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Process enhancement of hydrogen and methane production from palm oil mill effluent using two-stage thermophilic and mesophilic fermentation

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ABSTRACT

The present study investigates the technical possibilities of hydrogen and methane production from palm oil mill effluent (POME). The production was carried out in two stage (thermophilic and mesophilic) continuous phase with recirculation of the digestate sludge. The reactors used for the present study, up-flow anaerobic sludge blanket reactor (UASB) and continuous stirred tank reactor (CSTR) were operated under thermophilic and mesophilic conditions, respectively. The UASB reactor was operated at 2 days hydraulic retention time (HRT) and 75 kgCOD m³ d⁻¹ organic loading rate (OLR) for hydrogen production. The effluents from UASB reactor containing mainly with acetate and butyrate were directly fed into CSTR for methane production and 5 days HRT was maintained. Both UASB and CSTR reactors were operated for 120 days continuously, and a stable production of the hydrogen and methane was obtained in the separate reactors. The maximum hydrogen and methane production rate achieved was 1.92 L H₂ L⁻¹ d⁻¹ and 3.2 L CH₄ L⁻¹ d⁻¹, respectively. The cumulative hydrogen and methane yields were 215 L H₂/kgCOD⁻¹ and 320 L CH₄/kgCOD⁻¹, respectively with the total COD removal efficiency of 94%. *Thermoanaerobacterium* species was dominant in hydrogen reactor, while methane reactor was dominated with *Methanobrevibacter* sp.

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List of abbreviation

POME	Palm Oil Mill Effluent
UASB	Up-flow Anaerobic Sludge Blanket
CSTR	Continuous Stirred Tank Reactor
HRT	Hydraulic Retention Time
OLR	Organic Loading Rate
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
VFA	Volatile Fatty acids
TS	Total solids
VS	Volatile Solids
VSS	Volatile suspended solids
TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector
HPP	Hydrogen Production Potential
MPP	Methane Production Potential

Introduction

In recent times, hydrogen has captured an extraordinary consideration as a potential fuel for transport purposes and power generation [1]. Hydrogen is considered to be a promising and sustainable energy carrier of the future. It has a high heating value of 142 kJ/g and it doesn't release any greenhouse gases during combustion [2]. Conventional methods such as water electrolysis, steam reforming, and coal reforming are energy intensive (>840 °C) and non-eco-friendly [3]. In an attractive dark fermentation, maximum yield of 12 mol hydrogen per mole of glucose can be achieved at ambient temperature and atmospheric pressure using organic wastes [4]. Various waste materials such as starch and cellulose waste water, food waste, dairy waste, skim latex, kitchen waste water, and POME is being exploited as a renewable-energy source [5]. As per conservative estimates, the POME produced in Indonesia and Malaysia is more than 50 million m³/year, which is equivalent to power generation capacity of 800 GW [6]. The POME is rich in BOD, COD, proteins, lipids, nitrogenous compounds and minerals. The production of hydrogen from such organic waste is an ideal strategy in achieving the dual benefits of waste stabilization and energy recovery [7].

Usually, the hydrogen production is always accompanied by volatile fatty acids (VFAs) production such as acetate, butyrate, propionate and ethanol that are more appropriate substrates for methane (CH₄) production further in the second-stage [8]. Therefore, methane production is well considered as a suitable post-treatment unit of hydrogen production. In recent times, a two-stage process combining hydrogenesis and methanogenesis has been a focused technology. The significance of two-stage process includes, process stability, higher biogas yield, and high total energy recovery. Evidently, Cavinato et al. [9] compared the single-stage process with two-stage fermentation of organic waste and reported that overall energy recovery from two-stage was higher than single-stage fermentation. Likewise, Antonopoulou et al. [10] showed a feasibility of two-stage fermentation using sweet sorghum with a hydrogen yield of 10.41 L H₂/L

sweet sorghum and a methane yield of 29 L CH₄/L sweet sorghum utilizing dark fermented residues as a sole substrate in the second stage.

The UASB reactors are specifically designed for the anaerobic digestion, and it can handle high OLR, short HRT digestion of many organic wastes that may contain high undissolved solids. While, CSTR runs at a steady state with a continuous flow of reactants and products. It has good temperature control, continuous operation and high methane recovery [11]. However, hydrogen and methane yield is mainly affected by the environmental factors such as HRT, pH, and temperature. Sompong et al., [12] studied hydrogen production from palm oil mill effluent at 60 °C using *T. thermosaccharolyticum* PSU-2 species. In their study, it was observed that biogas production rate and hydrogen yield was affected by the HRT, pH, temperature and the substrate concentration utilized. Generally, the HRT for hydrogen and methane production using POME is 1–2 days and 10–15 days, respectively [13]. This implies that the reactor volume for methane production is about 5–6 times higher than hydrogen production. Hence, it is significant to develop the high-rate methane production system using POME. Normally, the optimum pH for hydrogen production is 5.5–6.0 and a large amount of sodium hydroxide, which is used for pH adjustment can increase the production cost as well [14]. The POME generated at a high temperature of around 80–90 °C from its source. Therefore, the biological conversion at thermophilic conditions eliminates the need for cooling systems. It favours thermodynamics system and maintains low hydrogen partial pressure [15]. In previous studies, successful hydrogen production from organic materials using single-stage fermentation under thermophilic condition was achieved by Noparat et al. [16]. They reported hydrogen production rate of 1973 ml H₂ L⁻¹POME using heat shocked sludge rich in *Clostridium* species at 55 °C with 3 days HRT in continuous stirred tank reactor.

Until now, the two-stage dark fermentation process has been operated with various types of organic waste, such as food [17], olive pulp [18] and red canary grass [19]. There is no published work in the development of a continuous sequential two-stage process for the hydrogen and methane production using POME as a substrate. Based on this information, herein we developed a two-stage process of hydrogen and methane production under thermophilic and mesophilic conditions using POME with an internal recirculation of the digestate sludge. The feasibility of support media polypropylene for the enhancement of methane production was also investigated for the first time to reduce the HRT in second stage methanogenic process.

Materials and methods**Preparation of inoculum**

The anaerobic sludge containing mixed microflora was collected from the bottom of the anaerobic pond at Felda palm oil industry, Lepar Hilir, Gombang, Malaysia. To enrich the sludge with hydrogen producing bacteria and inhibit the bioactivity of methanogens, the sludge was heat-treated at

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