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Pretreatment of oil palm empty fruit bunch (OPEFB) by *N*-methylmorpholine-*N*-oxide (NMMO) for biogas production: Structural changes and digestion improvement

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HIGHLIGHTS

- ▶ Oil palm empty fruit bunch was pretreated by NMMO.
- ▶ The pretreatment was performed at 90, 120 °C for 1, 3, 5 h using NMMO 73%, 79%, and 85%.
- ▶ The pretreatment increased the amorphous phase of OPEFB's cellulose up to 78%.
- ▶ Methane yield was improved up to 98.3% compared to the theoretical yield.

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ABSTRACT

Pretreatment of OPEFB (oil palm empty fruit bunch) by NMMO (*N*-methylmorpholine-*N*-oxide) on its subsequent digestions was investigated. The pretreatments were carried out at 90 and 120 °C for 1, 3, and 5 h in three different modes of dissolution (by 85% NMMO solution), ballooning (79% NMMO solution), and swelling (73% NMMO solution). The total solid recovery after the pretreatment was 89–94%. The pretreatment process did not have a major impact on the composition of OPEFB, other than a reduction of ash from 5.4% up to 1.3%. The best improvement in biogas production was achieved by a dissolution mode pretreatment of OPEFB, using conditions of 85% NMMO, 3 h, and 120 °C. It resulted in 0.408 Nm^3/kg VS methane yield and 0.032 Nm^3 CH_4/kg VS/day initial methane production rate, which correspond in improving by 48% and 167% compared to the untreated OPEFB, respectively.

1. Introduction

Biogas is a promising alternative energy source that can be used for different applications in heating, cooking, electricity production, vehicle fuels. 1 m^3 of biogas is approximately equivalent to 0.65 l fuel oil (ECO2L, 2011), depending on its methane content. Biogas production from various waste substrates is performed by different groups of anaerobic bacteria in a series of biochemical reactions including hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The ultimate products are methane and carbon dioxide, and a solid residue "digestate", which is a nutrient-rich product used as fertilizer (Seppälä et al., 2009). Biogas can be produced from a variety of available carbon sources such as manure, wastewater sludge, crops residuals, biological fractions of municipal wastes and lignocellulosic materials.

Oil palm empty fruit bunch (OPEFB) is a solid lignocellulosic waste generated as a byproduct of the palm oil industry. Annual world production of OPEFB in 2011 was approximately 14.5 million tons (dry base), where half of this amount was produced in Indonesia (USDA, 2012; DOA, 2006). OPEFB was previously considered as feedstock for production of a variety value-added products, such as citric acid (Bari et al., 2009), xylose (Zhang et al., 2012), activated carbon (Alam et al., 2009), butanol (Noomtim and Cheirsilp, 2011), hydrogen (Ismail et al., 2012), bio-oil (Abdullah and Gerhauser, 2008), ethanol (Jung et al., 2011), and biogas (Nieves et al., 2011).

In addition to cellulose, hemicellulose, and lignin, OPEFB is rich in inorganic elements such as silica and metal ions e.g. copper, calcium, manganese, iron and sodium (Law et al., 2007). The cell walls of OPEFB fibers are much thicker than hardwoods e.g. aspen, and as

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a result, OPEFB has a relatively high coarseness and rigidity index (Law and Jiang 2001). OPEFB fibers are considered to be difficult materials to digest. Therefore, pretreatment can significantly enhance their digestibility. The pretreatment can be performed by physical methods such as milling, thermal treatment, steam explosion, or by chemical methods e.g. acid or alkaline treatment, ammonia and carbon dioxide pretreatment as well as oxidative agents (Hendriks and Zeeman, 2009). Previous works on OPEFB pretreatment were conducted using chemical agents (Nieves et al., 2011; O-Thong et al., 2012), which could not be regenerated, resulting in a potentially negative impact on the environment.

NMMO (*N*-methylmorpholine-*N*-oxide) is nowadays used commercially for the spinning of cellulosic fibers (Lyocell process) in the textile industry. One of the main benefits of using NMMO is to develop an economically feasible and environmentally friendly process for the pretreatment step prior to biogas production. NMMO is a non-toxic solvent and can be recycled with up to 98% recovery (Hall et al., 1999). The cellulose could be dissolved using NMMO by breaking hydrogen bonds between the cellulose chains (Wendler et al., 2008). This chemical penetrates into the crystalline areas of cellulose, and new bonds are formed between NMMO and the cellulose (Cuissinat and Navard, 2006). Anti-solvent, usually water, could regenerate the cellulose by rapid precipitation (Kuo and Lee, 2009). By using NMMO in this way, the cellulose structure can be converted from a crystalline form into an amorphous form. Taking advantages of the NMMO characteristic, this solvent was used as chemical agent to pretreat OPEFB in this study. In a similar work, Teghammar et al. (2012) was able to improve biogas production from spruce, triticale, and rice straw up to 95%, 87%, and 79% of the theoretical yields, respectively.

In this work, the effects of NMMO pretreatment on OPEFB at different concentrations and temperatures were evaluated. The pretreated OPEFB was then used as a feedstock for anaerobic digestion, in which the effects of the pretreatments on the biogas production was evaluated.

2. Methods

2.1. Oil palm empty fruit bunch (OPEFB)

The OPEFB solid waste was obtained from an oil palm mill in Medan, Indonesia. It was sun-dried to achieve 6.5% moisture content, then shredded, ground, and sieved to achieve a particle size of 0.42 mm, and stored at room temperature before being pretreated.

2.2. NMMO pretreatment

OPEFB was pretreated using 73%, 79%, and 85% w/w NMMO solution (BASF, Ludwigshafen, Germany). The commercial NMMO (50% w/w in aqueous solution) was first concentrated to 73%, 79%, and 85%, using vacuum evaporator (Laborota 20, Heidolph, Schwabach, Germany) equipped with a vacuum pump (PC 3004 VARIO, Vacuubrand, Wertheim, Germany). Prior to the evaporation process, 0.6 g/l propyl gallate was added to the solution in order to avoid oxidation and degradation of NMMO during the pretreatment (Bang et al., 1999; Kim et al., 2006). Then, 6 g OPEFB was soaked in 94 g of 73%, 79%, and 85% NMMO solution, respectively, for 1, 3, and 5 h at 90 or 120 °C. During the pretreatment process, the mixtures of OPEFB and NMMO solution were stirred every 15 min. It was then terminated by adding 150 ml boiled deionized water to the suspension. The pretreated OPEFB was then separated by vacuum filtration and washed using hot water until a clear filtrate was obtained. Different analyses for the determination of weight loss, total and volatile solid content, crystallinity index, mode of swelling, and dimension of pretreated OPEFB fiber were carried out. The pretreated OPEFB was then used as feedstocks in the subsequent anaerobic digestion assays.

2.3. Anaerobic digestion

The batch anaerobic digestion experiments were carried out in thermophilic conditions (55 °C) using 120 ml-serum glass bottles (Hansen et al., 2004). Active inoculum was obtained from a full-scale municipal solid waste digester (Borås Energy and Environment AB, Borås, Sweden). Each bottle contained 27 ml of inoculum and 0.15 g VS (Volatile Solid) of NMMO-pretreated or untreated OPEFB. The VS ratio of the inoculum to substrate was 2.67. Blank samples were also prepared containing deionized water and inoculum. All these experiments were performed in triplicate and the accumulated methane production was determined under 50 days.

2.4. Analytical methods

The VS content of pretreated and untreated OPEFB was measured by determining total solid (TS) and ash content. The OPEFB was dried in an oven at 105 ± 3 °C to achieve a constant weight. For the ash determination, the OPEFB was placed in a muffle furnace and brought to a constant weight by igniting at 575 ± 25 °C (Ehrman, 1994). The acid insoluble lignin content and acid soluble lignin content of the OPEFB were determined according to the methods described by Templeton and Ehrman (1995) and Ehrman (1996), respectively. The fibers were hydrolyzed using a two-steps hydrolysis by 72% H_2SO_4 and followed by dilute sulfuric acid. After completion of the hydrolysis, the samples were filtered to separate the solid residue and the filtrate using a vacuum filter with a pore size of 15 µm. The aliquote was used for carbohydrate analysis and an acid soluble lignin analysis, while the residue was used for acid insoluble lignin analysis.

The crystallinity of the OPEFB was determined using Fourier transform infrared (FTIR) spectrometry (Impact 410, Nicolet Instrument Co., Madison, WI). The spectra were obtained with an average of 60 scans and a resolution of 4 cm^{-1}, in the range from 600 to 4000 cm^{-1} (Carrillo et al., 2004) controlled by Nicolet OMNIC 4.1 analyzing software (Jeihanipour et al., 2010). The swelling, ballooning, and dissolution of cellulose fibers were observed by optical microscopy. Gas samples taken during the anaerobic digestion assays were analyzed using a gas chromatograph (Varian 450-GC, USA) equipped with a capillary column (J&W Scientific GS-GasPro, 30 m × 0.320 mm, Agilent Technologies, USA) and a thermal conductivity detector (Varian, USA) with inject temperature of 120 °C. The carrier gas used was nitrogen operated with a flow rate of 2 ml/min at 75 °C using a split ratio of 10.

3. Results and discussion

The structural and compositional changes of oil palm empty fruit bunch (OPEFB) after pretreatment by NMMO were studied. The pretreated OPEFBs were then anaerobically digested to biogas in order to investigate the effect of NMMO pretreatment on the digestion. The results show that NMMO pretreatment did not change the major composition of OPEFB. However, the pretreatment resulted in several structural changes of OPEFB.

3.1. Effect of NMMO pretreatment on the composition and structure of OPEFB

OPEFB was pretreated using 73%, 79%, and 85% NMMO solution for 1,3, and 5 h at two different temperatures (90 and 120 °C). The chemical composition of OPEFB before and after pretreatment are