CHEMICAL ENGINEERING TRANSACTIONS
VOL. 57, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

Effect of Partial Ozonation and Thermal Pretreatment on Biogas Production from Palm Oil Decanter Cake

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In the present work, the effect of partial ozonation and thermal pretreatment on the CH_4 production by the anaerobic digestion of palm oil decanter cake was studied. Decanter cake is an attractive feedstock because of high biodegradable organic contents (50 and 31 %ww^{-1} cellulose and hemicellulose). Partial ozonation with 250 mg/hr O_3 loading for 20 and 60 minutes increased total sugar releasing and finally improved the performance of anaerobic fermentation based on the CH_4 yield and maximum biogas production potential (P). Xylose was the main pentose sugar hydrolyzed on hemicellulose structure for the partial ozonation pretreatment. Thermal pretreatment achieved higher total sugar releasing compared with the partial ozonation pretreatment for most cases. Besides, thermal pretreatment displayed strong effect on short lag time (1.8 d) for microbial adaptation in the fermentation system compared with ozonation pretreatment and non-pretreatment (2.6 and 4.3 d). However, the maximum methane yield (581 mL CH_4/g TS_{added}) and energy recovery (2.9 kJ) were obtained from the partial ozonation pretreatment for 60 min. Similarly, the maximum waste reduction based on TS removal was about 33% observed from the partial ozonation pretreatment for 60 min. Therefore, to improve the biogas production in overall process and enhance the waste utilization, integrating ozonation pretreatment with two stage fermentation would be suggested.

1. Introduction

Palm oil production is one of the important agro-industries in Thailand with major contribution to the country's development during the past 30 years. Palm oil product of Thailand is exported more than other countries and ranked in top-five of the world. The palm oil industry has a high potential for biomass energy utilization and therefore is one of the industrial sectors, which can contribute substantially to the supply of alternative sources of energy. From the processing for each tonne of fresh fruit bunches (FFB), 0.6-0.8 m^3 of palm oil mills effluent (POME), 23% of empty fruit brunch (EFB), 3.5% palm oil decanter cake (PODC) and 13.5% of palm mesocarp fiber (PMF) (Ooi and Kumar, 2008). The solid form of by-product, especially palm oil decanter would be focused in this study. Decanter cake is a solid waste produced in the purification process of crude palm oil after that the supernatant is separated as the purer palm oil and the sediment is the decanter cake. At the oil palm mill site, the decanter cake generated take up a lot of space. Moreover when dried, the decanter cake can be fired and contribute toward increasing the amount of suspended particles in the vicinities of mills. These waste products create an environmental hazard and entail high disposal costs every year. Generally, decanter cake has been utilized as feedstock for the production of cellulose and polyose (Nafis et al., 2012), biobutanol (Loyarkat et al., 2013), bio-diesel (Maniam et al., 2013), and bio-oil (Dewayanto et al., 2013). However, most decanter cake is used as animal feed and composting process (Yahya et al., 2010). According to characteristics of palm oil decanter cake, high cellulose hemicellulose and lignin were consisted. For enhancing biogas production, cellulose and hemicellulose have to be hydrolysed to sugar. However, both cellulose and hemicellulose are rigidly covered by lignin. Therefore, delignification of biomass was a necessary process to remove lignin. Pretreatment is essential for the removal of lignin, reduction of cellulose crystallinity and increased porosity of the material (Singh, et al., 2014).

Ozonation is an interested pretreatment option because ozone is a powerful oxidizing agent that can effectively degrade lignin and part of hemicellulose (Taherzadeh et al., 2008). The ozone could be used as a pretreatment process to improve substrate hydrolysis, increase cumulative methane production, and also improve anaerobic digestion efficiency (Almomani et al.,2017). Moreover, ozone technology has not been applied to palm oil decanter cake for biogas production by other researchers.

This research was to study and compare the efficiency of pretreatment method between the partial ozonation and thermal steam treatment including the effects of pretreatment method on biogas fermentation from palm oil decanter cake.

2. Materials and methods

2.1 Palm oil decanter cakes

Palm oil decanter cake was obtained from Suksomboon palm oil industry in Chonburi, Thailand. The sample was stored in a cold room at 4°C prior to use. The characteristic of decanter cake is shown in Table 1.

Table 1: Characteristics of palm oil decanter cake

Parameter	Decanter cake
Cellulose (%)	50.06
Hemicellulose (%)	30.74
Lignin (%)	10.40
Nitrogen (%)	1.70
Carbon (%)	44.77
Hydrogen (%)	6.46
Total solid (mg kg^{-1})	216,081

2.2 Microbial inoculum

Anaerobic sludge seed was obtained from a full-scale upflow anaerobic sludge blanket reactor treating beverage processing wastewater (Sermsuk Industry Co.Ltd., Pathumtani, Thailand). Prior to use the granule was sieved to the size <0.5 m to remove coarse matter and then washed twice with tap water The anaerobic granule sludge was recultivated in 0.5% (w/v) glucose solution until reach to steady state regarding the CH_4 content ad volume of CH_4 production and then washed with the distilled water twice before used as a seed microbial inoculum for the biogas fermentation.

2.3 Pretreatment process

In the study ozonation pretreatment, 2% wv^{-1}TS decanter cake was mixed in 500 mL deionized water and mixed sample until homogeneous. Ozone generator with loading of 250 mg/h was used to generate O_3 by adding into the samples with varying time of 20, 40 and 60 minutes respectively. For thermal pretreatment, the samples were heated by using water bath at 100 °C for 30, 60 and 90 minutes respectively.

2.4 Batch Fermentation

The batch test was carried out in 100 mL serum bottle (80 mL working volume) sealed with rubber with three replicates. Each serum bottle contained 3.7 g of the decanter (corresponding with 1% TS) and it was pretreated by ozonation and thermal steam according to pretreatment process. The pH of each test was adjusted to 7 with 3 N NaOH or 3 N HCl. The serum bottle was feed with nitrogen gas for 1 min (flow rate of 1,780 mL min^{-1}) to create an anaerobic condition. Biogas fermentation was conducted at mesophilic condition of 37°C with rotary shaking at 100 rpm. During the fermentation, total gas volume and composition were periodically monitored by gas counters and gas chromatography, respectively. All experiments were set up in triplicate.

2.5 Analytical methods

Total solids (TS), and chemical oxygen demand (COD) were measured according to Standard Methods 2540 G and 5220 B, respectively (APHA, 2005). The amount of generated biogas was recorded using liquid displacement gasometers. Biogas content (H_2, CH_4, and CO_2) was measured periodically everyday using a gas chromatograph (Shimadzu GC-8A, Kyoto, Japan) equipped with a thermal conductivity detector (TCD) with a Unibeads C 60/80 column (GL Sciences, Inc., Tokyo, Japan). Helium was used as a carrier gas. The temperatures of the injection port and the detector were 150 and 80◦C, respectively. The lignin, cellulose, and hemicellulose contents of the feedstocks and samples were measured by Klason Method (Lin and Dence, 1992). The total sugar concentration was determined by the phenol-sulfuric acid method (Dubois et al., 1956). The sugar components were determined by high performance liquid chromatography (HPLC) with a Zorbax carbohydrate column. The mobile phase was 80% acetonitrile a flow rate of 1.0 mL/min with a refractive index detector.

2.6 Kinetics analysis

The modified Gompertz equation (Eq.1) was used to fit cumulative hydrogen/methane production data obtained from each batch experiment (Kanchanasuta and Pisutpaisal, 2016). This model has long been used for describing hydrogen, methane, or biogas production in batch fermentation experiments.

$$H(t) = P \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \qquad (1)$$

Where *H(t)* is cumulative biogas production (mL) during the incubation time, *t* (h), *P* (H_{max}) is the biogas production potential (mL), R_m is the maximum production rate (mL hr^{-1}), λ is the lag phase duration (h), and e is the exp (1) = 2.718.

3. Results and Discussion

3.1 Pretreatment of palm oil decanter cake

The characteristics of palm oil decanter cake after pretreatment by partial ozonation and thermal steam treatment were summarized in Table 2. Pretreatment of lignocellulosic material is important to break down the lignin structure and increase the accessible surface area of cellulose and hemicellulose for hydrolysis. Results showed that the partial ozonation with O_3 loading 250 mg/h for 60 min achieved the maximum total sugar releasing (Figure 1) and it was higher than non-pretreatment condition by 67%. Besides, lignin content tended to reduce with the increase O_3 loading of 40 and 60 minutes (Figure 2).

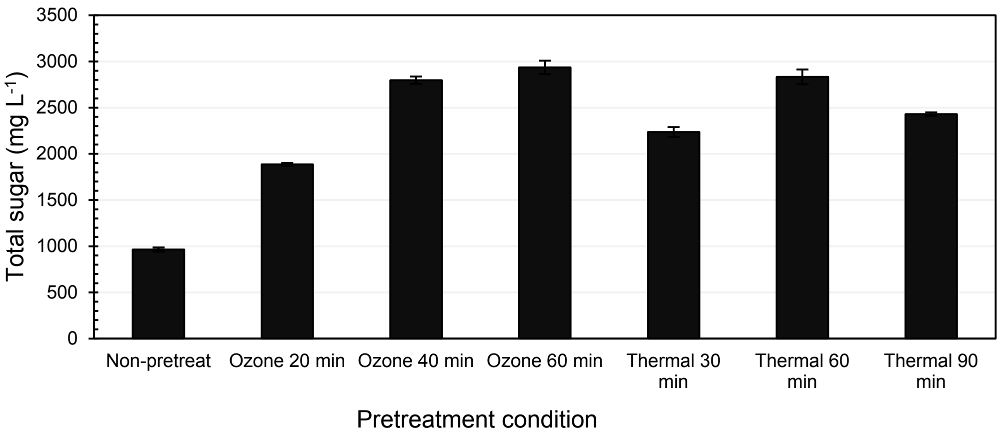

Figure 1: *Total sugar releasing from the different pretreatment processes*

Thermal steam treatment is an attractive pretreatment method for agro-industrial waste, especially, palm oil mill which has thermal steam as by-product during the production process. Regarding the reaction times of thermal steam pretreatment investigated, results indicated the highest total sugar was obtained when increasing reaction time of 60 min. On the other hand, the % holocellulose were decrease when increasing both ozonation and thermal times. It suggested that both pretreatement processes caused the degradation of complex raw materials and increased the soluble organic matter (Ariunbaatar, et al., 2014). Thermal steam treatment is an attractive pretreatment method for agro-industrial waste, especially, palm oil mill which has thermal steam as by-product during the production process. Types of sugar releasing showed that pentose sugar (xylose and arabinose) and hexose sugar (mannose and galactose) were the dominant sugar releasing from decanter cake pretreated by partial ozonation and thermal steam treatment while glucose was rarely observed. However, pretreatment process strongly resulted in hydrolysis of different type of sugar. Xylose was the main pentose sugar (C5) obtained from the partial ozonation pretreatment while it was not observed from the thermal steam treatment. On the contrary, arabinose was the main pentose sugar obtained from the thermal steam treatment. Results indicated that all sugar releasing obtained on hydrolysis of hemicellulose and pentose sugar (C5) was significantly observed for all cases. Therefore, to improve the sugar releasing from cellulose, enzymatic pretreatment has been further investigated.

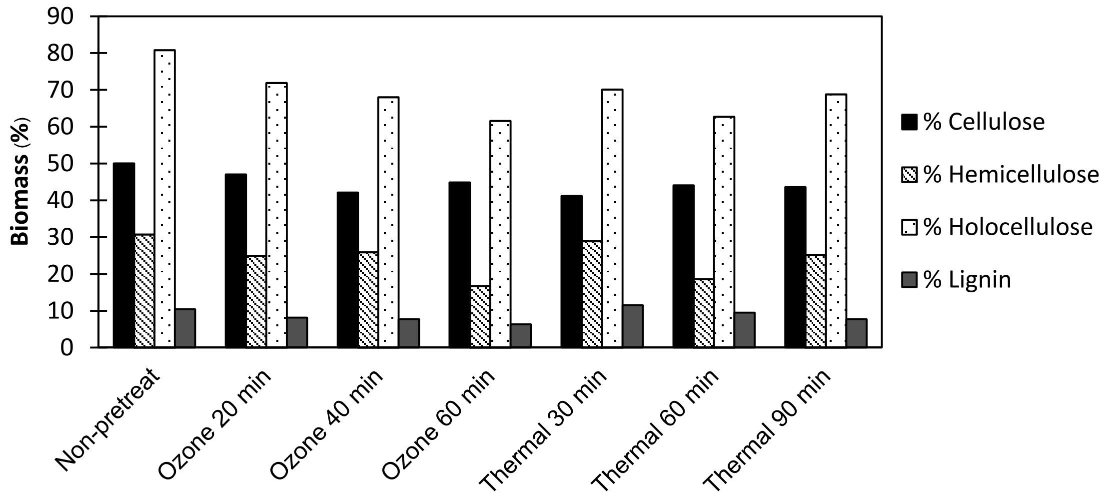

Figure 2: Biomass contents (%) in solid fraction of decanter cake after pretreatment process.

Table 2: Summarized the characteristics of palm oil decanter cake after pretreatment by partial ozonation and thermal steam treatment.

Condition	Total sugar (mg L^{-1})	Biomass (%)				Types of sugar
		Cellulose	Hemicellulose	Holocellulose	Lignin	
Non-pretreatment	964	50.06	30.74	80.8	10.4	galactose
Ozonation						
for: 20 min	1886	47.06	24.84	71.9	8.14	C5=xylose, C6=galactose
40 min	2797	42.12	25.9	68.02	7.72	C5=xylose,arabinose, C6=manose,glucose, galactose
60 min	2935	44.88	16.71	61.59	6.32	C5=xylose,arabinose, C6=manose,glucose, galactose
Thermal steam						
for: 30 min	2236	41.2	28.9	70.1	11.5	C5=arabinose C6=glucose
60 min	2833	44.1	18.6	62.7	9.5	C5=arabinose C6= manose
90 min	2429	43.6	25.2	68.8	7.7	C5=arabinose C6=manose,glucose, Galactose

3.2 Effect of partial ozonation and thermal steam treatment of decanter cake on biogas fermentation

The cumulative CH_4 fermentation profile data was S-shape trend and well fitted to the modified Gompertz equation (R^2> 0.99) for all experiments. The kinetics data from the equation, hence, was statistically significant. The highest methane contents in the range of 68-71% were observed at the 16^{th}-19^{th} fermentation for partial ozonation and steam thermal treatment (data not shown). The maximum methane production potential (P) was 465 mL obtained from the condition of pre-treated hydrolysate by ozonation for 60 min (Table 3). Similarly, the methane yield and energy recovery in all cases of ozonation pretreatment were higher than those observed in thermal steam and non pretreatment conditions. On the contrary, the maximum methane production rate 273 ml/L.h was obtained from non pretreatment condition. Besides, the lag time observed from the fermentation with non-pretreatment and thermal steam treatment condition were shorter than that observed from ozonation pretreatment. For the efficiency of waste reduction, the maximum waste reduction based on TS removal was about 33% observed from the condition of ozonation pretreatment for 60 min (Fig.2). Therefore, to improve the biogas production in overall process and enhance the waste utilization, integrating ozonation pretreatment with two stage fermentation would be suggested.

Table 3: The summary of biogas production rate, biogas yield and energy recovery compared between non-pretreated and pre-treated hydrolysate in fermentation process.

Hydrolysate after pretreatment	P (mL)	Lag time (d)	Yield ($mLCH_4/gTS_{added}$)	Biogas production rate (mL/L.d)	Energy Recovery (kJ)
Non pretreated	305.90	2.61	382.38	273.13	1.9
Ozone 20 min	381.10	2.69	476.37	176.43	2.4
Ozone 60 min	464.50	4.32	580.63	215.05	2.9
Thermal 30 min	314.95	1.88	393.69	145.81	2.0
Thermal 60 min	334.12	1.68	417.65	154.69	2.3

Note: Biogas yield is equal to the maximum biogas production potential (P) divided by the quantity of total solid of decanter cake which added in the fermentation bottle (P (mL) / TS (g)).

4. Conclusion

Pretreatment by partial ozonation of decanter cake has been suggested for enhancing the yield of methane production and energy recovery including improvement the overall fermentation process. The highest methane yield (581 mL CH_4/ g TS_{added}) and energy recovery (2.9 kJ/g TS_{added}) were obtained from the partial ozonation pretreatment (60 min). The partial ozonation pretreatment achieved the maximum total sugar releasing and xylose was the main sugar for all cases. However, the efficiency of hydrolysis on hexose sugar (C6) from cellulose could be improved by enzymatic pretreatment. Besides, integrated two stage fermentation is necessary for improvement of the overall biogas fermentation.

Acknowledgments

The authors would like to express their gratitude to Agricultural Research Development Agency (Public Organization) for the financial support (Grant no. PRP5805020300).

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