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Production of hydrogen energy from dilute acid-hydrolyzed palm oil mill effluent in dark fermentation using an empirical model

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ABSTRACT

Hydrogen generation was studied using palm oil mill effluent (POME) as an agro-industrial waste obtained from the palm oil industry. POME was subjected to a dilute acid hydrolysis step by HCl (37% v/v) to release fermentable sugars from cellulosic content. POME hydrolysate obtained was used as a substrate for hydrogen generation. The composition of POME hydrolysate showed glucose and xylose were the main monomeric sugars liberated. Hydrogen production was performed in dark fermentation process, in which the new bacterial strain *Clostridium acetobutylicum* YM1 was cultivated on POME hydrolysate based on a central composite design (CCD). CCD was constructed by considering three pivotal process variables including incubation temperature, initial pH of culture medium and microbial inoculum size. An empirical model, namely second-order polynomial regression model was generated and adjusted to CCD data. The analysis of empirical model generated showed that the linear and quadratic terms of temperature had a highly significant effect on hydrogen generation ($P < 0.01$). Furthermore, the quadratic effects of initial pH value of culture medium and inoculum size had a significant effect on hydrogen production at 95% probability level ($P < 0.05$). The regression model also showed that the interaction effect between temperature and initial pH value of the culture medium on the hydrogen generation was highly significant ($P < 0.01$). The empirical model suggested that the optimum conditions for hydrogen production were an incubation temperature of 38 °C, initial pH value of 5.85 and inoculum size of 17.61% with predicting the production of a cumulative hydrogen volume of 334.2 ml under optimum conditions. In order to validate the optimum conditions determined, C.

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acetobutylicum YM1 was cultivated on POME hydrolysate in optimum conditions. Verification test results showed that a cumulative hydrogen volume of 333.5 ml and a hydrogen yield of 108.35 ml H_2/g total reducing sugars consumed were produced.

Introduction

The current world energy demand mostly depends on the utilization of fossil fuels. The huge consumption of the fossil fuels over the years has caused various detrimental effects on the environment such as global warming, air pollution and severe climate changes [1–3]. On the other hand, increasing consumption of the fossil fuel-based energy with the high fluctuation in oil prices entails renewable and clean sources of energy which are compatible with climate issues [3–5]. In this view, hydrogen has been known as a clean and environmentally friendly source of energy since its combustion results in water [6–8]. Hydrogen is an adaptable energy carrier with an energy yield of 112–142 kjg^{-1} which is approximately three times of that for fossil fuels [1,3,6,9]. At present, hydrogen is mostly produced by processing the fossil fuels to hydrogen leading to the high release of greenhouse gasses [10–12]. Hence, it is important to generate hydrogen by clean technologies using renewable sources to dwindle environmental pollution and production costs. Varied methods for hydrogen generation from non fossil fuels have already been employed including thermo-chemical and biological technologies. However, biological processes have been known as an environmentally friendly and low energy intensive approach compared to chemical processes since biological processes can be operated at a mild temperature and normal pressure [13–17]. In this context, a number of biological processes have been utilized such as photo fermentation, dark fermentation, biophotolysis and water-gas shift reactions [18–24].

Dark fermentation is a biological process in which hydrogen-producing microorganisms grow on carbohydrate-based substances to generate hydrogen gas in anaerobic conditions under the lack of light [25]. It has been found that theoretically a maximum of 4 mol and 3.33 mol of hydrogen can be produced from one mol of glucose and xylose, respectively in dark fermentation in which acetic acid is the main fermentation metabolite [26,27]. Dark fermentation could be operated in various temperatures including mesophilic (25–40 °C), thermophilic (40–65 °C), extreme thermophilic (65–80 °C) and hyperthermophilic (>80 °C), depending on the microorganisms used [9,28,29]. A variety of bacterial strains have been found to convert carbon sources to hydrogen in dark fermentation process such as *Escherichia*, *Clostridia* and *Enterobacter* [15,30–32]. Bacteria of genus *Clostridium* are known as the main hydrogen-producing microorganisms in dark fermentation, which generate hydrogen from sugar-based substrates [33–37].

Dark fermentation offers several cost-effective advantages including the less time needed for hydrogen production by the quick growth of microorganisms in the culture, a low energy requirement for the systematic control of hydrogen production, utilization of cheap waste materials with adverse impacts on the environment, easy methods used in practical experiments and lessened environmental prerequisite requirements [38].

Different sugar and carbohydrate sources including glucose, xylose, sucrose, lactose, molasses and starch have been utilized for anaerobic fermentative hydrogen production [39–44]. In this regard, lignocellulose represents the most renewable source of fermentable sugars for hydrogen-producing bacteria to utilize them as an energy source in dark fermentation [3,45]. Lignocellulose is mainly composed of three polymeric components including cellulose, hemicellulose and lignin [46–48]. In order to liberate fermentable sugars from lignocellulose, the recalcitrant structure of lignocelluloses should be depolymerized to release soluble monomeric sugars from cellulose and hemicellulose components [49].

Production of oil from palm fruit is the main industry in Malaysia so that a total amount of 19,961,581 tons of crude palm oil was produced in Malaysia during 2015 [50]. Palm oil mill effluent (POME) is known as the liquid waste which is produced during the palm oil extraction process in the palm oil industry [51]. It has been estimated that 15.2 million tons of POME is annually produced in Malaysia. However, the huge production of POME deleteriously influences environment due to its high organic matters which show toxic characteristics. On the other hand, POME comprises of a mixture of carbohydrates. It has been found that the raw POME contains 38.36% cellulose and 23.21% hemicellulose and 26.72% lignin which represent a low-cost cellulosic substrate for the sustainable production of bio-based energy [52,53].

In this view, the dilute acid hydrolysis method has been found as an efficient method for liberating fermentable sugars including pentose (xylose) and hexose (glucose) using lignocellulosic substances [54–57]. It has well been established that hydrogen generation in the dark fermentation process is influenced by environmental parameters such as incubation temperature, initial pH of the culture medium and microbial inoculums. Hence, the optimization of the operating conditions is necessary to obtain the maximum hydrogen production [15,58–60]. In order to study the effects of process parameters, design of experiment techniques could be employed using different mathematical models such as factorial design, linear regression, taguchi method and response surface methodology (RSM) to further optimize operating conditions [61].

Response surface methodology (RSM) is known as a statistical method which is used in the generation of an empirical model to assess the effects of operating process parameters

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