

HYDROGEN PRODUCTION FROM BIOMASS

Marián Mešter, Jozef Rusnák

ABSTRACT

The future vision for hydrogen is that it will be cost-effectively produced from renewable energy sources and made available for widespread use as an energy carrier and a fuel. Biomass has the potential to accelerate the realisation of hydrogen as a major fuel of the future. The article describes the relevant technologies that convert biomass to hydrogen.

1. INTRODUCTION

Hydrogen is the lightest and most abundant element of the universe, represented by the symbol „H“. It is the first element in the periodic table with the atomic number 1. A hydrogen atom consists of one proton and one electron and a hydrogen nucleus is just a single proton. It is a major component of organic molecules, which are the building blocks of all organisms and it is found most frequently in water. At room temperature hydrogen is a gas, but when cooled to very low temperatures (below -253°C or 20 K) it becomes a liquid. Hydrogen occurs as H_2 at ambient temperature and pressure, colorless, odorless and extremely flammable gas.

It was discovered in 1766 by Henry Cavendish of England. In the first it was described as „inflammable air“ that Lavoisier later named „hydrogen“ (Greek: water former).

Even though hydrogen does not exist by itself on Earth, it can be produced from a wide variety of resources – coal, oil, natural gas, biomass, and water – using a variety of process technologies. Once hydrogen is produced, it must be transported to its point of use. Its low volumetric energy density makes it challenging to transport and deliver. Today hydrogen is stored and transported as a compressed gas or cryogenic liquid. [10]

2. HYDROGEN PRODUCTION FROM BIOMASS

Biomass and biomass-derived fuels are renewable energy sources that can be used to produce hydrogen sustainably. Using biomass instead of fossil fuels to produce hydrogen reduces the net amount of carbon dioxide released to the atmosphere, since the carbon dioxide released when the biomass is gasified was previously absorbed from the atmosphere and fixed by photosynthesis in the growing plants. Most regions of the world have enough suitable biomass – agricultural crops, crop residues, wood, agro-industrial waste, household waste, animal manure, sewage sludge and so on – to provide significant economic and environmental benefits. The eventual aim should be to coproduce hydrogen alongside other value-added by-products.

A wide range of technologies exists for transforming biomass into hydrogen (Figure 1). The conversion may take place either directly or via storable intermediates. Direct routes have the advantage of simplicity. Indirect routes have additional production steps, but have an advantage in that there can be distributed production of the intermediates, minimising the transportation costs of the biomass. [4]

Processes can be grouped into thermochemical and biological routes, both of which are relevant in the near- and mid-term. In the long term it may also be possible to produce hydrogen using photobiological processes, such as photosynthesis in cyanobacteria and algae. Hydrogen or hydrogen-rich gas derived from biomass can readily be used in most hydrogen energy conversion devices and fuel cells. However, no technology for producing hydrogen from biomass or microbes is yet economically competitive or commercially available. In particular, biomass cannot currently compete with steam reforming of natural gas as a source of hydrogen. [3]

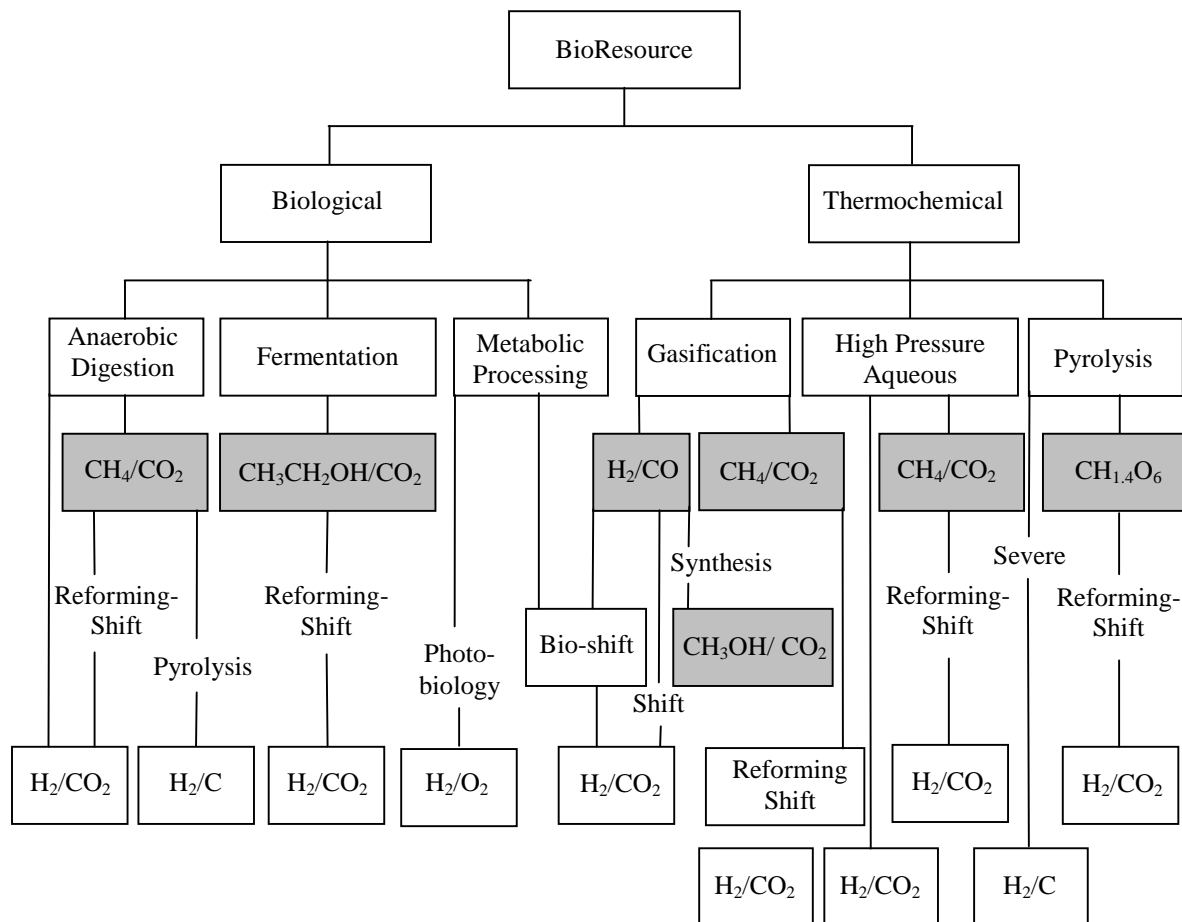


Fig. 1. Pathways from biomass to hydrogen. Storable intermediates are shown in grey boxes. [3]

2.1 Biological production

Biological methods present a less energy-intensive means of hydrogen production. These can occur at ambient temperatures and pressure and predominantly generate hydrogen and carbon dioxide.

Anaerobic digestion and fermentation

Anaerobic digestion is the biological degradation of organic material without oxygen present. This results in the production of biogas, a valuable (energy containing) product. Biological conversion via anaerobic digestion is currently being practised by workers around resulting in methane that can be processed to hydrogen by conventional steam reforming processes. [6]

The definition above contains four parts: biological, degradation, organic material and without oxygen.

- *Biological*: This implies that the process is carried out by bacteria, which have to be kept in a healthy condition and in good living conditions. The bacteria have to be grown and nurtured in the process to get a good production of biogas.
- *Degradation*: This means that the substrate/organic material is broken down into its building blocks and subsequently for a large part into biogas.
- *Organic material*: The (dry) material in greenhouse residues consists of organic, or natural, material and anorganic materials like sand. Part of the organic material is broken down into biogas.
- *Without oxygen*: This means that air is not allowed to interact with the greenhouse residues. In degrading greenhouse residues there are a few competing biological processes: with and without the presence of oxygen. To promote the production of biogas as a valuable product of the degradation, oxygen must be kept away from the reactor contents.

The biological anaerobic degradation of greenhouse residues can be divided into four steps [6]:

1. *Hydrolysis*: high weight organic molecules (like proteins, carbohydrates, fat, cellulosis) are broken down into smaller molecules like sugars, aminoacids, fatty acids and water.
2. *Acidogenesis*: further breakdown of these smaller molecules into organic acids, carbondioxide, hydrogen sulfide and ammonia occurs.
3. *Acetogenesis*: the products from the acidogenesis are used for the production of acetates, carbondioxide and hydrogen.
4. *Methanogenesis*: methane, carbondioxide and water are produced.

Fermentation is a sequence of reactions which release energy from organic molecules in the absence of oxygen. All beverage ethanol and more than half of industrial ethanol is made by this process. From ethanol it is possible to produce hydrogen.

The first reactor capable of producing hydrogen from a renewable fuel source - ethanol - efficiently enough to hold economic potential has been invented by University of Minnesota engineers. The invention rests on two innovations: a catalyst based on the metals rhodium and ceria, and an automotive fuel injector that vaporizes and mixes the ethanol-water fuel. The vaporized fuel mixture is injected into a tube that contains a porous plug made from rhodium and ceria. The fuel mixture passes through the plug and emerges as a mixture of hydrogen, carbon dioxide and minor products. The reaction takes only 50 milliseconds and eliminates the flames and soot that commonly accompany ethanol combustion. [9]

Metabolic processing

A third area of hydrogen production within biological processes is split water by photo biological organisms. The process called „biophotolysis“ or „photobiological hydrogen production“. Photobiological hydrogen production is based on photosynthesis in microorganisms, like green algae and cyanobacteria. The organism's photosynthetic apparatus captures light, and the resulting energy is used to couple water splitting to the generation of a reducing agent which is used to reduce a hydrogenase enzyme within the organism. Thus photosynthesis uses solar energy to convert water to oxygen and hydrogen. [3]

This photosynthetic pathway produces renewable fuels without producing greenhouse gases. The scientific challenge associated with the approach is that the enzyme (a reversible hydrogenase) that actually releases the hydrogen is sensitive to oxygen. The process of photosynthesis produces oxygen and this normally stops hydrogen production very quickly in green algae. So, to overcome this problem scientists are generating O₂-tolerant, H₂-producing mutants from photosynthetic microorganisms by various genetic approaches. The ultimate goal of this work is to develop a water- splitting process that will result in a commercial H₂-producing system that is cost effective, scalable to large production, non-polluting, and self-sustaining. [8]

2.2 Thermochemical production

Gasification

Gasification is one of the thermochemical conversion processes that can be used to transform biomass into thermal energy and electricity. The gasification process takes place at around (800-1000)°C and needs a moderate supply of oxidant, less than required for a combustion process.

There are several simultaneous thermochemical processes that are realising inside the gasification reactor. Once the biomass is heated, it first releases its volatile components (CO, CO₂, H₂, H₂O, CH₄, light hydrocarbons and tar). This process is known as pyrolysis and it takes place both in an inert or in an oxidant atmosphere. The remaining solid fraction (char) still contains a high amount of carbon and therefore, energy. The char reacts further with the gaseous products from pyrolysis mainly to produce H₂, CO. These reactions are endothermic and are known as the gasification reactions. The solid carbon and the volatile compounds can also burn if there is

some oxidant available. The combustion reaction is exothermic and therefore provides the heat for the gasification reactions. [1]

High pressure aqueous

When pulverized biomass is mixed with water to make a slurry and then put under high pressure, either a high or low temperature process can be used to produce oils and fuels, including hydrogen. After being subjected to high temperature, a pressurized slurry can be suddenly depressurized, or „flashed“, to produce high quality oils and gases. The low temperature, high pressure technology forces the slurry through a catalyst to produce fuels, including hydrogen. [2]

Pyrolysis

Biomass pyrolysis produces a liquid product (bio-oil) that contains a wide spectrum of components that can be separated into valuable chemical and fuels. In pyrolysis, biomass is broken down into highly reactive vapors and a carbonaceous residue, or char. The vapors, when condensed into pyrolysis oils, can be steam reformed to produce hydrogen. [7]

Pyrolysis is defined as chemical decomposition occurred in organic materials by heating it to a high temperature without oxygen, or with a so limited supply of oxidising agents that gasification does not take place or only little gasification occurs. Pyrolysis usually occurs under pressure higher than atmospheric pressure and at operating temperatures higher than 430°C. The mechanism of pyrolysis is that the atoms in the organic molecules of the materials vibrate apart at random positions due to the heavy vibrations at the temperature for pyrolysis. The products from pyrolysis are gases, liquid after condensation, and a solid residue containing fixed carbon. [5]

Liquid production from fast pyrolysis has become more important than solid charcoal production. In comparison to the traditional pyrolysis processes for charcoal manufacture, fast pyrolysis is an advanced process to produce a significant fraction of biomass as a liquid. In fast pyrolysis, the organic materials are heated to (450 – 600) °C in the absence of air very rapidly. Similarly, the products would be organic vapours, pyrolysis gases and charcoal under these conditions. The vapours are condensed to a liquid mixture, which is called bio-oil. [5]

3. CONCLUSIONS

At present hydrogen from fossil fuels is by far cheaper than hydrogen from other sources. A massive research effort in the biomass to hydrogen conversion technologies is necessary in order to decrease the cost of „renewable“ hydrogen. The main aim of this article was to describe some from these technologies that can be used to convert biomass to hydrogen.

4. REFERENCES

- [1] Barrio, M.: *Hydrogen from Biomass Gasification*. Trondheim: Norwegian University of Science and Technology, Institute of Thermal Energy and Hydropower, Norway. [online] [cit. 2005-07-14]
Available from: <<http://www.tev.ntnu.no/MariaBarrio/publikasjoner/H2%20conference.pdf>>
- [2] Brown, K.: *Producing Renewable Hydrogen from Biomass*. In: BioCycle Energy, January 2004. [online] [cit. 2005-07-14]
Available from: <<http://www.moea.state.mn.us/p2/forum/040129biocycle-biomass.pdf>>
- [3] Larsen, H., Feidenhans'l, R., Petersen, S. L.: *Risø Energy Report 3: Hydrogen and its competitors*. Roskilde: Risø National Laboratory, November 2004, Denmark.
- [4] Milne, A.T., Elam, C. E., Evans, J. R.: *Hydrogen from Biomass: State of the Art and Research Challenges*. Golden: National Renewable Energy Laboratory, USA.
- [5] Zhang, L.: *Sunlight Ancient and Modern: The Relative Energy Efficiency of Hydrogen from Coal and Current Biomass*. Atlanta: Georgia Institute of Technology, July 2004, Georgia, USA.

- [online] [cit. 2005-07-14] Available from: <http://etd.gatech.edu/theses/submitted/etd-08182004-145924/unrestricted/zhang_ling_200412_mast.pdf>
- [6] Biomass Technology Group: *Anaerobic digestion*. [online] [cit.2005-07-14] Available from: <<http://www.btgworld.com/technologies/anaerobic-digestion.html>>
- [7] National Renewable Energy Laboratory: *Advanced Hydrogen Production Technologies* In: Hydrogen energy for tomorrow, August 1995. [online] [cit. 2005-07-14] Available from: <<http://www.osti.gov/bridge/servlets/purl/161466-3AdeH0/webviewable/161466.pdf>>
- [8] National Renewable Energy Laboratory: *Hydrogen and Fuel Cells Research: Research Expertise*. [online] [cit. 2005-07-14] Available from: <<http://www.nrel.gov/hydrogen/expertise.html?print>>
- [9] University News Service: *New Reactor Puts Hydrogen From Renewable Fuels Within Reach*. [online] [cit.2005-07-14] Available from: <<http://www.ur.umn.edu/FMPro?-db=releases&-lay=web&-format=unsreleases/releasesdetail.html&ID=1155&-Find>>
- [10] U.S. Department of Energy: *Hydrogen Production and Delivery*. [online] [cit.2005-07-14] Available from: <<http://www.eere.energy.gov/hydrogenandfuelcells/production/basics.html>>

Authors` address:

Ing. Marián Mešter, PhD., Ing. Jozef Rusnák, PhD.
Department of Electric Power Engineering
Technical University of Košice
Mäsiarska 74
040 01 KOŠICE, Slovak Republic
E-mail: marian.mester@tuke.sk, jozef.rusnak@tuke.sk,
Tel: + 421 / 55 / 602 3556, + 421 / 55 / 602 3555
Fax: + 421 / 55 / 602 3552