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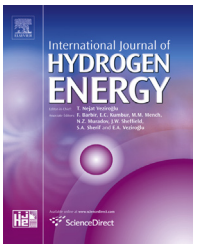

Optimization of bio-methanol production from goat manure in single stage bio-reactor

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ABSTRACT

Most of the previous studies only focused on either the production of biogas or liquid fuel, but this study introduces the production of bio-methane and bio-methanol in a batch bio-reactor. The optimization of the process was conducted via response surface method using Design Expert 6.0.10. Proximate and ultimate analysis of the solid waste from papaya peel, banana peel, vegetable waste, leftover rice, bagasse, pineapple peel, goat manure and poultry waste were conducted. The biogas content was analyzed using a gas chromatograph equipped with a thermal conductivity detector (GC-TCD), while bio-fuel was analyzed using High Performance Liquid Chromatography (HPLC). The screening test indicated that waste from goats fed grass and soy pellets was used for the bio-methanol production profiles because this biomass has the highest carbon (36.16%) and volatile solid (12.44 wt%) of the various tested biomass. From the profile analysis, the maximum value of bio-methanol produced is 2.49% with 74.24% of methane. The design of experiments shows that the actual bio-methanol concentration values vary from 0.51 to 5.19 gL^{-1}, and these values are not significantly different from the values (0.45–4.51 gL^{-1}) predicted by the model. The optimal conditions for the production of bio-methanol were temperature of 32.72 °C, 11 days of hydraulic retention time and 0.40 g/L cell concentration for the production of 6.80 gL^{-1} bio-methanol. The results showed that the goat manure had the most potential for bio-methanol production.

Introduction

Switching from fossil fuels to renewable energy could lead to positive impacts for most countries in the world, especially Malaysia, a country that faces a greenhouse gases problem [1], economic uncertainty from petroleum price fluctuations and potentially exhausted fossil fuel supplies within the next 20 years [2,3]. The expected population growth is 2% [4] and urbanization will increase municipal solid waste [5]. In 2007, the Northern and Southern Hemispheres released, respectively 1865 ppb and 1741 ppb of methane into the atmosphere [6,7]. These methane emissions have triggered a review of methane usage in the production of bio-methanol [8] by using low cost biomass as the feedstock [9].

About 100,000 tons of methanol used annually for the synthesis of other chemicals, electricity generation and as a transportation fuel (125 million liters) [10–12]. The flammability limit of methanol between 6 vol% and 36.5 vol%, and is

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higher than the flammability limit of gasoline (between 1 vol% and 7.6 vol%) [13]. The octane number of methanol (107) is also higher than that of gasoline (98) with energy density of 15.6 MJ L^{-1}, and stores more energy than hydrogen (8.49 MJ L^{-1}) [12]. Compared with biochemical route, thermochemical processes have several disadvantages. Namely among them are: 1) high energy consumption and are environmentally unfriendly [14–19]; 2) difficult to set up and the optimal temperature for fuel production differs depending on the type of biomass [20–23]; 3) promote low char yield that can corrode the equipment [24,25]; 4) bio-oil formed contain undesirable properties [26]. Thermochemical route in conversion of methane to methanol have been developed but fundamentally difficult to achieve under mild conditions [27–36].

Through biochemical route, methanotrophic bacteria that contain a methane monooxygenase (MMO) enzyme is used as it capable of activating the stable C–H bond under ambient conditions and easily found in animal waste, mud, sewage sludge, meadow soils and sediments [37,38]. To date, the biochemical route requires a high cost for the pre-treatment and production process due to the currently expensive enzyme price and inefficiency with respect to enzyme usage [39,40]. These barriers prevent the biochemical process from progressing towards commercialization. Therefore the biomass that already contains methanotrophic bacteria can be used as feedstock to form methane and bio-methanol without using single bacteria. The methane and bio-methanol accumulate were depended on environment factors such as pH, cell concentration, temperature and time for fermentation. Note that maximum yield of bio-oil the most effective temperature for methanogens activity were between 30 °C and 37 °C, at pH value 6 to 8, with duration time 0–20 days [41,42] and low cell concentration caused decreased in cell activity to form other product [38].

Thus, the main objective of this study is to optimize the production of bio-methanol from biomass via fermentation using a laboratory bioreactor. This study proposes an effective way to produce bio-methanol, specifically, the oxidation of methane that is formed by methanotrophic bacteria present in solid waste utilizing oxygen from the atmosphere. This study develops a fermentation lab scale reactor that produces methane from solid waste and the methane from this reaction is used as a feedstock for the production of bio-methanol in a single step. Moreover, the biochemical reactions occur in a mixed culture of bacteria, not in single culture bacteria; therefore, factors such as special medium and cell cultivation requirements and enzyme purification are not significant. Next, this paper determines the significant factors affecting the production of bio-methanol in the small scale reactor. Finally, parameters such as temperature, time and cell concentration are optimized using Response Surface Methodology and Design Expert 6.0.10.

Methodology

Sample preparation

Several types of solid wastes were chosen from agricultural waste such as pineapple peel, vegetable waste, bagasse, banana peel and papaya peel. In addition to those waste products, leftover rice, goat manure and poultry waste were selected for this experiment. Goat manure was selected based on different types of feeding, either feeding with palm leaves or grass and soy pellets. Goat manure and poultry waste were supplied from livestock locations at Dengkil and Banting, Selangor MALAYSIA. Agricultural waste and leftover rice were supplied from the market Shah Alam, Selangor, MALAYSIA. The physical pre-treatment process was conducted by grinding all of the samples into small sizes less than 5 mm. This mechanical pre-treatment process aims to reduce the crystallinity of cellulose in order to improve the digestibility and fermentation of the various types of biomass [43].

Proximate and ultimate analysis

Proximate analysis was performed to determine the total solid and moisture contents according to ASTM E949-88 [44], while volatile matter was determined according to ASTM E897-88 [45] using the Froilaba AC240 oven available in the Chemical Engineering laboratory, Universiti Kebangsaan Malaysia (UKM). In order to determine the total solids and moisture content, 3 g of each sample was heated at 110 °C for 30 min. Determining the volatile matter required heating the samples at high temperature (950 °C) for 10 min. After high-temperature heating, the ash content and fixed carbon were determined by procedures ASTM E830-87 [46] and ASTM D5681-98a [47]. The sample was dried to constant weight according to ESS Method 340.2 [48] before the sample elements were analyzed. A *ThermoFinnigan* (Italy) brand instrument (CHNS-O EA1112) was used to analyze the percentage of elements in the sample, specifically carbon, hydrogen, nitrogen, sulfur and oxygen. This instrument was from the Faculty of Science and Technology, UKM.

Batch bio-reactor

Fermentation conditions were established using an innovative batch glass bio-reactor (2 L) that included a *Daiichi Denko* brand air heater (240 V), temperature probe (0–50 °C), pH probe and fluorescence lamp. The set up of apparatus for batch bioreactor is shown in Fig. 1 where the sample used in each fermentation test was 200 g. The sample was mixed together with water in ratio 1: 3, then remained in the reactor for 44 days and after 4 days of operating time, the biogas was collected using the gas bag and the liquid product was analyzed. The temperature was maintained at 29 °C for the 44-days experiment. Before the experiment, approximately 1 g of sodium hydroxide (NaOH) was added into the sample feed and the bio-reactor was closed with a stainless steel flange (outside diameter: 12 cm). This system had four channels. The first channel was the biogas collection channel that emptied into measuring cylinder (1000 ml) containing water, and the second channel was for sample inlet and outlet. This second channel also used to inject 30 mL of air inside the bioreactor every time after sample was taken. Then for the other two channels are for temperature and pH probe inlet. Biogas quantity was determined by the water displacement technique, according to the principle of Mariotte [49], who stated

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