion of mixing brewery sludge with vinasse and silica mud at various ratios under thermophilic conditions was explored. Vinasse, silica mud and beer sludge (the sludge from the treatment of beer wastewater) are the main solid wastes of the beer production. Uncontrolled decomposition of these wastes could cause large-scale contamination of soil, water, and air. The results of the investigation showed that the optimal ratio of beer sludge and vinasse was 1:1 under total solids of 10%, producing the highest amount of gas of 1.34 cm^3/g within 24 h and 4.06 cm^3/g in 10 days. The silica mud weakened the fermentation process and reduced the gas production, and the concentration of total organic carbon, total nitrogen and volatile solids decreased during the digestion. For the mixture of brewery sludge and vinasse, the content of the total organic matter in the biogas manure was more than 60% and the value of pH was 6.5 after the anaerobic digestion, indicating that the manure can be used as an organic fertilizer.

1. INTRODUCTION

With the development of economy and the improvement of people's living standards, the beer production has been increasing at an annual rate of 15–20%. Vinasse, silica mud and sludge from the treatment of beer wastewater (beer sludge) are the main solid wastes of beer production. Uncontrolled decomposition of solid wastes could cause large-scale contamination of soil, water, and air. Vinasse is the most abundant brewing by-product, accounting to around 85% of total by-products which reached

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10 million ton per year in China. Nowadays, vinasse is simply used as livestock feed with a marginal profit. For example, the incorporation of brewery waste (spent grains) into fish-feeding was investigated by Kaur and Saxena in India [1]. However, the brewer's grain is characterized by high content of organic compounds and moisture, resulting in putrescibility. Moreover, the uncontrolled decomposition could result in large-scale environmental pollutions. Thus, efficient management and reuse technology is increasingly required due to environmental and economic concerns.

Over the years, innovative ideas for the utilization of wastes have been proposed, such as composting [2], incineration and land filling. Anaerobic digestion of organic wastes to produce energy in the form of biogas is the most promising [3]. In anaerobic digestion, complex organic materials are firstly hydrolyzed and fermented by acid bacteria into volatile fatty acids (VFAs). The VFAs are then consumed by hydrogen-producing acetogenic bacteria and methanogenic bacteria and converted into H_2 and CH_4 [4–6]. In this process, co-digestion is mainly used to treat complementary wastes. The benefits of the co-digestion include: 1) dilution of potential toxic compounds, 2) improving the balance of nutrients, 3) synergistic effects of microorganisms, 4) increasing the load of biodegradable organic matter, and 5) higher biogas yield. Additional advantages include hygienic stabilization, increased digestion rate while the process occurs under thermophilic conditions [7]. The course of a perfect anaerobic digestion includes two stage: acid stage and alkaline stage. The biogas production in the alkaline stage could be plentiful and much methane (CH_4) could be obtained [5]. However the reaction time can be more than 30 days which is too long from the standpoint of biogas producers. Therefore that method is inefficient due to its low productivity. The reaction time of acid fermentation is less than 15 days. In the course of acid fermentation, hydrogen could be obtained [5, 6], and at the same time more carbon could be captured in the products. The application of anaerobic digestion in treating organic wastes has been evaluated by a number of studies [8–15]. However, these studies mainly concentrated on the fermentation of municipal sludge and kitchen wastes [11–15]. Research on the performance of the anaerobic digestion for the brewery waste substrates, particularly for the green fuels production by acid fermentation is rare.

In this paper, the production of biogas (bio-hydrogen) during acid fermentation of sludge, vinasse and silica mud at high temperatures was studied in laboratory scale batch reactors. High temperature was used in order to reduce the fermentation time and improve the productivity. Main parameters of the process have been determined.

2. MATERIALS AND METHODS

Inoculum and substrate. Three different materials of brewery waste substrates were used in the course of anaerobic digestion. Brewery sludge, vinasse and silica mud were collected from the Tsingtao Brewery, China. Vinasse was mashed and stored for use.

Brewery sludge contained various microorganisms and was used as inocula, while vinasse and silica mud were mixed with brewery sludge before the anaerobic process.

Experimental set-up. The schematic diagram of the anaerobic digester used in this study is shown in Fig. 1.

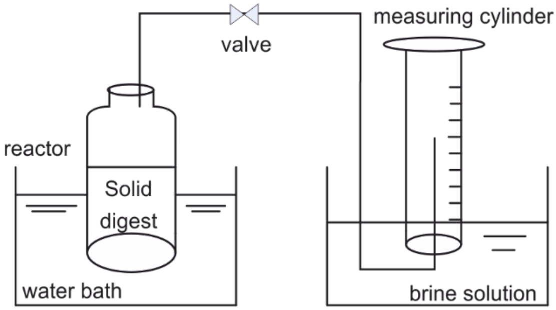

Fig. 1. Schematic diagram of anaerobic fermentation

The reactor consisted of glass jars 1.0 dm^3 in volume equipped with rubber stoppers and an outlet for biogas. The operation volume was approximately 0.8 dm^3. Brewery sludge, vinasse and silica mud were mixed at the ratios of 1:0:0, 1:1:0 and 1:1:0.2 by weight. The detailed compositions of the feedstock applied to the reactors are presented in Table 1.

Table 1

Composition of the experimental mixtures before the anaerobic fermentation

Group	Composition	Ratio by weight	TS [wt. %]
1	sludge	1	10
2	sludge + vinasse	1:1	10
3	sludge + vinasse + silica mud	1:1:0.2	10

Water was fed into the bioreactor to maintain total solids (TS) to be 10 wt. %. This batch experiment was conducted under thermophilic conditions for 17 days. The temperature was controlled with a water bath and maintained at the level of 50 °C. The bioreactor was stirred regularly to keep the substrates thoroughly mixed. Biogas production was measured on a daily basis by acid brine displacement.

Analytical methods. The digestion process was monitored by determining the following parameters: pH, volatile solids (VS), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP, calculated as P_2O_5), and total potassium (TK, calculated as

K_2O). Volatile solids were determined by using the ignite clean evaporating dish at 550 °C for 1 h in a muffle furnace [16]. TN, TP and TK were measured according to standard methods [17]. Total organic carbon (TOC) was measured by the potassium chromate method. Total organic matter (TOM) was 1.724 times TOC [17]. pH was measured using a potentiometer. The produced gas was collected in a gas displacement chamber which was directly connected to the headspace of the reactor, and measured continuously in the measuring cylinder. The main response variables used for evaluating the process performance were biogas productivity and the variations of the TOC, TN, TP and TK.

3. RESULTS AND DISCUSSION

3.1. PERFORMANCE OF GAS PRODUCTION

Figure 2 shows cumulative gas production during the fermentation of various brewery waste substrates. The biogas production showed a periodic trend. If just brewery sludge was used, only 0.08 cm^3/g of biogas was generated. The biogas production increased rapidly to 1.34 cm^3/g within 24 h when the vinasse was added. The process lasted for 10 days and the accumulative biogas production was noticeably higher than that of the former group. In comparison, a lower gas production was obtained when silica mud was added to the substrates. The bioreactor started to produce gases after 5 days and the accumulative gas increased only to 1.28 cm^3/g in 10 days.

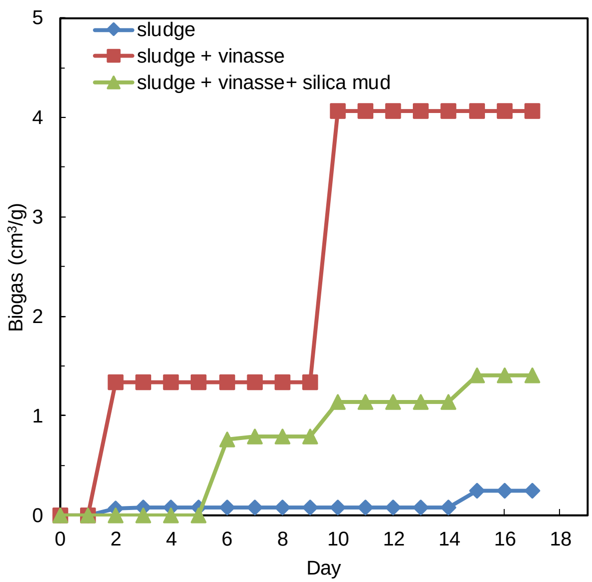

Fig. 2. Cumulative biogas production in the course of anaerobic digestion

The results indicate that the gas production from the mixture of brewery sludge and vinasse is more efficient. The presence of alcohols in silica mud may inhibit the activity of mixed microflora and reduce the biogas production. The results showed that there was a time when no biogas was generated (Fig. 2). Sharma and co-workers [18] also observed similar phenomenon. A similar result can also be found in Sosnowski's and co-workers' reports [5] probably due to temperature fluctuation during the digestion process, resulting in a periodic gas production. Mattocks [19] noted that the selection of appropriate operating temperature is vital but stabilization of temperature is even more important. That study also have shown that variations of ±1 °C in a day may force the gas producing organisms into periods of dormancy. Moreover, the substrates being in-homogeneous also result in a periodic gas production.

3.2. VARIATIONS OF VOLATILE SOLIDS CONTENT AND pH IN THE COURSE OF DIGESTION PROCESS

Anaerobic digestion can reduce the VS content in all digestions. Volatile solids are converted to organic acid during the process of hydrolysis acidification and in turn affect the pH value of the system.

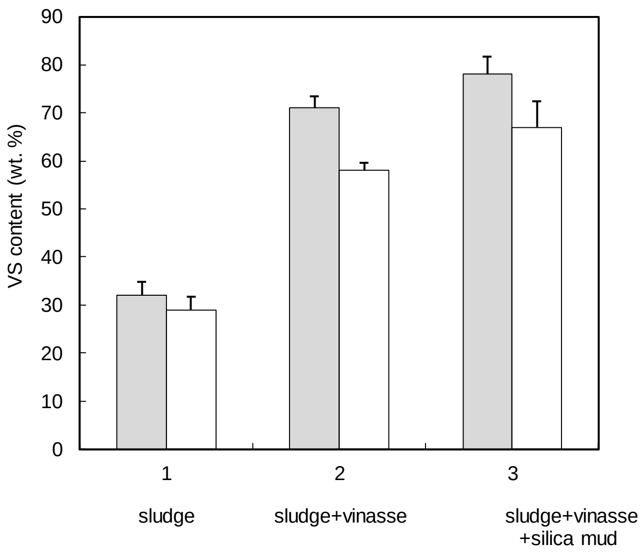

Fig. 3. Content of volatile solids (VS) in mixtures subjected to digestion process before (dashed bars) and after the reaction (white bars)

The results of the research (Fig. 3) showed that the VS content in brewery sludge was reduced by 3% (from 32 to 29 wt. %) after 17 days, compared to 13% in the presence of vinasse and 11% in the presence of both silica mud and vinasse. The mixtures of brewery sludge and vinasse were thoroughly decomposed during the digestion process, leading to the abrupt decrease by 13% of the VS content. Upon the addition of silica mud, the reduction decreased to 11% indicating that silica mud would inhibit the fermentation process and reduce the gas production. It should be noticed that the anaerobic removal of organic substances in our experiments was within the range of 3–13%. Tomei et al. showed that the removal efficiency of organic substances could reach 32±5% in the sequential anaerobic/aerobic digestion of municipal sewage sludge when the feed VS concentration was 1.6 wt. % [20]. The lower removal efficiency in our experiments may be caused by the lack of aerobic digestion and the high VS content.

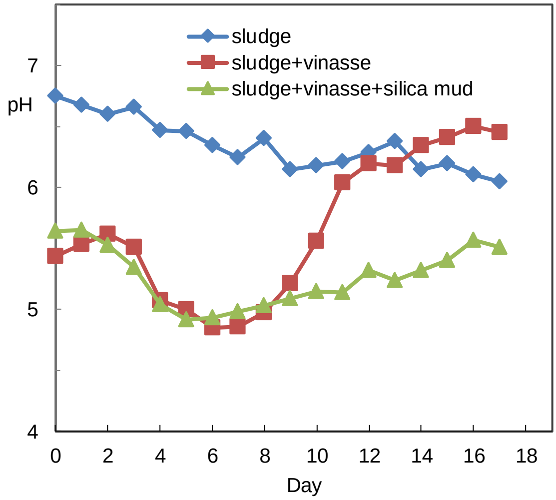

Fig. 4. pH of examined mixtures in the course of anaerobic digestion

Figure 4 shows time dependence of pH for different mixtures during fermentation. For the mixture of brewery sludge and vinasse, pH decreased to 4.85 in the first six days, and then increased slightly to 6.45. However, with the addition of silica mud pH decreased to 4.92 in the five days and then increased slightly to 5.51. In our experiments, pH did not exceed 6.75, while Macias et al. [4, 5] showed that pH in their study changed from acidic stage to alkaline stage due to the periodic accumulation of fatty acids in the solid phase reactor and subsequent transfer and consumption of VFA by methanogenesis [4], thus the fermentation could be divided into two stages, namely, acid fermentation and alkaline fermentation. At the beginning, VS was decomposed to VFAs during the hydrolysis acidification and the accumulation of VFAs led to a decrease of pH. Then, VFAs were utilized by methanogens and were converted to carbon dioxide and methanol. Consequently, the quantity of VFAs reduced gradually and pH would again increase. However, in our experiments the fermentation occurred only at the acid phase (Fig. 4). The results showed that there was an absence of alkaline stage, which indicated that the condition was not suitable for the growth of methanogenic bacteria and the component of biogas should be mainly hydrogen, which was similar with Godday's reports [6].

3.3. VALUES TOC, TN, TP AND TK IN THE COURSE OF ANAEROBIC DIGESTION

Table 2 summarizes the variations of TOC, TN, TP, TK, and pH of the outlet water (OW) before and after the anaerobic digestion. The values of TOC decreased after the digestion. The TOC of the mixture (brewery and vinasse) was reduced by 8.8 wt. % (from 43.9 to 35.1 wt. %) after 17 days, while those of the mixture of three materials (brewery, vinasse and silica mud) decreased by 5.8 wt. % (from 48.1 to 42.3 wt. %).

Table 2

TOC, TN, TP, TK (wt. %] and pH of OW in experimental mixtures before and after the anaerobic digestion

Mixture	Parameter	Group		
		1	2	3
Before the digestion	TOC	33.8	43.9	48.1
	TN	1.75	3.9	4.1
	TP	1.58	0.95	0.74
	TK	0.92	0.81	0.35
	pH	6.86	6.86	6.86
After the digestion	TOC	28.1	35.1	42.3
	TN	1.47	2.68	3.15
	TP	1.50	0.67	0.54
	TK	1.09	0.98	0.36
	pH	7.05	9.78	9.02

The results indicate that higher gas production results in larger reduction of TOC due to the conversion of organic carbon into H_2, CO_2 and other final products. Similarly the TN in the substrates also decreases after fermentation. The main transformations of nitrogen include the nitrogen fixation and release. This significant mass deficit in the TN balance also confirms that some gaseous products are generated. pH values of OW were both higher than 9, which indicated that the volatilization of ammonia contributed significantly to the reduction of nitrogen (Table 2). The maximum reduction of TOC and TN was observed in the mixture of brewery sludge and vinasse which indicates that a more thoroughly reaction occurred.

3.4. CHARACTERISTICS OF PRODUCTS AFTER THE ANAEROBIC DIGESTION

Characteristics of the products after digestion are shown in Table 3. The quality of biogas manure from the fermentation of brewery sludge was inferior. While for the mixture of brewery sludge and vinasse, the contents of TOM, total nutrients and pH were

60.5%, 4.32% and 6.5, respectively, which was optimum compared with the fermentation of other groups. The contents of the TOM and pH met the Standards for Organic Fertilizer of China [21].

Table 3

Characteristics of products after the anaerobic digestion

Group	Total organic matter [wt. %]		Total nutrient [wt. %] ($N + P_2O_5 + K_2O$)		pH	
	Standard[a]	Sample	Standard[a]	Sample	Standard[a]	Sample
1	≥45	48.4	≥5.0	4.06	5.5~8.5	6.37
2	≥45	60.5	≥5.0	4.32	5.5~8.5	6.50
3	≥45	72.9	≥5.0	4.05	5.5~8.5	5.51

[a]Refers to Standards for Organic Fertilizer of China -NY525.

Thus, the biogas manure can be applied to soil as a source of plant nutrients. Kütük et al. [22] found that the biogas manure had an obvious promoting effect on the growth of sugar beet plants, indicating that the byproducts can be used for agricultural use.

4. CONCLUSIONS

The feasibility of producing biogas and biogas manure from brewery waste substrates with thermophilic fermentation has been demonstrated. With respect to the amount of the biogas generated, the optimum ratio of brewery sludge and vinasse to generate the maximum quantity of biogas was 1:1. The maximum biogas production of 4.06 cm^3/g in 10 days was observed by hydrogen fermentation at the TS of 10 wt. %. The presence of silica mud would inhibit the fermentation and reduce the gas production. At the same time, high quality biogas manure, which could be applied to soil as a source of plant nutrients, would be obtained from the mixture of brewery sludge and vinasse after the anaerobic fermentation.

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