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Production of hydrogen from biomass and its separation using membrane technology

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ABSTRACT

Hydrogen is an important raw material for chemical industry and feasible renewable energy carrier that could replace fossil fuels. However, the specie seldom exists in a form of pure H_2. Therefore, to obtain hydrogen in volumes suitable to be used as a raw material it is necesary to decompose hydrogen-rich compounds. The carbohydrate-rich biomass can be an important source of hydrogen by applying the process of dark fermentation. In this paper potential ways of hydrogen production from organic wastes (biomass) by means of dark fermentation are reviewed and discussed. The bacteria used for dark fermentation are enlisted, characterized and compared. The pretreatment processes and various reactor designs are analyzed and discussed. The hydrogen separation by membrane method (which can provide the most pure hydrogen) are presented.

The paper describes recent achievements in optimizing parameters, conditions and reactors used to industrialize dark fermentation.

1. Background

Dark fermentation is a branch of science and technology which is developing very rapidly in every step of the process different substrates [1–3,5,8], including crop residues (such as corn [2,3], bagasse [3,4], carrots [5], Jerusalem artichoke roots [5], maize flour [5], oats [5]), potatoes [1,5], sugarbeet residues [2,6], wheat flour [7], rapeseed oil cakes [5], sunflower oil cakes [5], grape marc [8], vegetable waste from restaurants [8,9], fruit peels (orange peels and banana peels) [8], animal waste e.g. cow manure [7], chicken meat [8], fish residues [5,8], food residues like kitchen waste [5,7,8,10], sewage wastes [1,2,5,8,11], and other biodegradation methods leading to hydrogen production [10]. Sambusti et al. [12] and Saiffudin et al. [13] reviewed dark fermentation taking into account one kind of substrate i.e. algae. Ghimire et al. [14] compared different substrates and parameters. Bundhoo et al. [15] and Wong et al. [16] analyzed role of pretreatments and parameters effecting the process. Elsharnouby et al. [17] analyzed bacterial monocultures used for dark fermentation.

This review summarizes the role of substrates, bacteria and pretreatments, including parameters and reactors. In the article all the earlier steps and design of the dark fermentation process mentioned above are analyzed. Additionally in the article membrane separation methods are discussed.

Standard dark fermentation is an anaerobic process, which leads to the decomposition of sugar molecules (usually hexoses) into low-weight organic-acid, hydrogen and carbon dioxide. Hexoses and/or pentoses often originate from hydrolysis of higher carbohydrates such as starch, molasses and cellulose [15]. The great interest in dark fermentation based on different types of carbohydrates is generated because of the widespread availability of carbohydrate-rich materials (e.g. paper, wood, grass straws) with high hydrogen content and the low number of inhibiting byproducts that can occur during the process, together with the low amount of energy needed for bacteria to digest glucose.

According to Hallenbeck [19] and Gottshalk [20] dark fermentation can be a one-stage process, when the substrate contains simple sugars. Then, the general route of dark fermentation in the presence of water (for example, glucose or sucrose) is as follows [4,5] as in equation:

$$C_nH_{2n}O_n \rightarrow C_mH_{2m-1}COOH + zCO_2 + yH_2,$$

where: $n = m+z = 5,6, 12, \ldots$; $y=0.5(n-m)$, $y = 2$ or 4; $z=n-m-1$.

Extended dark fermentation includes other biomaterials used successfully in anaerobic digestion, like fats, proteins, in addition to pure carbohydrates [14,22–25]. In the case of dark fermentation of substrates with high protein content the process can be disrupted due to

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high nitrogen and resulting high ammonia concentration inhibiting hydrogen generation [14,22], however, due to Alibardi et al. [26], proteins does not influence on dark fermentation process. Fatty acids are substrates with high potential for dark fermentation and high efficiency (hydrogen yield for sugars is around 0.33 but 0.38 for glycerol) [10,25,27,28].

Dark fermentation is related to methane fermentation, but the standard process is limited to hydrolysis and acidogenesis. Hydrogen production is optimized during acidogenesis under low pH conditions. Processes leading to methanogenesis are at least partly inhibited. In the case of dark fermentation process led by acidogenic bacteria (like Clostridium) methanogenic processes can be inhibited by special pretreatment of inoculum. Extended fermentation may rely on more stages, i.e. hydrolysis, acidogenesis and acetogenesis, but again it obstructs methanogenesis.

2. Bacteria promoting dark fermentation

Anaerobic microorganisms generate hydrogen using hydrogenase enzymes. Anaerobic bacteria produce hydrogen as by-product of their metabolism. The presence of hydrogenase enzymes was proven in 1931 in Escherichia coli. Hydrogenases are enzymes that stimulate production and recycling of hydrogen in bacteria [20]. Anaerobic bacteria produce hydrogen as a by-product of their metabolism. The most common anaerobic bacteria enzymes are: [Fe]-hydrogenase, [NiFe]-hydrogenase, [NiFeSe]-hydrogenase [30]. [Fe]-hydrogenase catalyses generation of hydrogen, while [NiFe]–hydrogenase uptakes generated hydrogen, and [NiFeSe]-hydrogenase is bidirectional. [NiFe]-hydrogenase is 100 fold less active than [Fe]-hydrogenase, therefore more generated hydrogen is excreted from the organism than is adsorbed back [20]. Hallenbeck pointed out that hydrogen can be generated by both: [Fe]-hydrogenase and [NiFe]-hydrogenase [15]. Morra et al. [31] reported existence of [FeFe]-hydrogenase enzyme in strict and facultative bacteria.

Dark fermentation can be stimulated by anaerobic bacteria of several different phyla, families, genus and species, belonging to Gram-positive or Gram negative groups. According to Zajic et al. [18] there are several bacteria that produce hydrogen. Bacteria producing hydrogen are from a group of endospore-forming rods Bacillaceae (genuses Clostridum, Bacillus), Gram negative facultatively anaerobic rods (Enterobacteria, Vibrionaceae) and cocci (Veillonellaceae) [32], Gram positive cocci (Micrococcaceae), Peptococcaceae, Gram positive asporogenous rod-shaped bacteria (lactobacillae). Unfortunately, the majority of these bacteria produce hydrogen in amounts considered unsuitable for use in full-scale dark fermentation plants. Hydrogen is produced most efficiently by species of Clostridium, Bacillus, Enterobacter, and some thermophilic bacteria like Thermocellum and Thermatoga.

The role of these bacteria, strict bacteria (Clostridium) and facultative bacteria (Enterobacter, Bacillus) will be described below.

(a) Clostridium

One of the most relevant and the most efficient hydrogen producing groups of bacteria is Clostridium. An important feature of Clostridium is its ability to form protective spores. The protective spores allow surviving harsh conditions, like extreme temperature, low or high pH and chemical agents [33]. Another characteristic of clostridia is lack of cytochrome [34]. Therefore, inoculums containing Clostridium can be pretreated by means of heat, determined pH or chemicals for increase of the hydrogen production rate and to remove other bacteria. Hydrogen producing Clostridium are: *Clostridium acetobutylicum, Clostridium botulinum, Clostridium butylicum, Clostridium butyricum, Clostridium cellobioparum, Clostridium cellulosolvens, Clostridium dissolvens Clostridium fossicularum, Clostridium hydrogenicus, Clostridium kluyveri, Clostridium oedematis-maligni, Clostridium pasteurianum, Clostridium sporogenes, Clostridium tetani, Clostridium tetanomorphum, Clostridium thermocellum, Clostridium thermosaccharolyticum, Clostridium welchii, Clostridium werni*. Among these bacteria, beside thermophilic and *meso*philic, also psychrophilic species appear like *Clostridium algidixylanolyticum* [35]. The most efficient hydrogenic bacteria are *Clostridium butylicum, Clostridium butyricum, Clostridum* kluyveri and *Clostridum pasteuranium* [36]. A monoculture of *Clostridium sp*. can produce from 1.61 to 2.36 mol H_2 mol^{-1}glucose [36]. Clostridia belong to strict anaerobic bacteria, the most important bacteria in mixtures which task is to produce hydrogen with the highest possible efficiency. Despite the high yield of hydrogen production clostridium are very fragile to oxygen and to various form of substrate [28]. Some clostridium like Clostridium sp. strain No. 2 are able to convert glucose and xylose with similar efficiencies [37]. There are attempts to reduce oxygen sensitivity by using them in mixtures with other less air sensitive groups of bacteria termed facultative.

(b) Bacillus

Bacillus is another group of bacteria which like clostridium are made up of endospore forming rods. The most commonly used are Bacillus macerans (acetoethylicus), Bacillus cloacae (Enterobacter cloacae), Bacillus macerans, Bacillus polymyxa. Kumar et al. [27] isolated Bacillus licheniformis from cattle manure. The hydrogen yield of dark fermentation with Bacillus licheniformis was 0.37 mol H_2 mol^{-1} glucose in semi-continuous process and 1.1 mol hydrogen mol glucose in batch mode [28]. The hydrogen yields for Bacillus coagulants from carbohydrates like cellobiose (5.6 mol H_2 mol^{-1} cellobiose), L-arabinose (1.9 mol H_2 mol^{-1} L-arabinose), D-xylose (1.2 mol H_2 mol^{-1} D-xylose) [29] are higher than in the case of bacteria from the Enterobacter group (Citrobacter freundi, Enterobacter cloacae).

(c) Enterobacter

According to Zajic et al. [18] the family of Enterobacterae includes bacteria from seven groups. The genuses are: Escherichia coli (Genus I), Citrobater intermedius (Genus II), Salmonella enteritidis (Genus III), Genus IV (*Enterobacter (Aerobacter) aerogene*), *Enterobacter sp*, *Aerobacter cloacae*, *Aerobacte* indologenes).

Enterobacterae is a group of bacteria that grow anaerobically or aerobically depending on pH value. Enterobacterae are anaerobic bacteria of high air-resistivity. Although oxygen blocks the growth of bacteria it does not decrease hydrogen yield. Therefore, Enterobacter is often used in mixed cultures, which are more sensitive to oxygen. They are used more rarely in monoculture due to lower hydrogen yield than in the case of Clostridium. According to Yokoi et al. [30] for the *Enterobacter aerogenes* strain HO-39 hydrogen yield depends on the kind of carbohydrate substrate, i.e. from 0.83 mol of hydrogen for a mole of lactose to 2.16 mol of hydrogen for a mole of maltose. More detailed analysis of hydrogen production rate and yield are presented in Table 1.

Bacteria can produce hydrogen in the wide range of pH value from 4.00 to 7.8 [31]. Therefore, Enterobacter aerogenes in relation to other

Table 1
Dependence of hydrogen production rate and yield from carbohydrate in case of Enterobacter aerogenes strain HO-39 [31].

Carbohydrate	Hydrogen production rate (ml H_2 l^{-1}subsrate medium)	Hydrogen yield (mol H_2 mol^{-1} substrate)
Glucose	1.243	1.00
Galactose	1.181	0.95
Fructose	1.094	0.88
Mannose	1.218	0.98
Mannitol	2.066	1.68
Sucrose	1.237	1.89
Maltose	1.343	2.16
Lactose	0.514	0.83