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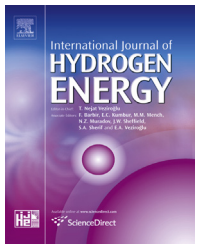

Crude glycerol by transesterification process from used cooking oils: Characterization and potentialities on hydrogen bioproduction

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ABSTRACT

This study evaluated the potential bioconversion of crude glycerol from biodiesel production, applying used cooking oil for biohydrogen production by fermentative bacteria consortia. The pretreatment of crude glycerol was made by pH adjustment. Heat treatment of the inocula and initial pH 5.5 were applied to select hydrogen-producing bacteria and inactivate hydrogen-consumers microorganisms. The inocula tested were: (I) granular sludge from the thermophilic UASB reactor used on the treatment of vinasse and (II) granular sludge from the UASB reactor used on the treatment of sanitary sludge for the assays (1) and (2), respectively. The characterization of crude glycerol presented high levels of alkalinity, methanol and soap that may be inhibitory to biologic processes of H_2 production. The assays were carried in anaerobic batch reactors in order to verify the efficiencies of crude glycerol to H_2 generations by the microbial consortia (20%) at 37 °C, initial pH 5.5, with 20.0 g COD L^{-1} glycerol. The cumulative production of hydrogen for the assays (1) and (2) were, respectively, (mmol H_2 L^{-1}) 28.49 ± 1.55 and 19.14 ± 1.67. The subsequent yields were obtained as follows: 2.2 moL H_2 mol^{-1} glycerol and 1.1 moL H_2 mol^{-1} glycerol, respectively. The used cooking oil was an efficient waste for bioconversion of crude glycerol to H_2 production.

Introduction

Biodiesel is an alternative fuel and a renewable energy source, due to its availability of feedstock, for its requiring a very simple technology for its production and its role in greenhouse gases reduction [1,2]. The global biodiesel production has increased significantly with an average annual growth of 42% and is expected to reach 37 billion gallons by 2016 [3]. Conventionally, triglycerides are employed for biodiesel

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production, such as virgin vegetable oils and animal fats, that are mixed with methanol and sodium hydroxide through catalyst processes [4]. The largest biodiesel marketing problem is the cost required for raw materials: about 70–95% of the total cost of production. The used cooking oil could be applied as a feedstock for biodiesel production with a reduction of costs of 60–70% [5], being two to three times cheaper than virgin vegetable oils [6]. The problems of the used cooking oil with your disposal via drainage or sanitary grounding, which may cause pollution of water and soil, they can be reduced using this waste as raw material for biodiesel production, that it can be an effective and economical approach to manage this energy source, providing a double benefit of fuel generation and environmental protection [7,8].

Brazil is among the largest producers and consumers of biodiesel in the world, with a monthly production, in February 2016, of 271,388 m^3 [9]. Since November 1st 2014, diesel marketed in Brazil contains 7% of biodiesel. This rule was established by the National Council of Energy Policy (CNPE) and increased from 5% to 7% the mandatory percentage of biodiesel mixture with diesel oil. The continuous increase in the percentage of biodiesel added to diesel has been demonstrating the success of the national program that tends to increase more and more the production of biodiesel.

A biodiesel production from a Brazilian pilot plant (University Center of Araraquara – Brazil) from used cooking oil by alkali-catalyzed transesterification processes has produced about 200 L of biodiesel through batch processes. The used cooking oils have been collected from houses, public schools and shops. The biodiesel produced supplies trucks that collect the used cooking oil, at a ratio of 50% diesel and 50% biodiesel, aiming at a cost reduction of 50%. For an input of 80 L of used cooking oil (feedstock) in the process, 20 L correspond to methanol (short chain alcohol) and 30% sodium hydroxide (catalyst) are pre-diluted in this alcohol, generating about 15 L of crude glycerol and 85 L of biodiesel.

Glycerol is the major byproduct of the biodiesel industry. In general, for every 100 kg of biodiesel that are produced, approximately 10 kg of crude glycerol (CG) are generated [10]. The glycerol is often called as crude glycerol due to its composition varies from one biodiesel plant to another in relation to feedstock oil composition and quality, the oil and methanol molar ratio, catalyst and the production process [11]. The impurities mainly present in this sample are soap, free fatty acids, methanol, unreacted triglycerides, diglycerides and monoglycerides [4]. The purification on CG was the most applied method before the boom of biodiesel production and utilized primarily in the cosmetic industry [11]. However, this purification is costly and hence its applications in food, pharmaceutical and personal care industries are not economically significant due to a decrease of the price of purified glycerol (1.54 US $/Kg before 2000 and 0.66 US $/Kg after 2007) [4,11].

The increase in CG production and management of such a huge amount of waste will be a problem for biodiesel manufacturers [2]. According to Sarma et al. (2013) [2], the CG is an environmental hazard and its disposal in landfills must meet the universal treatment that further increase biodiesel waste disposal cost, thereby increasing the cost of biodiesel production [2]. So, using the CG as a substrate for bioconversion to value products, such as hydrogen generation through anaerobic digestion [2], the cost for biodiesel production could be cut down.

The impurities present in CG may lead to the inhibition of microorganism's development during the biological processes. The pretreatment of the CG by pH adjustment to acidic conditions may convert the soluble soaps to insoluble free fatty acid, so they can be separated, removed from crude glycerol and recycled. The fraction containing free fatty acids is collected on the surface of the glycerol phase and can be removed and recycled for one more esterification process [4,12].

Dark Fermentation for the hydrogen production has advantages over photo-fermentation in terms of faster production, simple technique and no requirement of light energy [13]. The major advantage of dark fermentation consists of the wide range of organic substrates that fermenting bacteria can utilize for hydrogen production, such as wheat flour hydrolyzate and food waste hydrolyzate [14,15].

For biohydrogen production, a range of cheap and waste carbonaceous materials has been investigated as a substrate where good hydrogen yield has been achieved. In works involved pure glycerol as a feedstock for biohydrogen production, the high hydrogen yield has been reported. However, the cost to require pure glycerol is higher. So, the crude glycerol from biodiesel manufacturing process would be a preferred feedstock for hydrogen production. For large scale hydrogen production, CG seems to be the ideal substrate [4].

The amount of energy produced during the combustion of hydrogen per unit of weight is greater than the release for any other fuel, such as methane, gasoline, and others. Specifically, the amount of energy released during the hydrogen combustion reaction is about 2.5 times the power of combustion of a hydrocarbon. The main advantage of hydrogen as a fuel is the absence of CO_2 emissions and other pollutants [16,17].

Anaerobic processes of crude glycerol from biodiesel waste using either pure cell cultures (e.g. *Clostridium butyricum*, *Escherichia coli*) or mixed cultures (e.g. wheat soil, compost, and wastewater sludge) have been performed. Most of these studies were conducted in the anaerobic batch reactors, where the produced hydrogen is accumulated in the headspace of the bioreactors [2]. However, the majority of the researches are conducted with raw glycerol from virgin vegetable oils and animal fats [18]. In addition, the application of crude glycerol, from used cooking oils into biodiesel by transesterification processes, with fermentation by mixed cultures for H_2 generation has never been employed.

In these sense, the main goal of this study consisted in the use of crude glycerol as a carbon source, from the transesterification process of used cooking oils, to obtain biodiesel, in anaerobic batch reactors in order to generate H_2. The characterization of crude glycerol was performed and it was applied in assays of hydrogen bioproduction.

Materials and methods

Crude glycerol (CG)

CG was obtained from a Pilot Plant of Biodiesel Production from the Biotechnology Institute of Engineering Renewable Energy of