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Raw materials for fermentative hydrogen production

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ABSTRACT

The basics of hydrogen production by thermophilic fermentation and photofermentation are outlined. Various types of biomass, which can be used as raw materials for hydrogen fermentation are named and the methods of biomass pretreatment are highlighted. The approach to technical assessment of biomass suitability is reviewed and several promising raw materials are compared with respect to the attainable hydrogen yield.

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1. Introduction

The European Commission's Renewable Energy Roadmap sets out the objective of increasing the share of renewable energies to 20% of gross inland energy consumption by 2020 [1]. Amongst renewable energy sources, the biggest contribution is supposed to come from biomass. Biomass can be converted to energy carriers by thermal (combustion, pyrolysis and gasification) or biological (fermentation, digestion) processes [2,3]. An interesting and promising method of biomass utilisation is hydrogen production by fermentation. Hydrogen fermentation is the topic of Integrated Project HYVOLUTION, financed under the Energy Priority of the 6th Framework Programme of the EU [4]. The project is aimed at developing a blueprint for a complete hydrogen production plant employing two-stage hydrogen fermentation.

In the present paper, several vegetable raw materials are preliminarily evaluated from the point of view of their potential for fermentative conversion to hydrogen. The technical suitability of raw materials and the attainable hydrogen yield are taken into account. The economic aspects are not considered as the biomass cost will be only a fraction of the hydrogen cost which is known to depend also on the size of the production plant and the conversion technology which has not been developed. It is expected that realistic economic estimates will be available upon completion of the HYVOLUTION project in 2010. The commercialisation of fermentative hydrogen production technology is envisaged after 2015.

2. Hydrogen fermentation

The fermentative conversion of biomass to hydrogen builds on anaerobic digestion of carbohydrate-rich substances under influence of bacteria [5]. As a matter of fact, the well known putrefactive fermentation process converting organic substrates to methane also involves production of hydrogen as an intermediate product but under natural conditions this hydrogen is promptly consumed by methanogenic bacteria.

Microorganisms known to produce hydrogen include:

- strict and facultative anaerobic bacteria which convert fermentable sugars to organic acids, H_2 and CO_2; the highest rates of hydrogen production were obtained with certain species of thermophilic bacteria [6,7];
- photofermentative bacteria which use light energy for complete oxidation of substrates to H_2 and CO_2 [8].

Thermophilic fermentation consists in converting sugars or polysaccharides to hydrogen, carbon dioxide and organic acids. The fermentation can be carried out continuously or in batch mode. The typical chemical reactions of thermophilic fermentation of glucose, xylose and sucrose are presented below.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$$

$$3C_5H_{10}O_5 + 5H_2O \rightarrow 10H_2 + 5CH_3COOH + 5CO_2$$

$$C_{12}H_{22}O_{11} + 5H_2O \rightarrow 8H_2 + 4CH_3COOH + 4CO_2$$

The theoretical ratios of hydrogen yield to substrate equal 4 mol per 1 mol of glucose, 3.3 mol per 1 mol of xylose and 8 mol per 1 mol of sucrose.

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Photofermentation consists in converting organic acids to hydrogen and carbon dioxide. Assuming that acetic acid is the substrate, the photofermentation can be represented by the reaction:

$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2$$

The theoretical ratio of hydrogen yield to acetic acid equals 4 mol/mol. During photofermentation the photoheterotrophic microorganisms absorb and use the electromagnetic radiation as an energy source [8]. Due to the alkalinity of the fermentation broth, a volume fraction of carbon dioxide in hydrogen gas is 10–20%. After simple upgrading, the gas can be supplied to a fuel cell.

As the organic acids produced in thermophilic fermentation can be used as substrates for photofermentation, both processes can be coupled as schematically shown in Fig. 1. Compared to the attainable hydrogen yield of thermophilic fermentation, the yield of the two-stage process can be higher by a factor of up to almost 3 making it possible to obtain 70–75% conversion efficiency of fermentable substrates to hydrogen [4]. From the practical point of view, this is the upper limit of conversion efficiency as its value averaged over the period of running hydrogen production may be decreased by deviations from the most favourable process conditions, e.g. temporary instability of bacterial cultures, weather-induced reduction of the intensity of sunlight required for photofermentation, etc.

The main stages of the fermentative hydrogen production process are the following [9]:

- biomass pretreatment to give fermentable feedstock and non-fermentables;
- thermophilic fermentation in which fermentable feedstock is converted to hydrogen gas and organic acids;
- photofermentation in which organic acids are converted to hydrogen gas;
- upgrading of hydrogen gas to meet product specification;
- separation and treatment of non-fermentables.

Thermophilic fermentation is rather well understood but the knowledge of photofermentation is still far from complete. From the engineering point of view it is difficult to design a photofermenter to ensure an effective supply of light energy needed for achieving a satisfactory hydrogen yield. Other process stages, with the exception of pretreatment of certain kinds of biomass, can be based on well known technologies widely applied in agro-food or chemical industries.

3. Potential raw materials for hydrogen fermentation

With regard to the chemical composition there are three different kinds of biomass, which can be used as raw materials for thermophilic fermentation [7]:

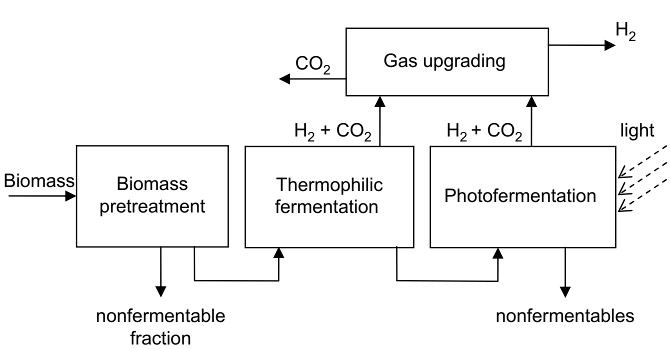

Fig. 1. Scheme of two-stage fermentative hydrogen production.

Table 1
Characteristic data of selected kinds of biomass.

Mass fraction of dry component, %	Raw material				
	Sugar beet	Potato	Wheat bran	Pressed beet pulp	Wheat straw
Sucrose	68	–	–	4	–
Starch	–	76	10	–	–
Cellulose	~4	~4	30	20	35
Hemicellulose	~5	–	25	32	25
Lignin	~1	–	8	4	18
Average yield of fresh biomass, t/ha	45	47	–	–	4,1
Mass fraction of water, %	75	75	10	75	17

- Sucrose containing biomass (i.e. sugar beet, sugar cane, sweet sorghum).
- Starchy biomass (i.e. potato, cereals).
- Lignocellulosic biomass (i.e. grass, wood, straw).

Apart from various kinds of crops, byproducts from biomass processing industries (beet pulp, molasses, potato peels, apple pulp, wheat bran, brewer's grain etc.) can be used for hydrogen production. Characteristic data including chemical composition of five selected kinds of biomass are given in Table 1 [10–13].

Bearing in mind that simple sugars (glucose, xylose, arabinose, etc.) are needed as substrates to thermophilic fermentation, each biomass type requires a proper pretreatment aimed at obtaining water soluble sugars. The method of biomass pretreatment depends mainly on the type and initial form of the raw materials. In the case of sucrose containing biomass, the pretreatment step consists in extracting raw juice which can be directly supplied to the thermophilic fermenter. The pretreatment of starchy and lignocellulosic biomass is more complex due to the necessary hydrolysis converting polysaccharides to simple sugars. An important problem is the removal of lignin before the fermentation unit as in contrast to cellulose and hemicellulose, lignin is not converted to simple sugars and moreover it may hamper the growth of hydrogen-producing microorganisms [7]. The non-fermentable fraction, which contains lignin can be utilised by combustion or gasification to generate energy. Alternatively, as pure lignin is a good raw material for the production of special chemicals and other products [14–16], it can be separated prior to hydrolysis.

On the basis of data given in Table 1 and information from literature, the theoretical and real yields of fermentable simple sugars and lignin were calculated under the following assumptions:

- 96% efficiency of raw juice extraction process in beet sugar factory [10];
- 94% efficiency of starch hydrolysis [17];

Table 2
Theoretical and real yields of simple sugars and lignin.

Theoretical/real yield, kg/t fresh biomass	Raw material				
	Sugar beet	Potato	Wheat bran	Pressed beet pulp	Wheat straw
Sucrose	170 163.2	–	–	10 9.6	–
Glucose	–	211.1 198.4	400 364	55.6 50	322.8 290.5
Xylose	–	–	255.7 230	90.9 81.8	235.8 212.2
Lignin	–	–	72 71.3	10 9.9	149.4 147.9

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