EFFECT OF PRE-TREATMENT AND BIOCHEMICAL METHANE POTENTIAL OF WASTEWATER FROM THE PRODUCTION OF BIODIESEL

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Abstract- This research aimed to study the effect of acidification in comparing with enzyme pretreatment on the biodegradability and BMP of biodiesel wastewater. The acid pretreatment can destroy emulsion form of this wastewater and resulted easier oil separation. Therefore the O&G was highly removed (95.27%), but it yielded higher VFA and acidity after treatment. For enzymatic pretreatment, it was also effective in O&G removal (78.63%) but the VFA was also decreased and pH after treatment was more suitable for biological treatment in following. The study of BMP for pretreated wastewater was conducted and it was found that the pretreated wastewater either by acidification or enzyme yielded higher methane production than that of non-pretreated biodiesel wastewater. However, the biodiesel wastewater pretreated with acidification gave higher accumulative methane volume than that pretreated by enzyme.

Keywords- Biodiesel Wastewater, Biochemical Methane Potential (BMP), Acidification, Enzyme.

I. INTRODUCTION

The wastewater from biodiesel processing contains high oil and grease (O&G), and lack of some nutrients elements. This result this wastewater was difficulty treated by biological process be caused of its characteristics are not suitable for the growth of microorganisms (Suehara et al., 2005). In addition it was also contaminated by methane and glycerol that can be harmful to the microorganism in the biological process.

However the biological wastewater treatment still be most suitable treatment method in the present because it has low cost and can product alternative energy like methane. To enhance the biological treatment of efficiencies biodiesel wastewater or Biochemical Methane Potential, this water requires the pretreatment process.

There are several pretreatment method have been investigated for oily wastewater (Kramer, 1971; Shamrani et al., 2002a; Ichikawa et al., 2004; Suehara et al., 2005; Bratskaya et al., 2006; Yang, 2007; Bensadok et al., 2008; Canizares et al., 2008; Mobarak-Qamsari et al., 2012).
The acidification was found that it is highly effective for demulsification of emulsified wastewater but the pH need to be adjusted again prior the biological process. The use of enzyme produced by microorganisms may be on alternative pretreatment method. There are many studies reported the effective of enzyme on oily wastewater treatment. This research, therefore, was interested to investigate the biodiesel pretreatment by hydrochloric acid pretreatment on biodegradability of biodiesel wastewater.

II. METHOD

A. Wastewater and Inoculums

Biodiesel wastewater was donated by Specialized Research and Development Center for Alternative Energy from Palm Oil and Oil Crops, faculty of engineering, prince of Songkla University.

It was help at 4 ^{o}C before experiment. The biological inoculum was collected from the palm oil industrial wastewater treatment plant. It was also kept at 4 o C until analysis and use.

B. Pretreatment method

The experiment was done in laboratory scale. For acidification process the 1 N HCl was used in this study. 1 L of wastewater was adjusted pH to be 3 and then was leave for 24 hr. After that the oil layer was separated by surface removal.

The treated wastewater in lower liquid phase was collected to be analyzed its chemical characteristics. Enzyme used in this study are produced by Pseudomonas fluorescens. The concentration used was 140 µg/ml of pretreated wastewater. The experiment was done at 40 o C and pH controlled at 8. The reaction time was 24 hr and the pretreatment wastewater was analyzed.

C. Biochemical methane potential (BMP) assay

The BMP batch experiments were investigated in 1 L reactor filled with 0.6 L of working volume. The temperature was controlled at 35 ^{o} C. The wastewater: Inoculum ratio was optimized by their variation from 1:0.1 to 1:1.5 (v/v). The initial pH was adjusted to be 7. The volume of biogas produced was measured once a day until the biogas was not produced anymore.

D. Analytical methods

The COD, BOD5, TS, SS, VSS, FFA, TKN, NH3-N, pH and O&G content were analyzed in according to the standard method for the examination of water and wastewater 22nd edition (WEF, AWWA, WEF, 2012). Protein of lipase is analyzed by Bradford method (1976). Enzyme activity analysis is done following Winkler and Stuckmann method (1979). Gas measured by displacement of water. Methane concentration in the biogas was measured by gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and helium was served as the carrier gas.

III. RESULT AND DISCUSSION

The characteristics of biodiesel wastewater was presented in table 1. The biodiesel wastewater is emulsified wastewater. Its discharged temperature was 40 ^{o}C. It contained high COD, TS and O&G. The BOD:COD ratio was 0.3 that can be suspected has it has low biodegradability.

III.I Characteristics of biodiesel wastewater after pre-treatment with acid and enzyme

Table 1 presented the characteristics of pretreated biodiesel wastewater samples and % impurities removal efficiencies by pretreatment methods.

Parameter	Biodiesel wastewater	After acidification	% remove	After enzyme pretreated	% remove
pH	12±0.15	3	75.00	8.05±0.07	32.92
TCOD	161,333±2,309.40	127,333±6,618.80	21.07	156,667±15,275.25	2.89
SCOD	118,889±9,924.60	114,000±5,000	41.08	96,000±8,000.00	19.25
SS	39,890±42.43	400±20	99.00	30,410±325.27	23.77
TS	134,565±200.75	40,168±10.61	70.15	40,040±169.71	70.24
VSS	12,748±267.32	5,535±21.79	56.58	10,735±403.05	15.79
O&G	17,140±4.00	810±5.00	95.27	3,662.5± 484.37	78.63
Alkalinity	6,158±12.02	-	100	22,150±353.55	*
VFA	952.1±8.84	1,350±70.71	*	17.5±3.54	98.10

Notation: The unit of parameters is mg/l, except pH.
:* Not remove but increase

The result showed that the addition of strong acid could charge the structure of composition in biodiesel wastewater reacts with acid, it will be transformed to be carboxylic acid and the small oil droplets was gathered to be larger droplets (Chen et al., 2000; Dukhin et al., 2001; Wengi et al., 2006; Ichikawa et al., 2007). When the oil droplets are large enough buoyancy to overcome the bonding forces between oil and water, it could float to the water surface. The combination of a lot of oil droplets on water surface would form oil layer that could be recovered. Hence the acidification resulted high reduction of O&G in biodiesel wastewater and also TS and SS. The pH of wastewater was decreased to be 3 because of acid addition, the COD had a few change, only 21.07 % of reduction but VFA was increased by 70.53%. These required the neutralization prior to the biological treatment or biogas system. The removal efficiencies obtained from enzyme pretreatment was lower than that of acid pretreatment. The O&G reduction was 78.63%. The COD, SS did not change but VFA was reduced by 98.10 %. But considering the VFA:alkalinity, it was found that the biodiesel wastewater pretreated by acid had not buffering capacity but the enzyme pretreatment degraded only O&G content while the wastewater composition did not change and still had high buffering capacity if it would be sent to biogas system.

III.II Methane production of pretreated biodiesel wastewater

The result from BMP assay for methane production showed the pretreated wastewater by acidification yielded higher methane production than that pretreated by enzyme and control respective. The biodiesel pretreatment with acid can enhance the Maximum accumulative methane (ml CH_4) most significantly when comparing with non-pretreatment wastewater.

The pretreatment by enzyme could increase methane production also but the methane produced was 28 times of that did not pretreated. This can be suspected that the useable substrate in the biodiesel for methanogenesis is organic content that suspend and dissolve in liquid phase after O&G removal. The oil content reduced by pretreatment step did not effect on methane production yield.

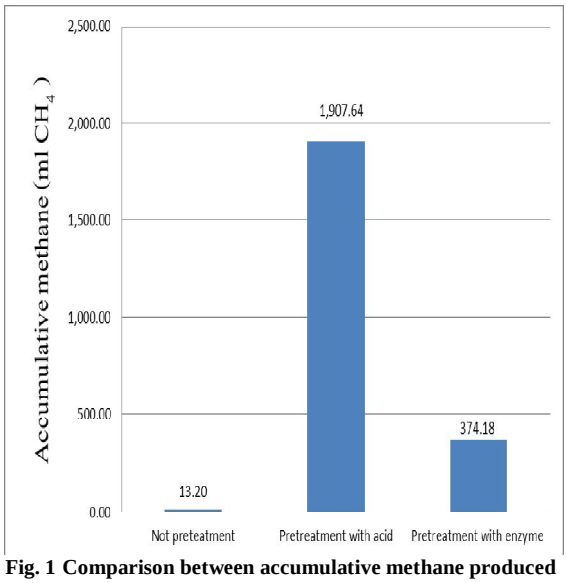


Fig. 1 Comparison between accumulative methane produced from biodiesel wastewater pretreatment with acid or enzyme and non- treated wastewater.

If comparing the methane production yield of wastewater inoculated with variation of wastewater:seed (v/v), if was found that the biogas volume and methane content increased with the increasing of the seed volume.

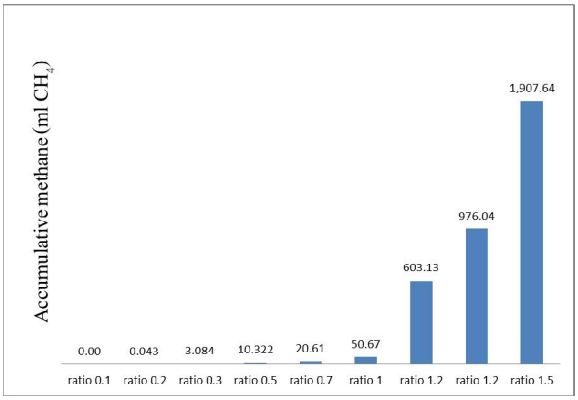


Fig. 2 The accumulative methane produced from the variation wastewater and acid ratios.

This cured by the high impact of seed composition on initial C:N ratio of substrate. The C:N ratio of biodiesel wastewater including that pretreated with acid was very high (300:1 approximately) that is imbalance of nutrients and result the unsuitable substrate for methane production. While the seed collected contains high nitrogen content therefore the increase of seed volume decreased C:N ratio to be close to suitable range. But the use of high volume of seed in the biogas system would not be practical; therefore the finding of nitrogen supplemental source for biodiesel co-digestion will be more appropriate.

CONCLUSION

The acid pretreatment gave higher efficiency in oil and grease removal than enzyme pretreatment and also BMP of pretreated wastewater. However, the enzyme pretreatment is low toxic and does not require neutralization prior biogas system. The methane production is satisfied from inoculated pretreated wastewater but the use of nitrogen rich substrate for co-digestion of biodiesel wastewater is necessary. The result from this study could be useful for biodiesel wastewater management after further up-scale experiment.

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