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Palm oil mill effluent (POME) as raw material for biohydrogen and methane production via dark fermentation

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ABSTRACT

The Palm Oil industry is growing faster, as the global demand for its products greatly overcomes its production. As palm oil production increases, also does its effluent, Palm Oil Mill Effluent (POME). POME is a complex effluent, which is not toxic, but due to its elevated organic content, it is considered extremely polluting. Generally, POME is submitted to both physical and chemical treatments before being discarded into receiving streams or other water bodies. This process might be costly for the industry and there 98is no income from effluent treatment, therefore another destination for this effluent is desirable. As an alternative, this residue could be exploited as raw material in biological processes, specially hydrogen and methane production, due to the presence of carbohydrates, lipids and proteins that might be metabolized during the dark fermentation process. Hydrogen can be used in different industries, such as chemical, biochemical and food industries. Methane is an important combustible, which could substitute natural gas and hydrogen as a very promising fuel. This review approaches sustainable and renewable processes for POME exploitation as raw material for renewable energy production.

1. Introduction

Palm oil is a major commodity for developing countries in Southeast Asia, specially Indonesia and Malaysia, which are responsible for 86% of the global production [1]. While global demand increases, Thailand, Colombia and, more recently, Brazil are also beginning to emerge as key players of that market [2,3].

The main reasons why palm oil consumption has been on the rise in the last years are their multiple uses (e.g., food industry, biofuels, cosmetics) and lower cost when compared to other oils [4]. The global palm oil market was valued at USD 62 million in 2014 and it is expected to reach USD 88 million by 2022, with a production of 128.20 million tons of oil/year, of which approximately 11.5% will be palm kernel oil [5].

In order to supply world demand for palm oil, its producers are augmenting the total production, also elevating the amount of residues generated in the process. The oil extraction generates a highly polluting residue, Palm Oil Mill Effluent (POME), which cannot be spilled directly into water bodies [6].

POME is a complex effluent, which is not toxic, but due to its elevated organic content, is considered extremely polluting [7]. Its characterization might vary according to the production process and raw material utilized [8–10]. While technologically advanced mills could process up to 150 MT of fresh fruit branches (FFB) per hour and generate POME with Chemical Oxygen Demand (COD) as low as 16 g O_2/mL, more primitive ones are able to process up to 2.5 MT of FFB and can originate POME with a COD as high as 100 O_2/mL [8,11]. There are several steps in the Palm oil production process, but POME is produced mainly during three of them: the sterilization of bunches, after kernel separation from the shells (in a hydrocyclone) and after oil clarification [12]. As observed, it is a complex material, containing high concentrations of organic material, oil and greases and suspended solids. Therefore, adequate treatment or usage is necessary before discharging it into rivers or seas [13–15].

Usually, treatment stations are considered non-profitable investments, leading to insufficient treatment of the effluent and, therefore, contamination of the surrounding area and water bodies. POME is usually treated by non-biological treatments as coagulation–flocculation,

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adsorption or membrane filtration [16–19]. Neither of those methods were able to treat POME adequately, while generating income to the industry [13]. A more economically, viable and environment friendly alternative is to use POME as raw material to biological processes [20], such as polymers production, methane and biohydrogen production and also for biodiesel synthesis [21–23].

As for hydrogen, this gas is very interesting since it could be used as feedstock in various processes, such as petrochemical, food, microelectronics, ferrous and non-ferrous metal processing, chemical and polymer synthesis, and metallurgical process industries [24] or as combustible in fuel cells [25]. Several researches have focused on the fuel application of hydrogen due to its clean combustion, high specific energy and non-toxicity; associated with the current scenario of depreciation of petroleum price and increment on sustainable development [23,25,26]. Although most hydrogen is produced by chemical routes from fossil sources [27], development of a biotechnological process to produce hydrogen is very attractive from a sustainable development perspective, since it applies renewable resources and requires low energy inputs as compared to chemical processes.

As for methane, it is a gas, whose world reserves have been dwindling quickly, as it is widely used. In addition to its elevated calorific power, the main reason for its fast depletion is its simple extraction process, as it is generally found in abundance in petrol wells [28]. It is widely used in industries or domestic houses to generate power [29]but more noble uses are being applied to it, such as methanol synthesis [30,31] or converting CH_4 and CO_2, two greenhouse gases, into synthesis gas [32]. Literature is extensive in what regards CH_4 production from biomass via chemical or biochemical processes. Amongst the biochemical processes, which can be carried under atmospheric pressures and room temperatures, anaerobic digestion is a traditional and well known technology, allowing high yields of CH_4. [33,34]. Furthermore, anaerobic digestion is an alternative solution for providing energy for remote areas, which is still an issue for the major producers of POME, such as Indonesia and Malaysia [35]. In addition to the fact that this energy can be used locally, it is also possible to supply the country's electrical system with the exceeding power generated by H_2 and CH_4 combustion.

This review approaches the employment of POME as raw material for hydrogen and methane production via a dark fermentation process, as well as a sequential production of hydrogen and methane, providing an interesting alternative that meets environmental conservation and energy production in a sustainable model, which could benefit local communities in remote areas.

2. The dark fermentation process

2.1. General aspects of dark fermentation

A Dark fermentation process consists in the application of strict or facultative anaerobic organisms for converting substrates, such as simple sugars, glycerol, fatty acids and carbohydrates into volatile fatty acids, alcohols, solvents, CO_2, H_2 and CH_4 [36,37].

The main advantages of dark fermentation as compared to other biological processes for hydrogen production lie in its light-independence and consequently low energy input requirement, the possibility of employing renewable biomasses as feedstock and faster H_2 production rates [37–39]. On the other hand, the bottlenecks of this process are low yields of H_2 and large quantities of by-products in the final medium [40]. However, most of these by-products are value-added, like organic acids, 1,3-propanediol and ethanol [34], which might be recovered from the medium.

Moreover, hydrogen production liquid waste (HPLW) might be applied as raw material for production of methane, lipid, bioplastic and electricity [34]. Also, HPLW could be utilized in a photofermentation system in order to provide electron donors, generating more H_2 in a hybrid process [41].

Dark fermentation of agro industrial wastes associated with the utilization of HPLW either for bioproducts recovery or as raw material in other processes represents a promising alternative to hydrogen production from a biorefinery perspective.

2.2. POME to H_2 via dark fermentation

As discussed in Section 1, POME is a complex material and its composition varies depending on palm oil processing. Generally, POME contains high concentrations of organic molecules such as fatty acids, proteins, carbohydrates, nitrogenous compounds, lipids (including triacylglycerol); and minerals [42]. This organic matter could be metabolized during dark fermentation processes either by pure culture or bacterial consortia.

Bacterial consortia, such as anaerobic sludge, are mainly used when complex materials are applied as feedstock, due to the presence of assorted organisms that could act synergistically, enhancing the degradation and consumption of these materials [43–45]. When a consortium of bacteria is used as inoculum, degradation of complex material occurs in four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis [43,46,47], in which different organisms act concurrently, as represented in Fig. 1.

Firstly, complex substrates, such as long chain fatty acids and triacylglycerols are hydrolyzed into simpler molecules, such as oleic acid, palmitic acid and glycerol by hydrolytic bacteria. In the second phase, acidogenic bacteria promote the conversion of those molecules into volatile fatty acids, typically acetic and butyric acids; and eventually alcohols, like 1,3-propanediol (formed by glycerol metabolism) and ethanol. In the sequence, the metabolism of organic acids generates acetate and butyrate and also cogenerates H_2 during acetogenesis. Finally, generated H_2 might be reduced to methane by methanogenic microflora [48]. However, since POME is a complex material, the substrates could not be easily available for bacterial cells, resulting in long adaptive phases and/or low conversion rates [49].(Fig. 2)

In order to produce hydrogen, it is mandatory to eliminate H_2-consuming bacteria from the medium, avoiding methanogenesis [38]. Since most of H_2-producing organisms are able to sporulate, it is relatively simple to eliminate H_2-consuming microorganisms when using mixed cultures [50]. The basis of pretreatment is to stimulate the sporulation of H_2-producing bacteria and to eliminate non-spore forming bacteria, typically H_2-consumers, by establishing a hostile environment. There are several types of pretreatment that can be chosen considering the microflora in the seed sludge [43,51]. An alternative

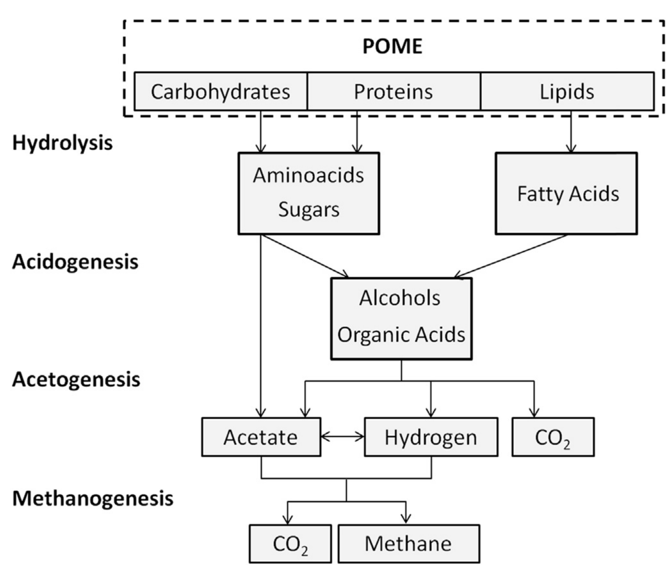

Fig. 1. Schematic model for dark fermentation of POME by bacterial consortia.