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Use of NMMO Pretreatment for Biogas Production from Oil Palm Empty Fruit Bunch

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***Abstract*—**Pretreatment of oil palm empty fruit bunch (OPEFB) with N-Methylmorpholine-N-oxide (NMMO) for enhancing biogas production was investigated. The pretreatments were performed at 90 and 120ºC for 1, 3, and 5 h using 73, 79, and 85% NMMO. The pretreated OPEFB was subsequently anaerobically digested to produce biogas. After the pretreatment, there were no significant changes of the main composition of OPEFB and the maximum total solid recovery was 92%. The amorphous phase was increased up to 78% at pretreatment condition using 85% NMMO solution for 3 h at 120°C. In general, higher concentration of NMMO and higher temperature resulted in increased amorphous form and higher biogas production. The best result of biogas production after the pretreatment was 0.408 Nm^3 CH_4/kg VS, which was 47.8% higher than that from untreated OPEFB.

***Keywords*—**Oil palm empty fruit bunch, pretreatment, NMMO, biogas.

I. Introduction

OIL palm empty fruit bunch (OPEFB) is a lignocellulosic waste of palm oil industry that can be used as feedstock for biogas production. In 2010, Indonesia had crude palm oil (CPO) production of 23.6 million tons with annual OPEFB production of 6.8 million tons (dry base) [1], [2]. Biogas is an energy source that nowadays is used for cooking, heating, electricity production, and after upgrading as car fuel (e.g. [3]). Hence, utilization of OPEFB for biogas production has benefits in both an environmental point of view by alleviating solid waste accumulation in palm oil industry and in the production of renewable energy.

One important step in the conversion of OPEFB to biogas is the pretreatment process. Pretreatment aims to render the cellulose fraction so that it can be easily degraded during anaerobic digestion. Pretreatment methods include physical, chemical, physico-chemical, and biological methods (e.g. [4]). Chemical pretreatments have shown to be very effective to increase digestibility of lignocellulosic materials for different purposes [5], [6]. In this work, the environmentally friendly solvent N-Methylmorpholine-N-oxide (NMMO) was used as the pretreatment reagent because it is non-toxic and can be recovered over 98% and reused [7]. NMMO has been proved to enhance biogas production from cellulose [8], rice straw, triticale straw, and softwood [9]. No literature was detected on pretreatment of OPEFB using NMMO for biogas pretreatment.

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II. Material and Methods

Oil palm empty fruit bunch were obtained from palm oil company in Medan, Indonesia. It was shredded, sun-dried until the water content was 10%, and ground to a particle size of 40 mesh.

NMMO (50% w/w solution) was provided by BASF (Ludwigshafen, Germany). This solution was vacuum-evaporated to 73%, 79%, or 85% concentrations. Prior to the pretreatment, propyl gallate 0.6 g/l was added in order to avoid NMMO degradation during pretreatment [10]. The pretreatments were performed by soaking 6 g OPEFB in 94 g of 73%, 79%, and 85% NMMO solutions for 1, 3, and 5 h at 90 and 120°C with stirring in every 15 min up to pretreatment time was over. Then, 150 ml of boiled-distilled water was added into the mixture immediately. The pretreated OPEFB was then separated from the mixture by vacuum filtration and washed using hot water until a clear filtrate was obtained. The pretreated samples were used to determine weight loss, volatile solid, glucan, lignin, and crystallinity.

Batch anaerobic digestion experiments were carried out in 120 ml-serum glass bottles at thermophilic condition (55ºC) for 50 days. The inoculum was obtained from a full-scale municipal solid waste digester, Sobacken (Borås, Sweden). Each bottle was filled with 27 ml of inoculum (0.4 g VS) and 3 ml of mixture of distilled water and NMMO-treated or untreated OPEFB as well as starch (Merck) as reference (0.15 g VS). Anaerobic digestion was also performed for blank sample that contained distilled water and inoculum. The anaerobic digestion experiments were run in triplicate.

National Renewable Energy Laboratory (NREL) Analytical Procedures were used to determine the total solid [11], glucan [12], acid insoluble lignin [13], acid soluble lignin [14], and ash [15]. The crystallinity was examined using FTIR spectrometer (Impact 410, Nicolet Instrument Corp., Madison, WI). Gas samples taken from the head space of glass digester were measured using GC (Varian 450-GC, USA).

III. Result and Discussion

A. Effect of Pretreatment on Composition of OPEFB and Structure

The untreated OPEFB contained 41.16% glucan, 28.43% acid insoluble lignin, 3.40% acid soluble lignin, 5.35% ash, and 21.65% of xylan. After being pretreated using 73, 79, and 85% NMMO for 1, 3, 5 h, the results showed that the composition of glucan, acid soluble lignin, and acid insoluble lignin remained relatively constant (data not shown). During the pretreatment, NMMO penetrates into microfibrils and affect the recalcitrant of the biomass to less crystalline structure while maintaining the composition of lignocellulosic material [16]. However, ash content decreased from 5.35% to 1.94%. The ash of OPEFB contains several salts and metal ions, such as calcium, sodium, copper, and iron which can dissolve in water [17]. The decrease in ash content could have been caused by the addition of water and washing after the treatment. After the pretreatment, the total solid recovery of OPEFB was relatively high in the range of 89% and 92%.

The structural changes in OPEFB were studied by FTIR. The absorbance band at 1427 cm^{-1} and 898 cm^{-1} are assigned to cellulose I (crystalline form) and cellulose II (amorphous form), respectively. The FTIR spectra of pretreated and untreated cellulose (cf. Fig. 1) shows a reduction in crystalline cellulose I and increasing in amorphous cellulose II. During the pretreatment, NMMO binds to the hydroxyl group at the 2^{nd} and 6^{th} carbons in glucose polymers [18].

TABLE I
Total Crystallinity Index

Temperature (°C)	Concentration of NMMO (%)	Time (h)	Total Crystallinity Index
90	73	1	0.60±0.07
		3	0.70±0.05
		5	0.65±0.03
	79	1	0.67±0.16
		3	0.66±0.05
		5	0.62±0.01
	85	1	0.57±0.03
		3	0.57±0.05
		5	0.58±0.11
120	73	1	0.57±0.03
		3	0.62±0.01
		5	0.61±0.08
	79	1	0.58±0.02
		3	0.60±0.07
		5	0.61±0.01
	85	1	0.70±0.05
		3	0.55±0.05
		5	0.57±0.03
Untreated OPEFB			2.50±0.08

When NMMO is removed during the washing, these chains will form a new bond in a reorganized state [19]. These phenomena might explain why crystalline cellulose of OPEFB was changed to the amorphous form after NMMO pretreatment.

Quantitatively, the degree of crystallinity is expressed by total crystalinity index (TCI), which was calculated based on the absorbance ratio A1427/A898 (Table I). The TCI of OPEFB which was treated with 73% and 79% of at 120ºC was lower than that of with 73% and 79% at 90ºC. The best results were obtained when 85% NMMO solution was used. The pretreatment condition at 120ºC using 85% NMMO

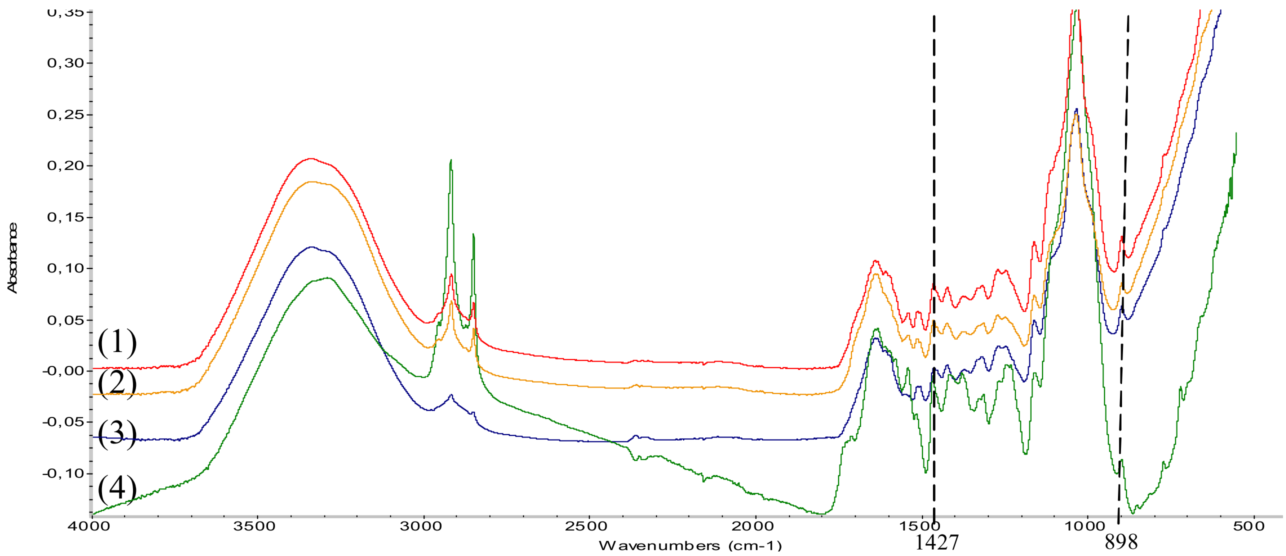

Fig. 1 FTIR spectra of pretreated and untreated OPEFB at 120ºC. The spectra are for (1) 1 h, (2) 3 h, (3) 5h pretreatment, and (4) untreated

solution for 3 h resulted in the lowest TCI. By comparing TCI between the untreated OPEFB and the pretreated OPEFB with the lowest TCI, it can be calculated that the increase of the amorphous part was achieved up to 78%.

B. Biogas Production

All pretreated and untreated OPEFB were subjected to anaerobic batch digestion. Enhancement of methane yield was obtained for pretreated OPEFBs compared to the untreated one. In general, the methane yields from the pretreated OPEFBs using NMMO at 85% were relatively higher compared to that of at 73% and 79% NMMO (data not shown). The highest methane yield was 0.408 Nm^3 CH_4/kg VS after OPEFB was treated with 85% NMMO solution for 3 h at 120°C. This value was an enhancement by 47,8% compared to methane production of 0.276 Nm^3 CH_4/kg VS from the untreated OPEFB and this value corresponds to 94% digestion compared to methane production of 0.443 Nm^3 CH_4/kg VS from starch which was used as reference for 100% digestion.

The values of methane yield from the untreated and pretreated OPEFBs were in good agreement with results from other studies using lignocellulosic materials. For example, untreated paper tubes could produce 0.238 Nm^3 CH_4/kg VS and after steam explosion with the addition of chemicals the paper tube residuals were reported to produce methane up to 0.493 Nm^3 CH_4/kg VS [20]. Meanwhile, the use of NMMO to pretreat cotton linter for ethanol and biogas production showed that pretreatment using 73% NMMO could improve the biogas production to 0.413 m^3 CH_4/kg VS in 15 days digestion [8]. It was an enhancement by 17% compared to 0.353 m^3 CH_4/kg VS from the untreated cotton linter.

TABLE II
METHANE PRODUCTION PROFILE FROM OPEFB TREATED WITH 85%NMMO

Pretreatment condition		Methane production profile					pH
Temperature (°C)	Time (h)	Initial rate[a] (Nm^3CH_4/kg VS/day)	Yield (Nm^3 CH_4/kg VS)	Ratio yield[b] (%)	Ratio Enhancement[c] (%)	$\%CH_4$[d]	
90	1	0.008±0.000	0.326±0.045	75.1	18.1	47.7	8.09
	3	0.011±0.000	0.360±0.000	81.3	30.4	48.4	8.17
	5	0.014±0.001	0.404±0.007	93.1	46.4	46.3	8.19
120	1	0.023±0.000	0.330±0.000	74.5	19.6	56.9	8.28
	3	0.030±0.003	0.408±0.000	94.0	47.8	55.0	8.27
	5	0.027±0.002	0.345±0.017	79.5	25.0	54.8	8.30
Untreated		0.012±0.003	0.276±0.002	63.6	0.00	55.4	8.26

[a]Methane production rates during the first 10 days

[b]Ratio of yield (%) $= \frac{\textit{Yield of methane production from pretreated OPEFB}}{\textit{Yield of methane production from Starch}} x100\%$

[c]Ratio of enhancement (%) $= \frac{(\textit{Yield of methane production from pretreated OPEFB} - \textit{Yield of methane production from untreated OPEFB})}{\textit{Yield of methane production from Untreated}} x100\%$

[d]% CH_4 $= \frac{\textit{Volume of methane}}{\textit{Volume of methane and carbondioxide}} x100\%$

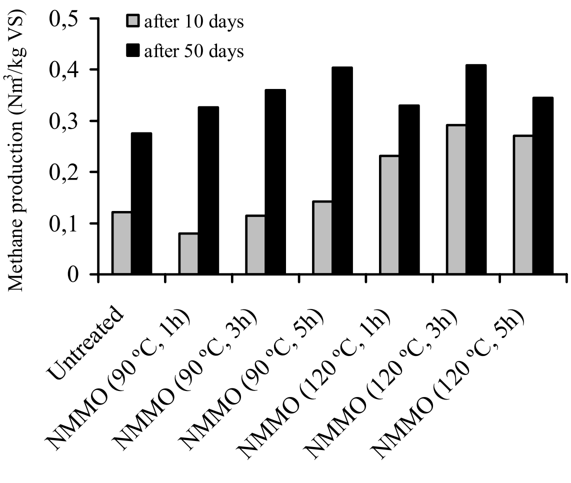

Fig. 2 Accumulated methane production (Nm^3/kg VS) after 10 (gray bars) and 50 days (black bars) of digestion from untreated OPEFB and treated OPEFB using 85% NMMO

Fig. 2 and Table II show the methane production and its values from the pretreated OPEFBs using 85% NMMO at 90ºC and 120ºC. It can be observed that higher pretreatment temperature accelerated the initial biogas production rate that was measured during the first 10 days of anaerobic digestion. In this study, high enhancement in methane yield was achieved using 85% NMMO, which gave low crystallinity index (Table I) of the pretreated OPEFB. It is in line with the data presented in previous reports [21], showing that the presence of high amount of amorphous phase increased the degree of enzymatic hydrolysis rate. The amorphous celluloses provide larger accessible surface area and an easily-attacked substrate for the enzyme of hydrolytic bacteria, allowing the hydrolysis process to be performed faster. This would lead to increased digestibility of OPEFB and increased accumulated methane production.

IV. CONCLUSION

Pretreatment with NMMO is effective to enhance the digestibility of OPEFB and the methane yield during the following biogas production. Major advantages of NMMO pretreatment that have been proved by this work are a) the composition of OPEFB after pretreatment did not change significantly b) small weight loss was detected after the treatment c) the treatment resulted in decreasing crystallinity of cellulose with increasing amorphous phase of OPEFB.

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