Efficiency analysis of hydrogen production methods from biomass

Krzysztof J. Ptasinski

Chemical Engineering Department,
Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven,
The Netherlands
E-mail: k.j.ptasinski@tue.nl

Abstract: Hydrogen is considered as a universal energy carrier for the future, and biomass has the potential to become a sustainable source of hydrogen. This article presents an efficiency analysis of hydrogen production processes from a variety of biomass feedstocks by a thermochemical method – gasification as well as biochemical methods – fermentation and anaerobic digestion. The exergetic efficiency of H_2 production by gasification of more dry biomass is comparable to that of the commonly used Steam Methane Reforming. The detailed exergy analysis of H_2 production by biomass gasification shows that the largest exergy losses occur in the gasifier.
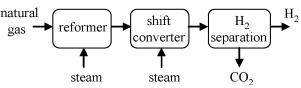
Biographical note: Krzysztof J. Ptasinski is an Associate Professor in chemical engineering at the Eindhoven University of Technology, Department of Chemical Engineering. He received an MSc and a PhD in chemical engineering from the Warsaw University of Technology, Poland. His research interest includes sustainable energy, applied thermodynamic and application of electrical energy to process engineering. He is the Author of more than 150 publications in various fields of chemical engineering, mainly chemical reactor engineering, separation processes and applied thermodynamics.

1 Introduction

The present world's energy demand is met by fossil fuels, i.e. petroleum, natural gas and coal. Two global problems related to the use of fossil fuels are a fast depletion and environmental damage due to emissions of various gases as CO_x, SO_x and NO_x. In future, our energy systems not only need to be renewable and sustainable, but also efficient, cost-effective and safe. It is widely acknowledged that the solution to the global problems would be to replace the existing fossil fuels by hydrogen as the universal energy carrier (Conte et al., 2001). The main advantages of the hydrogen system are that both production and utilisation of hydrogen can be emission-free and hydrogen can be obtained from a variety of feedstocks. Hydrogen can be used as a fuel in fuel cells for

power generation and in the transportation sector. Currently, however, hydrogen is produced mostly from fossil fuels, by steam reforming of natural gas (Steam Methane Reforming, SMR) and naphtha or coal gasification.

Figure 1   Schematics of the Steam Methane Reforming process

Today, most H_2 (90%) is generated from fossil fuels mainly by SMR what is not a sustainable process route. Generally, a SMR system is comprised of a reforming reactor, a shift converter and a H_2 separation, as shown in Figure 1. In the reformer, a synthesis gas containing H_2 and an appreciable amount of CO is produced. Further, this gas is processed in a shift reactor where CO is converted with steam into H_2. The final step is separation of H_2 from water and CO_2, usually by Pressure Swing Adsorption (PSA). The overall reaction of this process is

$$CH_4 + 2\,H_2O = CO_2 + 4\,H_2. \tag{1}$$

The future hydrogen energy systems must be based on hydrogen production from renewable energy sources. Actually, many new technologies are under development using water splitting by thermochemical or photo processes, solar- or wind-driven electrolysis or different biomass conversion processes. Biomass is the most versatile non-renewable resource that can be used for sustainable production of hydrogen. Renewable hydrogen technologies based on low value waste biomass as feedstock have great potential to become a cost-effective energy production.
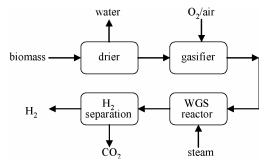
The objective of this article is to presented an efficiency analysis of different production technologies of hydrogen from biomass. The presented efficiency analysis is based on exergy analysis in order to take into account different quality of material and energy streams involved in considered technologies. In Section 2, both thermochemical and biochemical hydrogen technologies are discussed. The method of exergy analysis is explained in Section 3. Subsequently, in Section 4, an exergy analysis is performed for a thermochemical gasification process for a number of biomass feedstocks, such as wood, straw, sludge, manure and vegetable oil. Finally, the exergetic efficiency of thermochemical processes is compared with those of the biochemical processes as well as classical steam reforming of natural gas.

2   Hydrogen from biomass

Biomass has several important advantages which can accelerate the realisation of hydrogen economy. Key features are renewability and neutral CO_2 impact. Biomass has also unique versatility. A wide range of biomass sources, such as traditional agricultural crops, dedicated energy crops, residues from agriculture and foresting can be used to make hydrogen. These biomass feedstocks vary greatly in chemical composition, energy content, ash and moisture content. Generally, this is regarded as a real advantage, because it means that the best available and economically attractive feedstock can be selected.

The question is whether all the biomass type can be converted to hydrogen with reasonable exergetic efficiency. Relatively, the high efficiencies are very desired as the hydrogen content in biomass is low (approximately 6 wt% vs. 25% for methane) and energy content is also low due to high oxygen content (about 40 wt% of biomass).

Figure 2 Schematics of the thermochemical process for hydrogen from biomass

Biomass-to-H_2 conversion technologies can be divided into two categories: thermochemical and biochemical (Milne, Elam and Evans, 2002). The most widely practiced thermochemical process route for biomass-to-hydrogen is gasification coupled with Water Gas Shift (WGS, Figure 2). The first step drying is often needed for a wet biomass to assure autothermic gasification. Gasification is a high-rate pyrolysis carried out in the temperature range of 600–1,000 °C in fluidised bed reactors. The syngas produced in the gasifier contains mainly H_2, CO, moreover CO_2 and H_2O. In the WGS reactor, CO is subsequently converted into H_2 due to reaction

$$CO + H_2O = CO_2 + H_2. \tag{2}$$

The final step is separation of H_2 from CO_2 and water.

The biochemical conversion technologies are based on rather complex systems of biochemical reactions involving microorganisms, usually bacteria and enzymes. The main processes are photolysis, dark fermentation, photo fermentation, anaerobic digestion and are discussed in Section 5.

3 Method of exergy analysis

The exergy analysis is a relatively new analysis method in which the basis of evaluation of efficiency follows from the second law rather than the first law of thermodynamics. The exergy balance of a process can be represented in the following form using exergy values of all streams entering and leaving the process:

$$\sum_{\text{IN}} E_j + E^Q + E^W = \sum_{\text{OUT}} E_k + I \tag{3}$$

where $\sum_{\text{IN}} E_j$ and $\sum_{\text{OUT}} E_k$ are exergy flow of all entering and leaving material streams, respectively, E^Q and E^W are the sums of all thermal exergy and work interactions involved in a process. The difference between the concept of exergy and those of mass and energy is that exergy is not conserved but subjected to dissipation. It means that the

exergy leaving any process step will always be less than the exergy in. The difference between all entering exergy streams and that of leaving streams is called irreversibility *I*. Irreversibility represents the internal exergy loss in process as the loss of quality of materials and energy due to dissipation.

Table 1   Proximate and ultimate analysis of various biomass *Feedstock*

Feedstock	Proximate analysis (wt%)			Ultimate analysis (wt% of organic fraction)				
	Moisture	Ash	Organic fraction	C	H	O	N	S
Wood	19.8	1.84	78.4	50.8	6.06	42.7	0.36	0.07
Straw	12.7	6.37	80.9	48.9	5.97	43.9	0.82	0.15
Sludge	32.5	25.72	41.8	50.2	7.09	34.9	5.63	1.77
Manure	43.6	17.20	39.2	50.2	6.50	34.6	5.19	0.85
Vegetable oils	0	0	100	75.4	11.7	12.9	0	0

The quality of material streams can be expressed using their physical and chemical exergy.

$$E = E_{ph} + E_{ch} \tag{4}$$

where E_{ph} is the physical exergy and E_{ch} is the chemical exergy. The standard chemical exergy of a pure chemical compound ε_{ch} is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterised by the environmental temperature T_0 (298.15 K) and environmental pressure P_0 (1 atm), to the dead state, characterised not only by the same environmental conditions of temperature and pressure, but also by the concentration of reference substances in standard environment. The physical exergy is equal to the maximum amount of work obtainable when a compound or mixture is brought from its temperature T and pressure P to environmental conditions, characterised by environmental temperature T_0 and P_0.
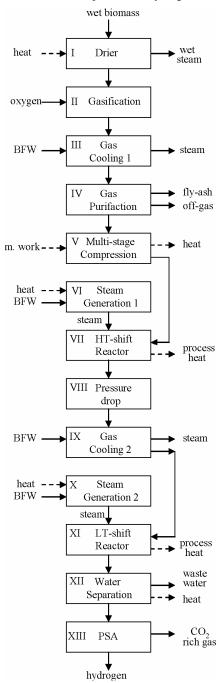
4   Exergy analysis of hydrogen production from biomass gasification

Exergy analysis of thermochemical H_2 production has been performed for different biomass feedstocks, including wood, straw, sludge, manure and vegetable oil. Table 1 shows proximate and ultimate analyses of considered feedstocks taken from the Phyllis database (2002).

The conversion of all biomass feedstocks to H_2 have been simulated using the flow sheeting program Aspen Plus. First, the process has been modelled and simulated for a standard set of conditions shown in Table 2. The most important parameters are the gasifier temperature and moisture content of biomass leaving the drier; the standard values of these parameters are 1,173 K and 10 wt%, respectively. Subsequently, the process conditions have been modified to determine the influence of the operating conditions on the overall efficiency and total exergy loss of the process.

Figure 3 shows the flow sheet of the H_2-from-wood process. The wood is first dried in the thermal drier to its final moisture content, which was varied between 5 and 17.5 wt%. The partially dried wood enters the gasifier, where it is exposed to a limited amount of oxygen. The gasifier temperature was varied between 973 and 1,373 K. In the gasifier, a syngas containing H_2, CO, CO_2 and H_2O is produced due to equilibrium chemical reactions. The syngas composition has been computed by Aspen Plus by

minimisation of the Gibbs free energy of the system. The syngas leaving the gasifier is first cooled down to 623 K and next cleaned from ash and tar (off-gas). Subsequently, H_2 content in the syngas is increased in two WGS reactors. The first reactor operates at High

Figure 3 Flow sheet of the thermochemical process for hydrogen from wood

Temperature (HT) of 623 K and the pressure of 30 bar whereas the second one – at Low Temperature (LT) of 423 K and 25 bar. Both shift reactors are modelled as equilibrium reactors. The steam needed in shift reactors is generated in separate units. The gas leaving the LT-shift reactor contains H_2, water and CO_2. Water is separated in a flash unit at 20 bar and 298 K, whereas CO_2 is separated from H_2 by PSA. The PSA process is modelled in Aspen Plus assuming H_2 separation efficiency equal to 85 and 100% purity of hydrogen as the main product.

Figure 4 The influence of the gasifier temperature on the exergetic efficiency and exergy loss for the H_2-from-wood process
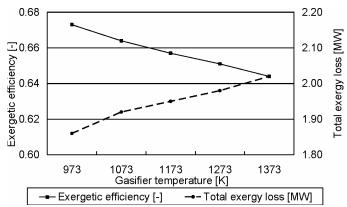

Table 2   Flow rate, temperature, pressure and exergy flow rate of the main process streams of the hydrogen-from-wood process (standard conditions)

Process stream	Flow rate (kg hour^{-1})	Temperature (K)	Pressure (bar)	Exergy flow rate(MJ s^{-1})
Biomass:				
Feed	1,000	298	1	4.64
Leaving drier	891	423	1	4.65
Wet steam from drier	109	423	1	0.017
Oxygen	396	298	1	0.137
Syngas:				
Leaving gasifier	1,287	1173	1	3.48
Leaving compressor	1,269	620	30	3.40
Steam produced from gas cooling 1	361	773	50	0.15
Gas purification:				
Fly-ash	15	623	1	0.008
Off-gas	3	298	1	0.004
H_2-rich gas:				
Leaving HT shift reactor	1,955	623	30	3.44
Leaving LT shift reactor	1,973	473	25	3.35
Steam produced from gas cooling 2	195	473	10	0.05
Wastewater	567	298	1	0
PSA products:				
CO_2-rich gas	1,330	298	1	0.61
Hydrogen	76	298	19	2.54

Table 2 summarises flow rate, temperature, pressure and exergy flow rate, calculated according to Szargut, Morris and Steward (1988), for the main streams of the H_2 – from wood process at the gasifier temperature of 1,173 K and the moisture content of biomass leaving the drier of 10 wt%. The exergy of oxygen is taken as the product of its chemical exergy and the exergetic cost of making oxygen from air, equal to 10% (Simbeck, Dickenson and Oliver, 1983). Exergy analyses were performed for the overall process as well as for separate process units indicated in Figure 3. Figure 4 demonstrates that the overall exergetic efficiency increases with decreasing gasifier temperature, and consequently the total exergy losses (internal and external) decreases with decreasing this temperature. The overall exergetic efficiency at the standard conditions is 65.7% what is calculated as the ratio between the exergy of useful process output: H_2, CO_2-rich gas and utilities (process heat from both shift reactors, steam from gas cooling 1 and 2 and drier) and the exergy of the process input: biomass, oxygen, utilities (compressor work, heat for steam generation 1 and 2 and drier). External exergy losses take place in the gasifier (ash and off-gas) and water separation (wastewater and heat).

A breakdown by process units of the total exergy losses for this process is shown in Figure 5 for different gasifier temperatures and the standard value of the moisture content of biomass leaving the drier of 10 wt%. The principal exergy losses occur in the gasifier and these losses decrease with decreasing gasifier temperature which also influence the total exergy losses, as shown in Figure 4. The exergy losses during water separation, gas compression, and both shift reactors are lower than that in the gasifier but still substantial. Figure 6 demonstrates that the total exergy losses decrease with decreasing moisture content in the biomass leaving the drier for both gasifier temperatures of 973 and 1,173 K.
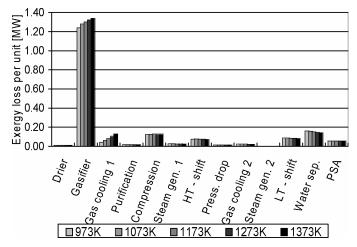
Figure 5 Exergy losses per unit for the hydrogen-from-wood process

Figure 6   The influence of the moisture content in the biomass leaving the drier on the exergetic efficiency and exergy loss for the H_2-from-wood process
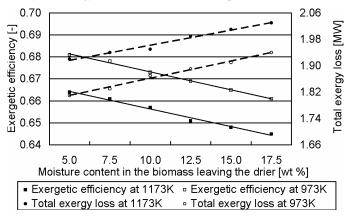

Figure 7   The influence of the original moisture content in biomass feed on the exergetic efficiency of thermochemical hydrogen production
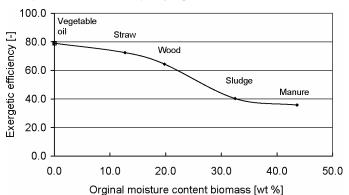

Table 3   Exergetic efficiency and amount of produced hydrogen for thermochemical processes (standard conditions)

Biomass	Exergetic efficiency (%)	Amount produced H_2 (kg hour^{-1})
Wood	65.7	75.1
Straw	72.5	83.5
Sludge	40.3	23.4
Manure	35.8	17.5
Vegetable oil	79.1	55.1

Table 3 summarises the overall exergetic efficiency as well as amount of produced H_2 for all investigated biomass feedstocks. The results of exergy analysis for H_2 production from straw, sludge and manure are similar to those presented for wood in Figures 4–6. On the other hand, the results of exergy analysis for H_2 from vegetable oil are different from those for other feedstocks. Table 3 shows that the highest amounts of H_2 are obtained from straw and wood, followed by vegetable oil, and much lower H_2 is obtained from sludge and manure. Finally, it is interesting to note that the exergetic efficiency of investigated processes depends clearly on the original biomass feedstock, as indicated in Figure 7.
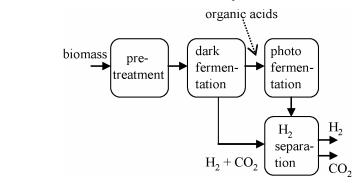
Figure 8   Schematics of the combination of dark and photo fermentation

5   Comparison of thermochemical H$_2$ with alternative H$_2$ production processes

As previously discussed, biomass gasification is the most widely practiced process to produce bio-hydrogen. In this section, the exergetic efficiency of H$_2$ from biomass gasification is compared to that of classical SMR and biochemical processes. The exergy analysis of SMR is presented by Rosen (1996), where the overall exergetic efficiency of 78.0% is reported. The main process losses are internal losses in the reformer furnace due to methane combustion. In general, biochemical processes for H$_2$ production are small-scale with a laboratory of pilot-scale status. The most promising methods are biophotolysis of water, fermentation and anaerobic digestion of biomass (Hallenbeck and Benemann, 2002).

The combination of dark and photo fermentation is shown in Figure 8. In this process, a high conversion of the (hemi) cellulosic part of biomass into H$_2$ and CO$_2$ is achieved. A wet biomass after pretreatment (hydrolysis) enters the dark fermentation reactor where at 70 °C and 0.5 bar H$_2$ and CO$_2$ are produced, in addition to organic acids, according to the chemical reaction:

$$C_6H_{12}O_6 + 2\,H_2O = 4\,H_2 + 2\,CO_2 + 2\,C_2H_4O_2. \qquad (5)$$

The photo fermentation reactor is used to convert organic acids into H$_2$ and CO$_2$ at 35 °C and 2.5 bar according to the chemical reaction:

$$C_2H_4O_2 + 2\,H_2O = 2\,CO_2 + 4\,H_2. \qquad (6)$$

In the Netherlands, a process is under development by the University of Wageningen in which potato peels are converted into H$_2$; the other products are cattle feed and CO$_2$ (Claassen, de Vrije and van Groenestijn 2004). The plant converts 793 kg hour^{-1} of potato peels (dry weight) into 57 kg H$_2$ hour^{-1} of which 40 kg H$_2$ hour^{-1} are produced in the photo-reactor. In the design study, hydrogen gas can be used for a stationary Polymer Electrolyte Membrane fuel cell and as transportation fuel.
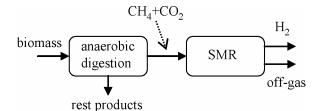
Figure 9   Schematics of the combination of anaerobic digestion and Steam Methane Reforming

Table 4   Exergetic efficiency of Steam Methane Reforming and biochemical processes for hydrogen production

		Exergetic efficiency (%)	
Process	*Biomass feed*	*Biomass-to-biogas*	*Biomass-to-H_2*
Steam methane reforming SMR	Natural gas	–	78.0
Dark and photo fermentation (UW)	Potato peels	–	29.1
Anaerobic digestion (Vagron)	Grey waste (organic fraction)	46.5	36.3

Anaerobic digestion is the most well-known technology for biochemical conversion of biomass into biogas. In this process, microorganisms derive energy and grow by metabolising organic material in an oxygen-free environment. The product gas is a mixture of primarily CH_4 and CO_2, which can be further converted into H_2 by a conventional technique like SMR, as shown in Figure 9. World-wide, a large number of anaerobic digestion plants are in operation and the systems currently operating in Europe have a total capacity of 1,500 MW. The anaerobic digestion plant Vagron operating in Groningen in the Netherlands (Luning, et al., 2001) have been analysed. This plant converts the wet organic fraction of the household waste (grey waste), containing mainly kitchen waste and some garden wastes. A biogas containing 65% CH_4 and 35% CO_2 is produced at the temperature of 52 °C. The specific gas production is 0.26 m^3 methane per kg of organic material. The other products of the plant are compost and wastewater.

Table 4 summarises the overall exergetic efficiency of the above-mentioned biochemical processes based on the plant data in addition to the SMR process. In the case of the anaerobic digestion, the efficiency of biomass-to-H_2 is evaluated as the product of the efficiency of biomass-to-biogas and that of the SMR. The exergetic efficiencies of biochemical processes are lower than those for H_2-from-biomass gasification of more dry biomass but comparable to those of more wet feedstocks (see Table 3).

6   Conclusions

Hydrogen production from biomass can play a major role in future because it utilises the renewable sources of energy. The exergetic efficiency of hydrogen production by gasification of more dry feedstocks, such as vegetable oil, wood and straw (65.7–79.1%) is comparable to that of the current hydrogen production by SMR (78.0%) based on fossil fuels. However, SMR is not a sustainable process and if the additional sequestration of produced CO_2 would be taken into account to make SMR more sustainable, than the exergetic efficiency of this process will be lower than the reported value of 78%.

Biomass wastes which are more wet, such as sludge, manure and various household organic wastes, are also interesting feedstock for hydrogen production as they can be converted by gasification or by biochemical methods. However, the exergetic efficiency for H_2 production from these feedstocks is lower both for gasification (35.8–40.3%) as well for biochemical processes (29.1–36.3%).

During H_2 production by gasification all solid biomass is converted into gas in which H_2 is the main exergetic output. On the other hand, during H_2 production by biochemical processes not only H_2 or H_2-rich gas is produced, but also some solid by-products are formed which could be eventually used, e.g. in agriculture (cattle feed and compost). If the exergetic values of these by-products would be taken into account than the overall exergetic efficiency of biochemical processes will increase till 36.2% for the fermentation and 56.1% for anaerobic digestion process.

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