Development of fermentation based process for biomass conversion to hydrogen gas

Pieternel A.M. Claassen¹, Truus de Vrije¹, Krzysztof Urbaniec², Robert Grabarczyk²
¹Wageningen UR Biobased Products, POBox 17, 6700 AA Wageningen, The Netherlands
²CERED Centre of Excellence, Warsaw University of Technology – Plock Campus, Jachowicza 2/4, 09-402
Plock, Poland

The production of hydrogen gas from biomass to meet the foreseen demand arising from the expected introduction of fuel 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, H₂ and CO₂; 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 H₂ and CO₂ [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:

\[
\begin{align*}
C_6H_{12}O_6 + 2H_2O & \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \\
3C_3H_{10}O_5 + 5H_2O & \rightarrow 5CH_3COOH + 10H_2 + 5CO_2 \\
C_{12}H_{22}O_{11} + 5H_2O & \rightarrow 4CH_3COOH + 8H_2 + 4CO_2
\end{align*}
\]

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.

![Diagram of two-stage fermentative hydrogen production](image)

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 of 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]

<table>
<thead>
<tr>
<th>Bacteria species</th>
<th>H$_2$ production efficiency (% of theoretical efficiency)</th>
<th>Efficiency of light energy conversion (%)</th>
<th>H$_2$ production rate on dry biomass (mmol/g·h)</th>
<th>Critical value of H$_2$ partial pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Caldicellulosiruptor saccharolyticus</em> (thermophilic)</td>
<td>74-80</td>
<td>not applicable</td>
<td>29</td>
<td>20-56</td>
</tr>
<tr>
<td><em>Rhodopseudomonas sp.</em>, <em>Rhodobacter capsulatus</em> (photoheterotrophic)</td>
<td>26-87</td>
<td>1-2</td>
<td>0.8-1.6</td>
<td>&gt;90</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Method</th>
<th>Efficiency of biomass energy conversion to H$_2$</th>
<th>Estimated production cost* (EUR/GJ H$_2$)</th>
<th>Production scale (m$^3$ H$_2$/h·1000)</th>
<th>State of development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasification of dry biomass</td>
<td>0.55-0.70</td>
<td>3-5</td>
<td>&gt;100</td>
<td>pilot/demo</td>
</tr>
<tr>
<td>Supercritical water gasification</td>
<td>0.70</td>
<td>10-15</td>
<td>10</td>
<td>R&amp;D/pilot</td>
</tr>
<tr>
<td>Hydrogen fermentation</td>
<td>0.40-0.70</td>
<td>15-25</td>
<td>&lt;1</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Methane fermentation and steam reforming</td>
<td>0.35-0.60</td>
<td>30-45</td>
<td>&lt;1</td>
<td>R&amp;D</td>
</tr>
<tr>
<td>Electrolysis of water using PV, wind, hydro etc.</td>
<td>not applicable</td>
<td>20-300</td>
<td>variable</td>
<td>state of the art</td>
</tr>
</tbody>
</table>

*/* biomass excluded

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

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Polysaccharides content (% of dry mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sucrose</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>68</td>
</tr>
<tr>
<td>Pressed beet pulp</td>
<td>4</td>
</tr>
<tr>
<td>Potato steam peels</td>
<td>-</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>-</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Mass of sugars (kg per 1000 kg dry mass of raw material)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>glucose</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>-</td>
</tr>
<tr>
<td>Potato steam peels</td>
<td>550</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>270</td>
</tr>
</tbody>
</table>

*/ 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]

<table>
<thead>
<tr>
<th>Initial substrate concentration (g/l)</th>
<th>H₂ yield (mol H₂/mol substrate)</th>
<th>Acetate yield (mol acetate/mol substrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>glucose</td>
<td>xylose</td>
<td>sucrose</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>10.6</td>
<td>3.9</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>10*</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>10**</td>
</tr>
</tbody>
</table>

*/ 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.
Acknowledgement

Support of the European Commission under contract 019825 HYVOLUTION is gratefully acknowledged.

References


