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Development of fermentation based process for biomass conversion to hydrogen gas

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The production of hydrogen gas from biomass to meet the foreseen demand arising from the expected introduction of fuell cells is envisaged. Apart from the well known gasification method, the fermentative conversion can be applied for this purpose. Two options of the latter method, that is, thermophilic fermentation and photofermentation can be combined in a two-stage process in which about 70% of hydrogen present in biomass is converted to gaseous form. It is expected that this process can be applied in decentralised, small scale production units.

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

- 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.

In order to develop a sustainable hydrogen production route based on fermentation, it is necessary to improve the existing knowledge of these process stages and carry out process optimisation studies. As a major step in this direction, European research project HYVOLUTION has been organised under the 6th Framework Programme of the EU.

Keywords: hydrogen fermentation, biomass

1. Introduction

In pursuit of reduction of carbon dioxide emission, there is an increasing interest in the replacement of carbon-containing fuels by hydrogen. The use of hydrogen - in fuel cells or by direct combustion - results in the formation of water with virtually no other emissions. However, as production of hydrogen from fossil fuels is concurrent with carbon dioxide production, the real benefit for carbon dioxide abatement can only be obtained if hydrogen is produced from renewable resources. Various hydrogen production techniques exploiting these resources are currently under investigation [1, 2].

The fermentation based biomass conversion to hydrogen builds on anaerobic digestion of carbohydrate-rich substances under influence of bacteria. As a matter of fact, the well known 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 sugars to organic acids, H_2 and CO_2; the highest rates of hydrogen yield were obtained with certain species of thermophilic bacteria [3,4];
- photofermentative bacteria which use light energy for complete oxidation of substrates to H_2 and CO_2 [5].

Prospects for the application of thermophilic fermentation and photofermentation in commercial hydrogen production are discussed in the present paper.

2. Thermophilic fermentation and photofermentation

Thermophilic fermentation consists in converting simple sugars or disaccharides to hydrogen, carbon dioxide and organic (typically, acetic or lactic) acids. The fermentation can be carried out continuously or in batch mode.

Assuming for simplicity that acetic acid is the main product, the thermophilic fermentation of glucose, xylose and sucrose can be represented by the corresponding reactions:

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

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

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

The maximum theoretical yields of hydrogen per 1 mole of glucose, xylose and sucrose are 4, 3.3 and 8 respectively. Experimental results indicate that yield values close to the theoretical limit can be obtained [3].

Optional raw materials for thermophilic fermentation are sugar- and starch containing plants or byproducts from biomass processing industries: sugar beet, sweet sorghum, potato, cereals, potato peels, wheat bran etc. Lignocellulosic biomass or byproducts like grass, wood, straw, beet pulp, carrot press cake (residue from carrot juice production) etc. can also be used but are more difficult to hydrolyse and the residual lignin may hamper the growth of microorganisms.

Photofermentation consists in reducing substrates 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 advantage of photofermentation is the production of hydrogen-rich gas containing very little carbon dioxide due to the alkalinity of the fermentation broth. After simple upgrading, it can be supplied to a fuel cell.

Thermophilic fermentation is rather well understood but application suffers from hydrogen inhibition at partial pressure of more than 20 kPa. The knowledge of photofermentation is still far from complete. From the engineering point of view it is difficult to design a photofermenter ensuring effective supply of light energy needed for achieving a satisfactory hydrogen yield.

3. Two-stage fermentative hydrogen production

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 from biomass about 70 % of theoretically available hydrogen.

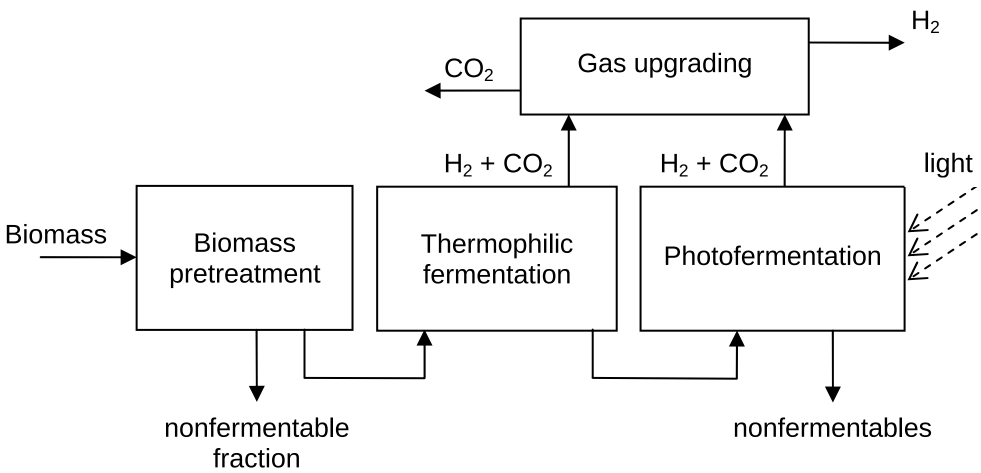

Fig. 1. Scheme of two-stage fermentative hydrogen production

In view of the existing research results, the practicability of two-stage fermentation has been proved but up to now, the experimental work has been carried out on laboratory or pilot scale only. Key parameters of hydrogen production from sugars by selected bacteria species are shown in Table 1 and a selection of data on the present stage of development of various techniques of hydrogen production from renewable resources is given in Table 2.

In order to investigate the suitability od various raw materials for fermentative hydrogen production, tests were made with sugar beet, potato steam peels (starchy material) and pressed beet pulp and miscanthus (lignocellulosic materials). The content of polysaccharides in these materials is given in Table 3.

Table 1. Parameters of hydrogen fermentation of sugars [6]

Bacteria species	H_2 production efficiency (% of theoretical efficiency)	Efficiency of light energy conversion (%)	H_2 production rate on dry biomass (mmol/g·h)	Critical value of H_2 partial pressure (kPa)
Caldicellulosiruptor saccharolyticus (thermophilic)	74-80	not applicable	29	20-56
Rhodopseudomonas sp., *Rhodobacter capsulatus* (photoheterotrophic)	26-87	1-2	0.8-1.6	>90

Table 2. Comparison of parameters of various techniques of hydrogen production from renewable resources [6]

	Efficiency of biomass energy conversion to H_2	Estimated production cost* (EUR/GJ H_2)	Production scale (m^3 H_2/h·1000)	State of development
Gasification of dry biomass	0.55-0.70	3-5	>100	pilot/demo
Supercritical water gasification	0.70	10-15	10	R&D/pilot
Hydrogen fermentation	0.40-0.70	15-25	<1	R&D
Methane fermentation and steam reforming	0.35-0.60	30-45	<1	R&D
Electrolysis of water using PV, wind, hydro etc.	not applicable	20-300	variable	state of the art

*/ biomass excluded

Table 3. Content of polysaccharides in potato steam peels and miscanthus [7, 8, 9]

Raw material	Polysaccharides content (% of dry mass)			
	sucrose	starch	cellulose	hemicellulose
Sugar beet	68	-	4	5
Pressed beet pulp	4	-	20	32
Potato steam peels	-	51	-	-
Miscanthus	-	-	38	24

Miscanthus biomass was pretreated by a combination of mechanical and chemical methods [7], that is, extrusion followed by enzymatic hydrolysis, and potato steam peels were pretreated by enzymatic hydrolysis [8]. The resulting amounts of glucose and xylose that can be directly converted to hydrogen by thermophilic fermentation are given in Table 4 where an estimate of the amount of sucrose which can be obtained from sugar beet is also added.

Table 4. Yield of fermentable sugars obtained from sugar beet, potato steam peels and miscanthus biomass

Raw material	Mass of sugars (kg per 1000 kg dry mass of raw material)		
	glucose	xylose	sucrose
Sugar beet	-	-	653*
Potato steam peels	550	-	-
Miscanthus	270	100	-

*/ calculated assuming 4 % sucrose loss during hot water extraction

It should be added that during pretreatment of each 1000 kg dry mass of potato steam peels, 546 kg dry mass of protein-rich solids are produced, which can be used as cattle feed [8].

Experimental results of fermentative hydrogen production from xylose, glucose, a mixture of these two simple sugars and sucrose are given in Table 5. The tests were performed at 70-72 °C in laboratory bioreactors operated in batch mode, using thermophilic bacteria *C. saccharolyticus.*

Table 5. Experimental results of hydrogen fermentation by *C. saccharolyticus* [10, 11, 12]

Initial substrate concentration (g/l)			H_2 yield (mol H_2/mol substrate)	Acetate yield (mol acetate/mol substrate)
glucose	xylose	sucrose		
10	-	-	2.52	1.44
-	10	-	2.24	1.17
10.6	3.9	-	3.3	1.6
-	-	10*	5.7	2.68
-	-	10**	6.71	3.35

*/ pure sucrose solution; **/ sugar beet juice

On the basis of available experimental data, the complete hydrogen production process based on two-stage fermentation can be envisaged to include the following main steps:

- 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 residual non-fermentables.

Preliminary economic estimates tentatively indicate that industrial-scale applications of the two-stage hydrogen production process can be economically viable. Decentralised production seems to be preferred, that is, hydrogen production plants employing this process should preferably be located close to biomass sources in agricultural regions. Similar to other hydrogen production technologies, logistical factors including raw-material production and transportation, and hydrogen supply to the distribution system will play an important role [13].

4. Concluding remarks

Research on fermentative hydrogen production from biomass received funding under the Energy Priority of the 6th Framework Programme of the EU. In January 2006, a 5-year project titled "Non-thermal production of pure hydrogen from biomass – HYVOLUTION" was started [14, 15]. The work is coordinated by Wageningen UR Biobased Products, The Netherlands, and the project consortium is composed of 21 partners representing 11 European countries plus Republic of South Africa.

The project is aimed at developing a blueprint for a complete hydrogen production plant employing two-stage fermentation. Suitable biomass resources - energy crops and bio-residues - are tested for fermentability and economically evaluated, and pretreatment technologies for optimal biodegradation of selected biomass types are under development. Among raw materials under investigation, sugar beet juice, molasses, potato steam peelings, miscanthus, barley straw, wheat bran and carrot press cake can be named.

Concurrent experimental work on thermophilic fermentation, photofermentation and gas upgrading is under way. It includes testing of prototype equipment units with the aim to provide necessary data for process modeling, simulation and integration. Simulation studies aimed at maximising the efficiency of biomass conversion to hydrogen and minimising the energy consumption make it possible to work out schemes of the production plant and specifications of the necessary equipment.

The project also includes socio-economic research on issues of key importance to future implementation of fermentative hydrogen production: life cycle analysis, identification of future stakeholders, ways to increase public awareness and societal acceptance, etc. To carry out this part of project work, necessary data are collected from experiments, simulation studies and literature.

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References

[1] Hallenbeck P., Benemann J.R.: Biological hydrogen production; fundamentals and limiting processes. Int. J. Hydrogen Energy, 27:1185-1193, 2002.

[2] Levin D.B., Pitt L., Love M.: Biohydrogen production: prospects and limitations to practical application. Int. J. Hydrogen Energy, 29:173-185, 2004.

[3] van Niel E.W.J., Budde M.A.W., de Haas G.G., van der Wal F.J., Claassen P.A.M., Stams A.J.M.: Distinctive properties of high hydrogen producing extreme thermophiles, *Caldicellulosiruptor saccharolyticus* and *Thermotoga elfii.* Int. J. Hydrogen Energy , 27:1391-1398, 2002.

[4] de Vrije T., Claassen P.A.M.: Dark hydrogen fermentations. In: Reith J.H., Wijffels R.H., Barten H. (editors): Bio-methane & Bio-hydrogen. The Hague: Smiet offset, 103-123, 2003.

[5] Basak N., Das D.: The prospect of purple non-sulfur (PNS) photosynthetic bacteria for hydrogen production: the present state of the art. World Journal of Microbiology and Biotechnology, 23:31-42, 2007.

[6] Claassen P.A.M, van Groenestijn J.W., Janssen A.J.H., van Niel E.W.J., Wijffels R.H.: Feasibility of biological hydrogen production from biomass for utilisation in fuel cells. Paper presented at the 1st World Conference and Exhibition on Biomass for Energy, Sevilla, 2005.

[7] de Vrije T., de Haas G.G., Tan G.B., Keijsers E.R.P., Claassen P.A.M.: Pretreatment of Miscanthus for hydrogen production by *Thermatoga elfi.* Int. J. Hydrogen Energy, 27:1381-1390, 2002.

[8] Claassen P.A.M., de Vrije T., van Groenestijn J.W.: Biological hydrogen production from biomass. ntp procestechnologie, 3, 2004.

[9] Bohn K., Clarke M.A., Buchholz K.: Composition of sugar beet and sugarcane and chemical behavior of constituents in processing. In: van der Poel P.W., Schiweck H., Schwartz T. (editors): Sugar technology. Berlin: Bartens, 115–208, 1998.

[10] Kadar Z., de Vrije T., van Noorden G.E., Budde M.A.W., Szengyel Z., Reczey K., Claassen P.A.M.: Yield from glucose, xylose, and paper sludge hydrolysate during hydrogen production by extreme thermophile *Caldicellulosiruptor saccharolyticus*. Appl. Biochem. Biotechnol., Vol. 113-116:497-508, 2004.

[11] Panagiotopoulos I.A., Bakker R.R., de Vrije T., Urbaniec K., Koukios E.G., Claassen P.A.M.: Prospects of utilization of sugar beet carbohydrates for biological hydrogen production in the EU. Journal of Cleaner Production (in press).

[12] de Vrije T., Bakker R.R., Budde M.A.W., Lai M. H., Mars A. E., Claassen P.A.M.: Efficient hydrogen production from the lignocellulosic energy crop Miscanthus by the extreme thermophilic bacteria *Caldicellulosiruptor saccharolyticus* and *Thermotoga neapolitana*. Biotechnology for Biofuels, 2(12): 12-26, 2009.

[13] Ball M., Wietschel M. (editors): The hydrogen economy: opportunities and challenges. Cambridge University Press, 2009.

[14] Claassen P.A.M., de Vrije T.: Non-thermal production of pure hydrogen from biomass: HYVOLUTION. Int. J. Hydrogen Energy, 31:1416-1423, 2006.

[15] Project HYVOLUTION, http://www.hyvolution.nl