Chapter 22

# Glycerol as a Raw Material for Hydrogen Production

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Additional information is available at the end of the chapter

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## 1. Introduction

Fossil fuels continue to be the primary global energy sources, suppling approximately 80% of global demand. However, such energy sources can cause the greenhouse effect with the generation of harmful gases such as COx, NOx, SOx, CxHx and other organic compounds. These pollutants are released into the atmosphere as a result of fossil fuel combustion [1]. Renewable technologies, such as biofuels, present possible alternative sources of energy that are carbon neutral.

Approximately 68% of global biodiesel supply is produced by five countries: Brazil, Germany, USA, France and Argentina. Brazil is among the largest producers and consumers of biodiesel in the world, with a production capacity of 8539 million liters [2]. Several factors favour the cultivation of different plants for biodiesel production in Brazil, especially the climatic condition, and the availability of arable land. The increase in the production of biodiesel makes Brazil a strategically important country for the whole world, due to the depletion of already known fossil energy reserves.

Biodiesel is a biofuel obtained by the transesterification of raw materials such as animal fats and vegetable oils. In Brazil, sources like soybeans and palm are economically attractive for biodiesel production due to their abundance. Approximately 80% of the biodiesel produced in Brazil is derived from soybean [3]. In Brazil, the addition of 2% biodiesel in diesel fuel has been mandatory since 2008, this amount was increased to 6% in July 2014 and then increased to 7% in November 2014 [4].

The large surpluses of glycerol that are generated in this process require new commercial uses to be identified. Brazil will become a major producer and consumer of biodiesel due to strong

strategy for biofuel production. This is possible due to exceptional conditions for the cultivation of oilseeds for oil extraction. The selection of feedstock depends strongly on potentialities of each region [5].

When biodiesel is produced from vegetable oils and animal fats through transesterification process, high amounts of waste are created. This waste chiefly consists of crude glycerol, which has limited commercial value, unless expensive purification processes are performed. Even when purified, there is such a large global overproduction that traditional markets find difficult to absorb it. Each ton of biodiesel produced generates approximately 100 kg of crude glycerol. However, the amount of crude glycerol generated in biodiesel production can vary from 1% to 85% (v/v), depending on operating conditions of the transesterification plants. Thus, to overcome these issues it is necessary to discover new uses for this significant residue.

Ethanol has been primarily produced from sugarcane in Brazil since 1975, encouraged by the implementation of the National Program for Alcohol (1975–1985). Brazil produces (in 2011/2012) nearly 571 million tons of sugarcane, which is processed by sugar mills to produce 36.9 million tons of sugar and 22.9 billion liters of ethanol [6]. The ethanol could potentially be used in the esterification process of biodiesel [7] to develop cheaper and more environmentally friendly processes. Several studies have been developed to obtain hydrogen gas, as a renewable energy source that can be generated from waste glycerin, a byproduct of biodiesel production.

In this sense, this chapter presents a comparative study on biological hydrogen production from crude glycerol, the microorganisms involved in the biological processes for hydrogen production and some of the strategies applied in the literature for the improvement of these systems. It will contribute to innovation in research into the reuse of crude glycerol, in a sustainable manner, thus leading to potential cost reduction and clean energy generation.

## 2. Glycerol: A byproduct of biodiesel production

Glycerin is the principal byproduct of biodiesel production, with waste streams containing at least 95% glycerol; however its purity can vary depending on the efficiency of the production process [8].

Glycerol is generated by the process for obtaining biodiesel from vegetable oils or animal fats. This process often uses the addition of catalysts, such as sodium hydroxide, and alcohols, such as methanol or ethanol, with reactors maintained under heat and agitation (Figure 1).

However, during the transesterification process a high volume of glycerol is produced as a byproduct: for 90 $m^3$ of produced biodiesel, approximately 10 $m^3$ of glycerin is generated [8]. Pure glycerol can be used in many different applications, mainly in textile, chemical, pharmaceutical and food industries. However, to use it in these applications is necessary a degree of purity higher than 95% [9]. To achieve this, the crude glycerin must be submitted to a purification process, often resulting in high financial costs.

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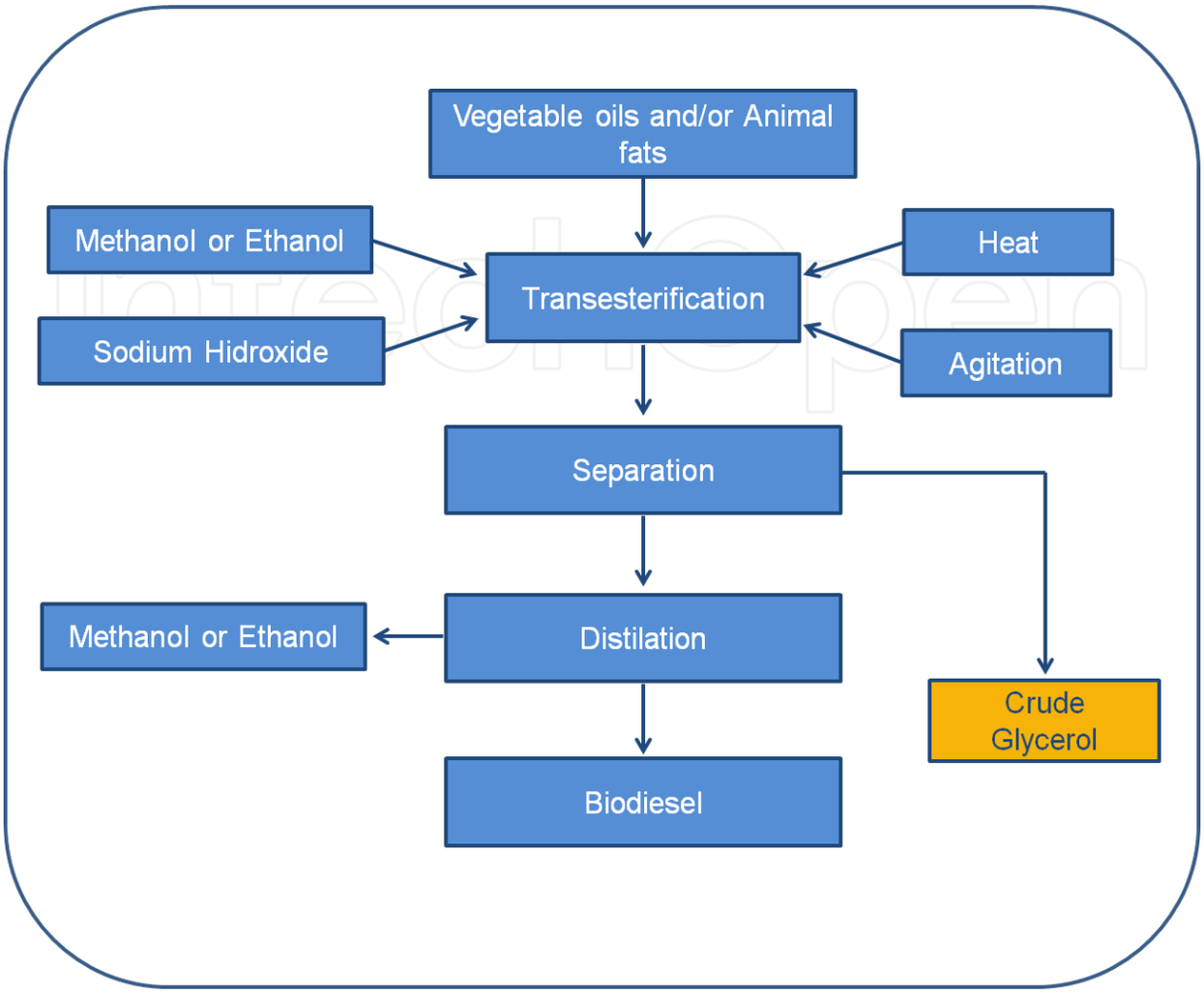


**Figure 1.** Representation of Biodiesel production by Transesterification Process (adapted from [10]).

Due to the significant amount of unwanted glycerol generated in the biodiesel manufacturing process [11], traditional markets have not found the capacity to absorb it, as described above. Depending on the purity, the main uses for glycerol are direct burning for energy production, inputs for various industrial segments and as raw material in animal feed [8].

## 3. The impurities present in crude glycerol

The main impurities present in crude glycerol are soap, free fatty acids, methanol, unreacted triglicerides, diglycerides and monoglycerides [10]. The exact composition of the waste glycerol often differs depending on the manufacturing process employed (Table 1). Silva et al. [12] observed methanol, water and sodium chloride, in samples of crude glycerol during the biodiesel production in a Brazilian plant with soybean oil as raw material.

Crude glycerol should be pre-treated before being used as feedstock. Methanol or ethanol can be removed using heating or distillation processes. Soap is another impurity present in the

crude glycerol and can be removed by precipitation from the liquid medium through pH adjustment. Sodium ions can be removed from crude glycerol by neutralization with addition of phosphoric acid and lime in excess, in order to crystallize/precipitate hidroxyapatite [17]. However, these treatments are costly and not economically justifiable. Alternatively, there are many studies covering the use of crude glycerol for bio-hydrogen production without pre-treatments [11]. These bioconversions of the crude glycerol may be suitable and economically attractive alternatives to the industrial processes.

| Source of biodiesel | Glycerol content w/wProduct Yield | | Impurities | Ref. |
|---|---|---|---|---|
| Nittany Biodiesel, State College, PA | 69.5% | 0.41 $m^3H_2$. $m^3$ $d^{-1}$ | MeOH, NaOH and sodium methylate | [13] |
| Integrity Biofuels, Indiana, USA | 67.5±3.2% | Phytase (1125 U $ml^{-1}$ supernatant) | $NaSO_4$, MeOH, Water, | [14] |
| Virginia Biodiesel Refinery (West Point, VA, USA) | 84% | Docosahexaenoic acid (4.91 g $l^{-1}$) | Soap, FFA, MeOH, Mono, Di or Triglycerides | [15] |
| Biodiesel factory, Portugal | 86% | 710.0 $cm^3H_2$ $dm^3$ medium | OMNG, ash and methanol | [16] |

OMNG - Organic Matter Not Glycerol; FFA – Free Fat Acids; MeOH – Methanol

**Table 1.** Impurities present in the crude glycerol during the biodiesel production

## 4. Applications of crude glycerol in biological processes

Glycerol can be consumed by microorganisms in biological processes to generate byproducts with added value, such as ethanol, 1,3-propanediol (PD), $H_2$ and organic acids, among others. PD may be used in industrial applications such as polymers, cosmetics, foods, adhesives, lubricants, laminates, solvents, antifreeze and pharmaceuticals [9]. Ethanol has been used in the pharmaceutical industry, solvent, cleaning products and personal hygiene. In Brazil, its use is remarkable mainly due to the sugarcane producing. In 2011 over 27 billion liters of ethanol was produced in Brazil from sugarcane. Most of it was destined for use as a fuel[18], mainly hydrid vehicles that can be driven by mixtures of gasoline and ethanol [19]. $H_2$ has been utilized as a reactant in the chemical and petroleum industries during the production of ammonia, petroleum processing and methanol [2].

The energy content of the pure glycerol is 19.0 MJ/kg, however for crude glycerol it is 25.30 MJ/kg, possibly due to presence of methanol and biodiesel [10]. Such high energy content of crude glycerol indicates its potential to be an effective carbon source for hydrogen, PD and ethanol bioproduction.

The microorganisms involved in hydrogen production may be classified in four groups: strictly anaerobic, facultative anaerobic, aerobic and phototrophic [22], for example, green algae,

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cyanobacteria, phototrophic bacteria and fermentative bacteria. However, higher yields of $H_2$ generation are obtained by fermentation processes. The main fermentative bacteria known to produce hydrogen include *Enterobacter* sp., *Bacillus* sp., *Clostridium* sp., *Klebsiella* sp. and *Citrobacter* sp.[9,21]. The process of dark fermentation from crude glycerol may be followed by fotofermentation [9] because phototrophic bacteria grow with organic acids (the possible metabolites from fermentation) and they may produce more hydrogen [22].

Glycerin may have different yields of hydrogen per mole of organic substrate, depending on the route of the fermentation used and the exact composition of the end products. According reference [9], the end products of the fermentation process may be acetic acid (equation 1); butyric acid (equation 2), butanol (equation 3) and ethanol (equation 4). Furthermore, as reported by several authors, it may also generate PD (equation 5),[23,24]. Generation of acetic acid (equation 1) and butyric acid (equation 2) are accompanied by higher yields of $H_2$, as observed in the fermentation of sugars [25].

$$C_3H_8O_3 + H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \quad (1)$$

$$2\,C_3H_8O_3 \rightarrow C_4H_8O_2 + 2CO_2 + 4H_2 \quad (2)$$

$$2\,C_3H_8O_3 \rightarrow C_4H_{10}O + 2CO_2 + H_2O + 2H_2 \quad (3)$$

$$C_3H_8O_3 \rightarrow C_2H_6O + CO_2 + H_2 \quad (4)$$

$$2\,C_3H_8O_3 \rightarrow CH_3COOH + C_3H_8O_2 + CO_2 + 2\,H_2 \quad (5)$$

Glycerol can also produce lactate (equation 6) and succinate (equation 7) [26].

$$C_3H_8O_3 \rightarrow C_3H_6O_3 + H_2 \quad (6)$$

$$2\,C_3H_8O_3 \rightarrow C_4H_6O_4 + 2\,CO_2 + 5\,H_2 \quad (7)$$

Fermentation processes of hydrogen production using anaerobic acidogenic bacteria have been extensively described by several authors [27-31]. Additionally there are several key intermediate products created during the fermentation of glycerol: mainly organic acids, such as acetic acid and butyric acid and alcohols, such as ethanol and PD [9].

The following metabolites are obtained from the fermentation of glycerol: dihydroxyacetone, succinic acid, citric acid, docosahexaenoic acid, propionic acid, hydrogen, ethanol, and PD.

Figure 2 demonstrate that during the oxidative metabolism of glycerol, pyruvate is formed as an intermediate.

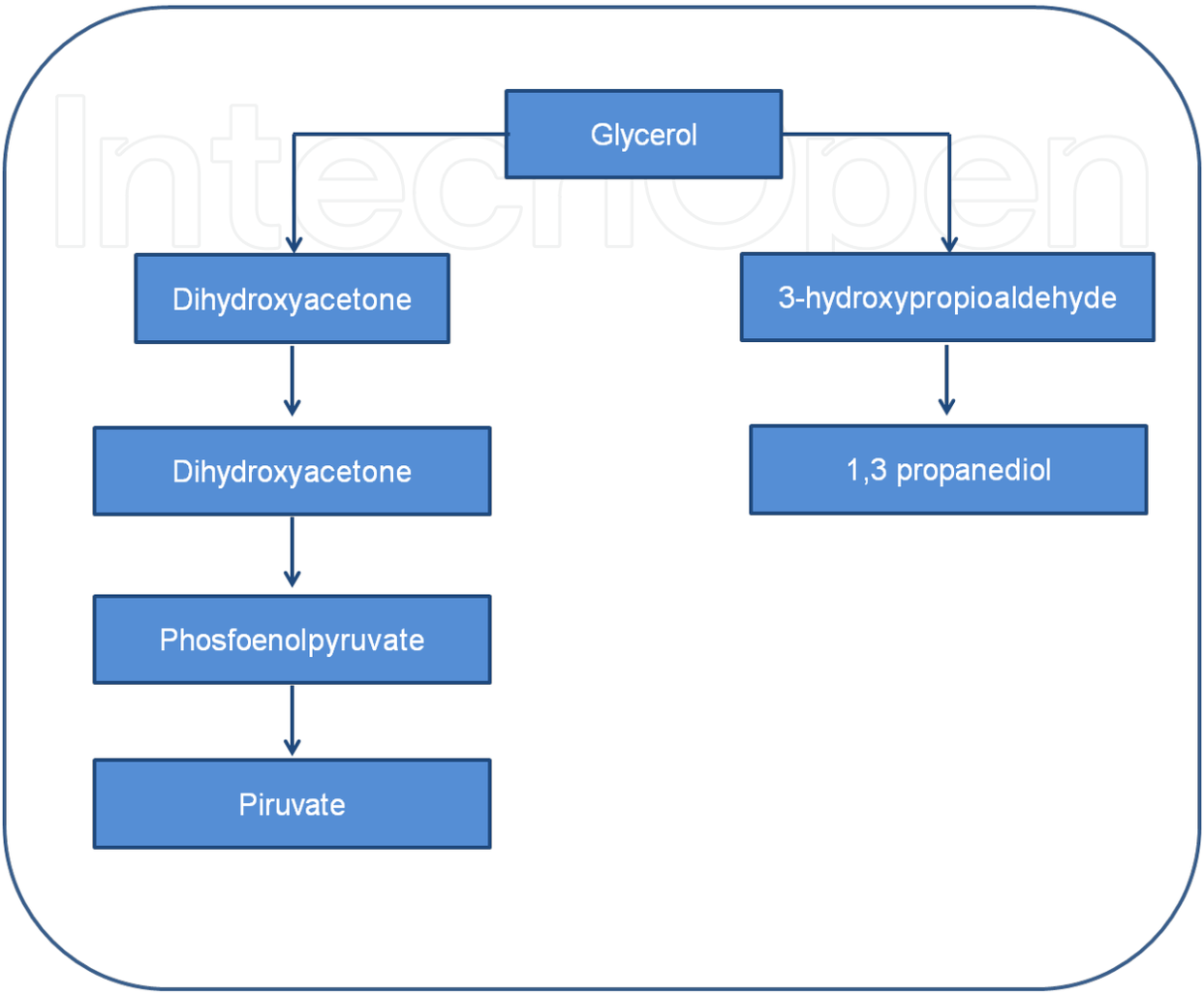


**Figure 2.** Glycerol metabolism during anaerobic fermentation (adapted from [10])

The production of PD is achieved through a reductive pathway in the anaerobic fermentation of glycerol. However, production of $H_2$ and other metabolites (ethanol, butanol, acetone, acetate, butyrate and lactate) compete with the production of PD by oxidative pathways [24].

However pyruvate formed during the conversion of glycerol (using the oxidative route) may be employed in various ways by microorganisms. The pyruvate is responsible for the formation of numerous metabolites such as lactate, ethanol, acetone, butanol and butyrate, as demonstrated during glucose metabolism (Figure 3). A similar metabolism using glycerol first produces pyruvate, before conversion to different metabolites and $H_2$ [10].

In many bacteria there are two biochemical pathways for glycerol metabolism: an oxidative pathway, where $H_2$ is generated and a reductive pathway leading to PD generation. When both pathways exist in the same microorganism PD production is preferential against $H_2$ [10].

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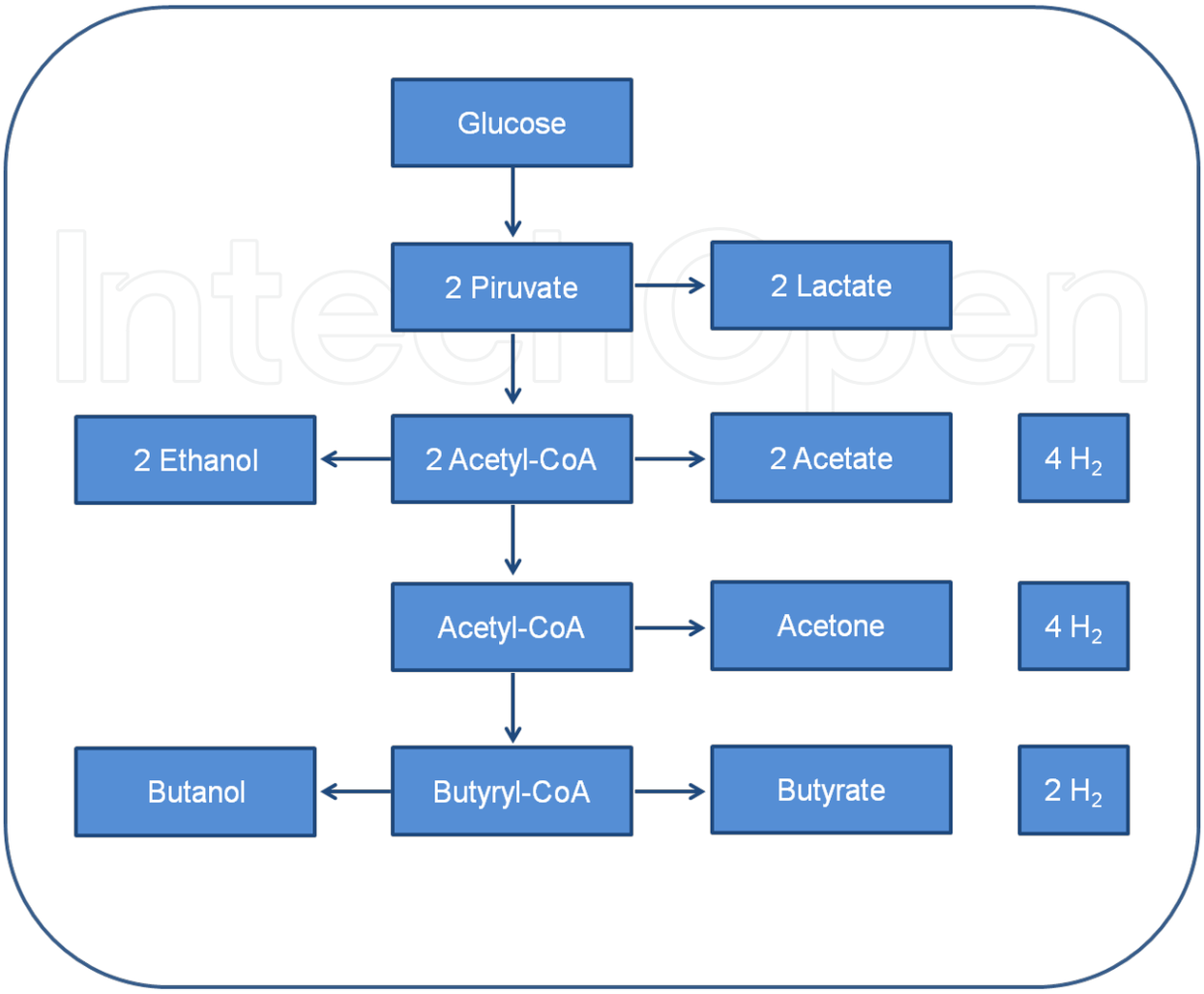


**Figure 3.** The glucose metabolism to pyruvate and hydrogen (Adapted from [10])

The biotechnological production of $H_2$, ethanol and PD from glycerol has been demonstrated by several bacteria species. The species of anaerobic bacteria as *Klebsiella* sp., *Enterobacter* sp., *Citrobacter* sp., *Lactobacillus* sp., *Bacillus* sp. [32] and some *Clostridium* sp., have demonstrated the ability to ferment glycerol or mixtures of glycerol and sugars [9]. In addition to the anaerobic microorganisms, nutrients are required in the reaction medium. These allow growth and fermentation of organic substrates leading $H_2$ production. Complex compounds used as nutrients include: peptone, tryptone, polypeptone, yeast extract, vitamin solutions, among others. Such bacterial species may generate $H_2$ from various carbon sources, particularly sugars [33] and glycerol.

Table 2 shows some studies about the bioconversion of glycerol using pure cultures or mixed microbial consortia to generate $H_2$ and other byproducts.

PD and $H_2$ are the two major products which can be obtained by bioconversion of crude glycerol. A co-culture of anaerobic bacteria, which can simultaneously use PD and produce $H_2$ via glycerol fermentation, may be a suitable option for crude glycerol bioconversion [10].

However, a combined production process of hydrogen and ethanol provides higher energy yield when compared with hydrogen or ethanol alone [40].

| Microorganisms | Hydrogen Yield | Other by products | Ref. |
|---|---|---|---|
| *Enterobacter aerogenes* HU-101 | 63 mmol $H_2$ $l^{-1}$ $h^{-1}$ | 0.85 mol ethanol $mol^{-1}$ glycerol | [34] |
| *Klebsiella pneumoniae* ATCC 25955 | - | PD | [35] |
| Mixed micro-flora of organic waste or soil | 11.5-38.1 ml $H_2$ $g^{-1}$ COD | PD | [36] |
| Mixed culture | 0.31 mol $H_2$ $mol^{-1}$ glycerol | 0.59 mol PD $mol^{-1}$ glycerol | [37] |
| Anaerobic digested sludge | 0.41 mol $H_2$ $mol^{-1}$ glycerol | 0.784± 0.063 L $CO_2L^{-1}$ media | [38] |
| *Halanaerobium saccharolyticum* | 0.62 mol $H_2$ $mol^{-1}$ glycerol | PD, butyrate, ethanol | [39] |
| *Halanaerobium saccharolyticum* | 1.61 mol $H_2$ $mol^{-1}$ glycerol | 1.11 mol $CO_2$ $mol^{-1}$ glycerol, acetate | [39] |

COD- Chemical Oxygen Demand; PD - Propanediol

**Table 2.** Bioconversion of glycerol to $H_2$ and other products

A range of reactor types has been used in hydrogen production that utilizes organic waste materials such as crude glycerol or pure glycerol. They may be simple serum bottles [33], laboratory scale fermenters, pack-bed or up flow reactors [41] (Figure 4). However, it should be noted that most of the studies were performed in batch anaerobic reactors on laboratory scale (Table 3). To the best of our knowledge, there are no studies with pilot scale reactors, this suggests that the research into the bio-production of hydrogen using glycerol is currently in a preliminary phase.

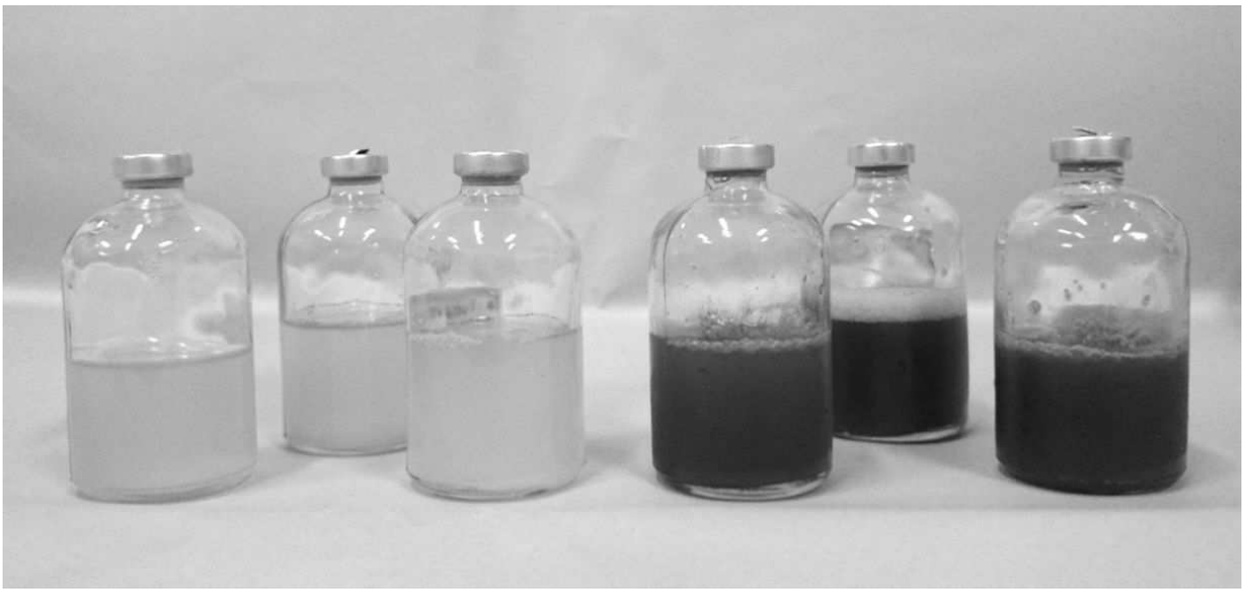

**Figure 4.** Anaerobic batch reactors applied on laboratory scale

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| Substrate | Inocula | Reactor | T (°C) | pH | $H_2$ Yield [a] | Ref. |
|---|---|---|---|---|---|---|
| Crude glycerol | Kefir | Batch | 25 | 5.2 | 0.22 | [42] |
| Crude glycerol | *Enterobacter aerogenes* | Batch | 37 | 6.8 | 1.12 | [34] |
| Crude glycerol | Mixture(wheat oil) | Batch | 30 | 6.2 | 0.31 | [13] |
| Pure glycerol | *Enterobacter aerogenes* | Continuous | 37 | 6.8 | 0.94 | [34] |
| Pure glycerol | Wastewaters | Continuous | 30 | 8.0 | 0.05 | [41] |
| Crude glycerol | Soil from blueberry farm | Batch | 30 | 5.5 | 0.18 | [43] |
| Crude glycerol | Organic Soil | Batch | 30 | 6.0 | 0.75 | [24] |
| Crude glycerol | *Enterobacter aerogenes* | Batch | 37 | 6.5 | 0.12 | [44] |

[a] mol-$H_2$.mol$^{-1}$ glycerol

**Table 3.** Different bioreactors applied for bioconversion of glycerol

However there are many promising results of hydrogen generation using different configurations of anaerobic reactors fed with industrial wastewater, sugars, starch and others. The configurations of anaerobic reactors applied for biological $H_2$ production are AFBR (Anaerobic Fluidized-Bed Reactor), CSTR (continuously stirred tank-reactor), EGBS (Expanded granular sludge bed reactor) and UASB (Up-Flow Anaerobic Sludge Blanket reactor) (Table 4).

| Substrate | Inocula | Reactor | $H_2$ Yield [a] | Ref. |
|---|---|---|---|---|
| Sucrose | UASB Sludge | Batch | 1.2 | [25] |
| Starch | Anaerobic Sludge | CSTR | 2.3 | [45] |
| Glucose | UASB Sludge | AFBR | 2.45 | [46] |
| Waste water of coffee | Anaerobic Sludge | UASB | 1.29 | [47] |
| Glucose and L-arabinose | CSBR and UASB Sludge | EGBS | 2.71 l$^{-1}$d$^{-1}$ | [48] |

[a] mol-H2 mol-1 substrate

**Table 4.** Different configurations of anaerobic reactors applied for $H_2$ production

The UASB reactor is a single tank process where the wastewater enters from the bottom and flow upward (Figure 5). A suspended sludge blanket filters treats the wastewater flows through it and bacteria living in the sludge break down organic matter by anaerobic digestion, transforming it into biogas. Some advantages of this configuration are: the conversion of the organic matter in all reactor areas (bed and sludge blanket); the microorganisms can grow close to the bottom of the reactor in the form of flocks or granules (1 to 5 mm); the mixing of the system is promoted by the upward flow of wastewater and gas bubbles [49,50].

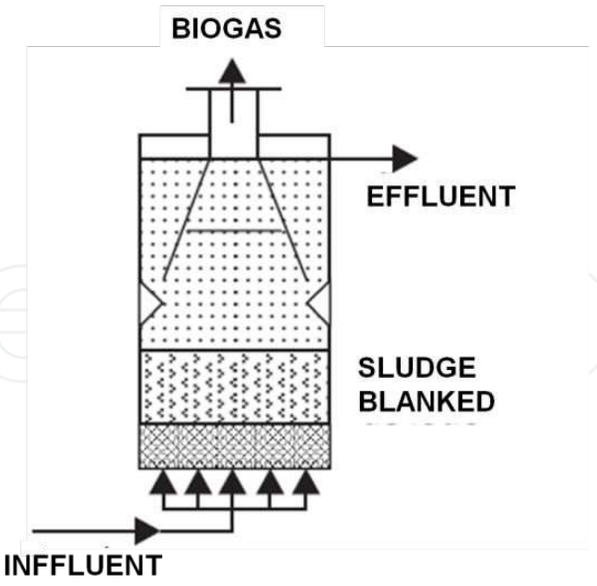


**Figure 5.** Schematic representation of UASB reactor (Adapted from [50])

The EGBS reactor has a cylindrical structure, packed with inert particles (0.3 to 3.0 mm of diameter) as support for microorganisms to form the biofilm (Figure 6). Several types of materials may be used as support mediums such as sand, coal, PVC, resins, ground tire and PET [51], etc. The biofilm may develop on the particles surface [49].

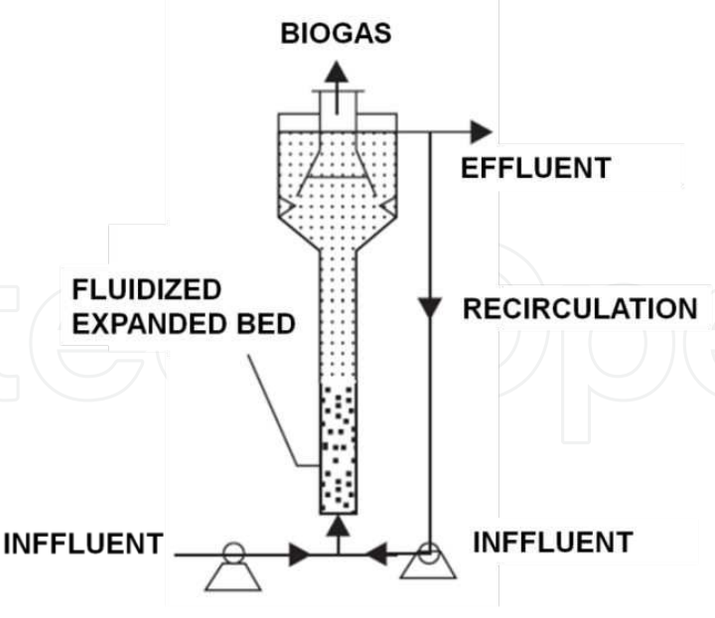


**Figure 6.** Schematic representation of EGBS reactor (Adapted from [50])

AFBR has the same operating principles of the EGBS reactors, except the particles size (0.5 to 0.7 mm) of the support medium and the expansion rates (Figure 7). The upward velocity of

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the liquid must be enough high to fluidize the bed until it reaches the point at which the gravitational force is equaled by the upward drag force. A high recirculation rate is necessary and the particles do not stay a fixed position inside the bed [49].

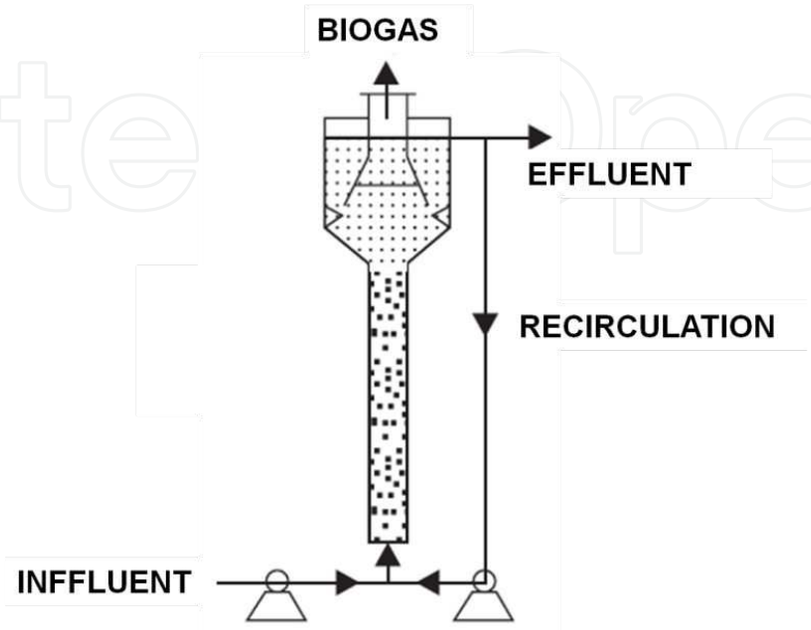


**Figure 7.** Schematic representation of AFBR reactor (Adapted from [50])

CSTR is known as a mix batch reactor and is an ideal type reactor in chemical engineering, for studies on laboratory scale [50]. CSTR can provide continuous or intermittent flow and comprises the follow steps: (1) filling (input of organic matter and microorganisms); (2) reaction (organic matter come into contact with microorganisms and they will degraded it); (3) sedimentation (settling of anaerobic sludge) and (4) emptying (removal of treated effluent) (Figure 8).

Studies on anaerobic fermentation of glycerol present major advances in pure cultures, such as with *Enterobacter aerogenes*. However, pure cultures do not represent real situations, such as those found in industrial waste [43]. To address this, research has been conducted onto hydrogen generation with mixed cultures obtained from anaerobic microorganisms present in biological treatment system sludge [39]. However, $H_2$-generating bacteria may be present in addition to bacteria that consume this gas, such as methanogenic archaea.

The fermentative production of hydrogen can be facilitated with methanogen inhibition, since methanogenic archaea use hydrogen in anaerobic biological processes [25]. To inhibit this methane formation process, reagents can be introduced, such as 2-brometanosulfonic acid (BES) and acetylene [2]. Additionally, pH control and heat treatment may provide other effective ways to prevent methanogens [25]. These methods may promote hydrogen production and encourage the growth of endospore-forming bacteria which are tolerant to high temperatures and adverse environmental conditions [21].

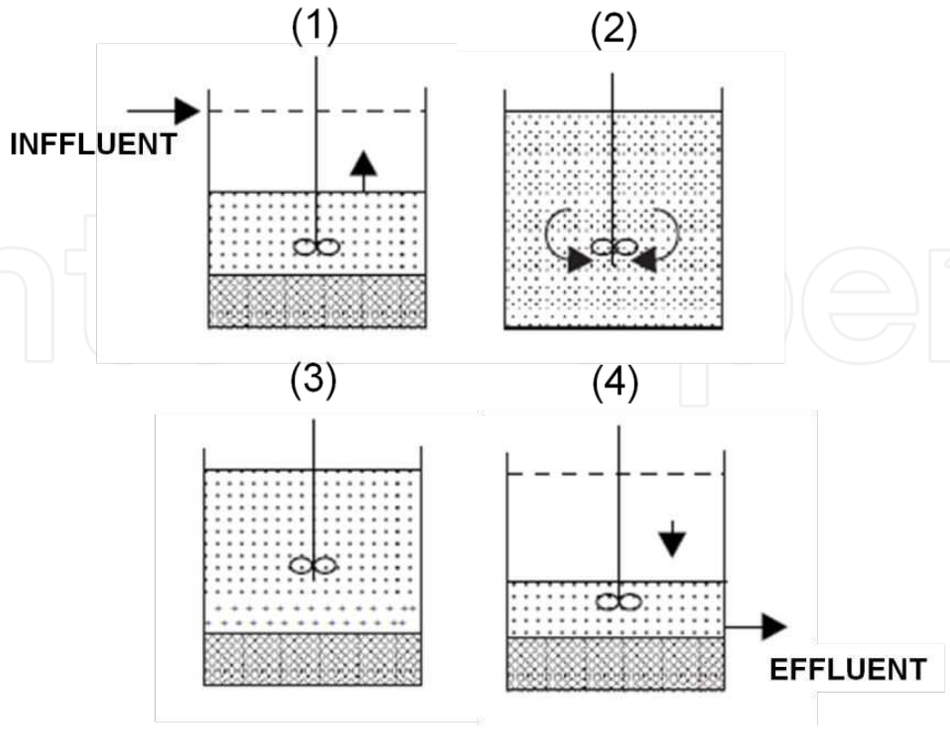


**Figure 8.** Schematic representation of CSTR reactor: (1) filling; (2) reaction; (3) sedimentation and (4) emptying (Adapted from [50])

When the pH is controlled, organic acids that favor microbial selection and the consequent production of hydrogen gas are formed. Other methods for elimination hydrogen consumers utilize ultra-sonication, acidification, sterilization and freezing/thawing [10]. Sá et al. [52] studied the biological hydrogen production using anaerobic sludge of the sewage treatment system of Rio de Janeiro city, Brazil. The authors (op cit.) applied heat treatment (120 °C for 1 h) upon the sewage to inhibit methanogenesis. Tests in anaerobic batch reactors using glycerin for $H_2$ production were obtained of 0.80 mol-$H_2$.mol glycerine$^{-1}$. Therefore, all such methods need to be verified for crude glycerol fermentation and hydrogen production efficiency.

## 5. Energetic applicarions and storage of $H_2$

Hydrogen can be used as energetic source in different systems and technologies, such as vehicular, stationary or portable devices.

In vehicular applications, hydrogen can be used as a supplemental fuel in conventional spark ignition engines without extensive engine modifications, reducing CO and hydrocarbons emissions, improving engine performance characteristics, such as thermal efficiency and specific fuel consumption. The researches show that when $H_2$ is used as a sole fuel in spark ignition engine, it is more efficient (and cleaner, since its combustion produces only water) than fossil fuel [53].

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Another option for vehicular transportation is use hydrogen in fuel cells (Figure 9). Fuel cells are high-efficiency power generation systems that convert hydrogen and oxygen directly into electricity using a low-temperature electrochemical process assisted by catalysts, emitting only water and virtually no pollutant. This system consists mainly of two electrodes (where electrochemical reactions takes place) separated by electrolyte or a membrane. Hydrogen and oxygen (i.e. from air) are fed into the fuel cell. The flow of ions between the electrodes occurs through electrolyte, while the excess electrons flow through an external circuit, providing electrical power [54].

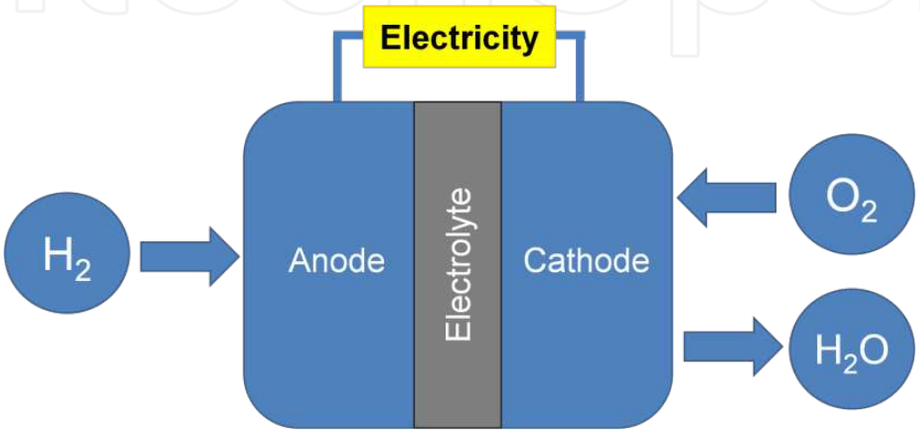


**Figure 9.** Simplified schematic representation of a fuel cell

Fuel cells convert hydrogen into electricity at high efficiency since they are not subject to the Carnot cycle limitations [55]. In present-day vehicles, a petrol-driven car engine operates at 25% efficiency, in the other hand a hydrogen fuel cell engine can operate at more than 65% [54].

Several types of fuel cells have been developed at different scales and characteristics (Table 5). The Brazilian government (Ministry of Mines and Energy - MME) plans introduce $H_2$ in the national energy matrix until 2025 not only as fuel for vehicles, but also as a clean source for stationary power generation for energy supply. According the MME plans, after 2020 the hydrogen produced in Brazil should be mostly provided from renewable sources [56].

Many global electronic companies such as Samsung, Sony, Toshiba, Motorola, Panasonic, Fujitsu, NEC, Hitachi and others have been developed patents and prototypes using fuel cells portable systems. Even though the market is not yet mature, the volume of investments of these companies indicates that technology should be consolidated in a few years [57]. However, the widespread utilization of $H_2$ as an energy source requires solutions to several problems: the gas must be able to be produced from a cheap and renewable source; safe storage and handling of $H_2$ must be addressed and refueling infrastructure developed.

A significant challenge regarding the large scale use of hydrogen gas is its storage. A storage device is an important part of the hydrogen energy system and it is a serious problem due to high inflammability, adequate safety measures should be taken during the production, storage, and use of $H_2$ fuel.

| Fuel cell type | Operating temperature (ºC) | Eletrical power range (kW) | Eletrical efficiency (%) |
|---|---|---|---|
| Proton exchange membrane | 60-110 | 0.01-250 | 40-55 |
| Alkaline | 70-130 | 0.1-50 | 50-70 |
| Direct methanol | 60-120 | 0.001-100 | 40 |
| Phosphoric acid | 175-210 | 50-1000 | 40-45 |
| Molten carbonate | 550-650 | 200-100,000 | 50-60 |
| Solid oxide | 500-1000 | 0.5-2000 | 40-72 |

**Table 5.** Characteristics of various fuel cell types (adapted from [54])

Hydrogen is quite difficult to store or transport with current technology. There are many ways for storing hydrogen fuel; as a gas (hydrogen compressed), a liquid (liquid hydrogen) and chemicals (metal hydride) [53].

Hydrogen compressed in tanks (with similar technologies applied in natural gas compression) is the easiest and cheapest way to store it. These tanks can store hydrogen at a high pressure (about 25 MPa - 35 MPa), but even under these conditions the energy density by volume for hydrogen is lower than for gasoline or diesel as can be seen from Table 6. In liquid form (-253 ºC), the energy density has higher value than hydrogen in compressed form [58]. However, it is necessary to spend more energy to liquefy hydrogen than to compress it (up to 20% of the energy content of hydrogen is required to compress the gas and up to 40% to liquefy it), so the cryogenic process efficiency demands elevated costs [54].

| Fuel | Way of storage | Energy density by weight (kWh/kg) | Energy density by volume (kWh/L) |
|---|---|---|---|
| Hydrogen | Gas (20 MPa) | 33.3 | 0.53 |
| | Gas (30 MPa) | 33.3 | 0.75 |
| | Liquid (-253 ºC) | 33.3 | 2.36 |
| | Metal hydrides | 0.58 | 3.18 |
| Natural gas | Gas (20 MPa) | 13.9 | 2.58 |
| | Gas (30 MPa) | 13.9 | 3.38 |
| | Liquid (-162 ºC) | 13.9 | 5.8 |
| Methanol | Liquid | 5.6 | 4.42 |
| Gasoline | Liquid | 12.7 | 8.76 |
| Diesel | Liquid | 11.6 | 9.7 |

**Table 6.** Energy density for some fuels (adapted from [58])

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Metals and metal alloys can also be used as a storage medium for hydrogen (hydrides form), i.e. chemical hydrides, $Ca_2H$, LiH, $NaBH_4$, $MgH_2$, $LiAlH_4$ and $H_3NBH_3$ have been widely studied as storage materials [53]. The positive aspects of this storage technology are low risk of unwanted losses, low pressures and energy densities greater than liquid and compressed hydrogen. The greatest disadvantage is the weight of these storage systems, about three times heavier than compressed hydrogen tank [58]. Probably, for this reason Toyota chose to use high-pressure tanks to equip the "Mirai" - its first commercial car powered by hydrogen produced on industrial scale [59].

The massive use of energy from hydrogen is expected to be gradual, with production and utilization initially on-site, with the development of new strategies environmentally friendly without the necessity for storage and transportation. For ex, initialy the hydrogen produced in a treatment plant can be used as energy source for its production plant; the use of $H_2$ for energetic necessity to maintaining a pump system would be appropriated.

## 6. Conclusion

The use of crude glycerol by biologic processes that generate PD, hydrogen and ethanol should be ensured for large scale production. Therefore, detailed economic studies and the optimization of such processes are interesting subjects for future investigations. New strategies may involve developing a proper market for the bioconversion of crude glycerol, as this would determine the economic viability of obtains clean energy from the glycerol feedstock.

Crude glycerol from the biodiesel manufacturing processes is a potential feedstock for bacterial hydrogen, PD and ethanol production. It can be used as substrate for the production of these bio products instead of other more expensive, carbon sources such as sugars.

A high hydrogen yield is possible when acetic acid is produced as the end product of crude glycerol fermentation. Other similar strategies should be developed for a metabolic route of acetic acid generation during the fermentation of crude glycerol.

Most investigations on crude glycerol bioconversion have been performed in serum bottle scale batch reactors. Only a few studies have been performed in a continuous mode. The continual improvement of investigations into bacterial hydrogen production using the continuous mode is recommended.

Consortia of anaerobic bacteria from environmental sources or pure cultures may be used for bioconversion of crude glycerol to hydrogen PD and ethanol. However using co-cultures may reduce the accumulation of metabolites and improve hydrogen yield. Application of the biological processes to directly convert abundant crude glycerol into higher value products may represent a promising route to achieve economic viability in the biofuels industry.

The widespread utilization of $H_2$ as an energy source requires solutions to several problems: the H2 must be able to be produced from a cheap and renewable source; refueling infrastructure must be developed for fuel cells. The appropriate utilization of energy from hydrogen in

large scale must be initially expected on-site. Further investigations for safe and economic storage of hydrogen are recommended.

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