## ARTICLE IN PRESS

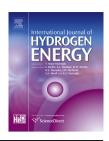
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## Determination of bio-methanol as intermediate product of anaerobic co-digestion in animal and agriculture wastes

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### ABSTRACT

Many researchers have reported on the end products of the anaerobic digestion process as biogas and methane but the useful intermediate products in the anaerobic digester effluent, such as bio-methanol have typically been ignored. Bio-methanol is an auspicious substitute for fossil fuels with a variety of fuel applications and advantages with regard to the environment, the economy, and consumers. Thus the main objective of this study is to investigate the intermediate product of anaerobic co-digestion of animal and agriculture wastes. The wastes are characterized based on proximate and ultimate analyses. This study was conducted in a room temperature, lab-scale reactor with a fixed retention time. Methanol was analyzed using high-pressure liquid chromatography (HPLC). It was observed that, banana peel (61.51 wt.%) and boiled rice (81.25 wt.%) substrates with cow dung inoculum have the greatest potential for bio-methanol production via anaerobic co-digestion. This study proves that the methanol exists as intermediate product of anaerobic co-digestion. Finally, this study concludes that by enhancing the production of methanol at intermediate phase can reduce the production of methane gas.

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## Introduction

Fossil fuels have become an important source of energy in the last 20 years and account for 80.9% of the total world energy supply [1]. However, fossil fuel use is responsible for the emission of atmospheric pollutants, including greenhouse gases [2]. In Malaysia, population and economic growth as well as the increasing demand for energy have triggered a

search for alternative energy sources. Renewable energy is expected to become an important source of energy and will contribute 18% of the global energy supply by 2030 [3]. Switching from fossil fuels to renewable energy brings positive impacts such as reduced emissions of toxic and greenhouse gases, a greener environment and healthier community, as well as the promise of a sustainable future. Although renewable technology currently incurs high development and management costs for large-scale energy and

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renewable material production, further research to develop cheap, clean and eco-friendly products is underway.

Methanol has attracted attention as an alternative transport fuel when blended in various proportions and is currently under consideration for wider use [4]. Methanol that falls into the liquid biofuel category is currently under development by researchers. The steadily increasing prices of crude oil and petroleum have increased the viability of commercial-scale biofuel production. Methanol is a major feedstock in the petrochemical industry and has recently been considered as an emerging renewable liquid transportation fuel and a replacement for non-renewable fossil fuels. Alcohol fuels from methanol have been well known in the racing community for years because of their safety and performance advantages compared to gasoline as well as their higher octane number, which offers a slight edge in power compared to ethanol [5]. Agarwal et al. [6] studied on methanol-gasoline blended fuel in a medium duty spark ignition transportation engine and it was found that the gasohol emitted lower CO, NO and smoke than gasoline, combustion characteristic of gasohol blends are similar to gasoline and suggested that the methanol can be excellent substitute for gasoline for transportation engines without any hardware amendment. Besides that, methanol can also be used as a source of energy for direct methanol fuel cell, a type of proton exchange membrane fuel cells (PEMFCs) which can be used for portable electronics and vehicle applications due its benefits of cheap, small, ecofriendly and able to replace conventional batteries in the future [7,8]. Based on from the research conducted by Rashidi et al. [9], it is remarkable to found that DMFC system is lowcost, occupies less space than Li-ion battery to store energy and higher exegetic efficiency of DMFC causes less emissions of carbon dioxide.

The majority of the methanol produced for commercial applications is synthesized through the pyrolysis conversion pathway to synthesis gas (syngas). However, the feedstocks may vary. Pyrolysis is a thermal decomposition process in which organic matter in the biomass is converted into bio-oil (methanol) in the absence of oxygen or in an atmosphere containing significantly less oxygen than is required for complete combustion [10,11]. These processes are characterized by high energy consumption, low conversion efficiency rates, and high capital costs [12]. However, bio-methanol can be produced via a cheaper process that consumes less energy and space by anaerobic digestion.

Many researchers have conducted research on the yield of valuable products and by-products that can be extracted or produced through the anaerobic digestion of biomass, solid waste, or sewage. Wang & Blaschek [13] studied the fermentation of mixed sugar from tropical maize stalk juice with Clostridium beijerinckii NCIMB 8052 to produce butanol. Zhu et al. [14] studied anaerobic co-digestion of municipal food waste and sewage sludge for the production of biohydrogen. Sharma et al. [15] were successful in the increased production of biogas and methane by anaerobic co-digestion of poultry litter and thin stillage in a pilot-scale thermophilic continuous stirred tank reactor (CSTR). Liu et al. [16] conducted a research study on the anaerobic co-digestion of municipal biomass waste and dewatered sewage sludge and achieved a stable operation with high biogas production. Anaerobic mesophilic

co-digestion of pig manure and glycerin was studied by Astals et al. [17], who found that, interestingly, co-digestion increased methane production. Rivero et al. [18] investigated on anaerobic co-digestion of mixed sewage sludge and crude glycerol from biodiesel industry at mesophilic condition in a laboratory scaled semi-continuous CSTR, found that high removal of volatile solids, the hydrogen and methane yield enhanced significantly. Although many researchers have reported on the manufacture of end products of the anaerobic digestion process, particularly biogas and methane [19–21], the useful intermediate products in the anaerobic digester effluent, such as bio-methanol, have typically been ignored. Bio-methanol is an auspicious substitute for fossil fuels with a variety of fuel applications and advantages with regard to the environment, the economy, and consumers.

Thus, this work is an exploratory study of bio-methanol as intermediate product via anaerobic digestion. In this work, anaerobic digestion of different types of bio-solids was investigated using laboratory-scale reactors. The main objective of this study was to determine the bio-methanol yields for the solid-state digestion of different livestock and agricultural wastes via anaerobic digestion.

The anaerobic digestion of bio-solids involves biological conversion of soluble, dissolved organic matter into biogas (methane and carbon dioxide), alcohols (bio-methanol and other higher molecular weight alcohols), volatile fatty acids and nitrogen-rich organic residues. Anaerobic digestion offers many benefits, including low levels of biological sludge, high efficiency, and low nutrient requirements [22]. It is also an attractive waste treatment practice to control pollution and recover energy [23]. It is experimentally proven herein that the performance and yield of a digestion process can be improved when different wastes are mixed and digested together. This process is termed as anaerobic co-digestion. Anaerobic codigestion is a waste treatment method in which different wastes are mixed and treated together [24]. Co-digestion has been used to increase the yield of anaerobic digestion of organic waste. Cuetos et al. [25] have observed that codigestion stabilizes the bio-solid mixture in the bioreactor, increases the C/N ratio and reduces the nitrogen concentration. Khalid et al. [26] stated that the utilization of cosubstrates with low nitrogen content promotes the production of biogas because the different features of each type of waste are complimentary, thus reducing the problems associated with single-substrate anaerobic digestion, including the accumulation of volatile compounds and high ammonia concentrations. The recent research conducted by Miao et al. (2014) [27] to evaluate methane production by co-digestion at different inoculum to substrate ratios (ISRs) of Taihu blue algae and swine manure. The results indicated that codigestion of blue algae and swine manure at produced high methane yield than the digestion of blue algae inoculated with granular sludge.

Besides, poorly managed and untreated animal manure can become a major cause of water and air pollution. Livestock sector releases about 14.5% of total global greenhouse emissions, which is more than direct emissions from the transport sector [28]. Manure can be a beneficial resource for the production of renewable energy and as a source of nutrient-rich agricultural fertilizer [29]. Glucose and other

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