

# THERMODYNAMIC INVESTIGATION OF SELECTED PRODUCTION PROCESSES OF HYDROGEN FROM BIOMASS

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## 1. Introduction

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 [1]. Hydrogen can be used as a fuel in fuel cells for power generation and in the transportation sector. However, hydrogen currently is produced mostly from fossil fuels and the future hydrogen energy systems must be based on hydrogen production from renewable energy sources. Biomass is the most versatile non-renewable resource that can be used for sustainable production of hydrogen. Biomass has several important advantages which can accelerate the realization of hydrogen economy. Key features are renewability and neutral CO<sub>2</sub> impact. Biomass has also unique versatility. A wide range of biomass sources, such as traditional agricultural crops, dedicated energy crops, residues from agriculture and forestry can be used to make hydrogen. These biomass feedstocks vary greatly in chemical composition, energy content, ash and moisture content. The question is whether all the biomass type can be converted to hydrogen with reasonable exergetic efficiency. The relatively high efficiencies are very desired as the hydrogen content in biomass is low (approximately 6 wt% versus 25% for methane) and energy content is also low due to high oxygen content (about 40 wt% of biomass).

Biomass-to-H<sub>2</sub> conversion technologies can be divided into two categories: thermochemical and biochemical [2]. The most widely practiced thermochemical process route for biomass-to-hydrogen is gasification coupled with water gas shift (WGS). 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 they all are discussed in section 4.

The objective of this paper is to present a second law analysis of different production technologies of hydrogen from biomass. In the next section the method of exergy analysis is explained. Subsequently, in section 3, 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. Method of Exergy Analysis

The exergy balance of a process can be represented in the following form using exergy values of all streams entering and leaving the process:

$$\sum_{IN} E_j + E^Q + E^W = \sum_{OUT} E_k + I \quad (1)$$

where  $\sum_{IN} E_j$  and  $\sum_{OUT} E_k$  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.

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

$$E = E_{ph} + E_0 \quad (2)$$

where  $E_{ph}$  is the physical exergy and  $E_{ch}$  is the chemical exergy. The standard chemical exergy of a pure chemical compound  $\epsilon_0$  is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterized by the environmental temperature  $T_0$  (298.15K) and environmental pressure  $P_0$  (1 atm), to the dead state, characterized 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, characterized by environmental temperature  $T_0$  and  $P_0$ .

### 3. 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 [3]. Table 2 shows lower heating values (LHV), the ratio  $\beta$  between the chemical exergy and LHV, and chemical exergy for all feedstocks. Chemical exergy of biomass is calculated from the correlation for technical fuels given by Szargut and Styrylska [4].

The conversion of all biomass feedstocks to  $H_2$  have been simulated using the flow sheeting program Aspen Plus. First, the process has been modeled and simulated for a standard set of conditions shown in Table 3. The most important parameters are the gasifier temperature and moisture content of biomass leaving the drier; the standard values of these parameters are 1173 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.

Table 1. Proximate and ultimate analysis of various biomass feedstocks.

Feedstock	Proximate analysis (wt%)			Ultimate analysis (wt% of organic fraction)				
	Mois- ture	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

Table 2. Lower heating value and chemical exergy of various biomass feedstocks.

Feedstock	LHV <sub>org</sub> (kJ/kg organic)	$\beta$ (-)	$\epsilon_{ch}$ (kJ/kg biomass)
Untreated wood	18904	1.122	16634
Straw	18064	1.128	16506
Sludge	19617	1.118	9249
Manure	19148	1.116	8427
Vegetable oils	37558	1.074	40338

Figure 1 shows the flow sheet of the H<sub>2</sub>-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 1373 K. In the gasifier a syngas containing H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O is produced due to equilibrium

chemical reactions. The syngas composition has been computed by Aspen Plus by minimization 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<sub>2</sub> content in the syngas is increased in two WGS reactors. The first reactor operates at high 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 modeled as equilibrium reactors. The steam needed in shift reactors is generated in separate units. The gas leaving the LT-shift reactor contains H<sub>2</sub>, water and CO<sub>2</sub>. Water is separated in a flash unit at 20 bar and 298 K whereas CO<sub>2</sub> is separated from H<sub>2</sub> by pressure swing adsorption (PSA). The PSA process is modeled in Aspen Plus assuming H<sub>2</sub> separation efficiency equal to 85% and 100% purity of hydrogen as the main product.

Table 3 summarizes flow rate, temperature, pressure, and exergy flow rate, calculated according to Szargut et al. [5], for the main streams of the H<sub>2</sub>-from-wood process at the gasifier temperature of 1173 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% [6]. Exergy analyses were performed for the overall process as well as for separate process units indicated in Fig. 1. Figure 2 demonstrates that the overall exergetic efficiency increases with decreasing gasifier temperature, and consequently the total exergy losses (internal and external)

Table 3. 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	Temperature	Pressure	Exergy flow rate
		(kg/hr)	(K)	(bar)	(MJ/s)
Biomass:	feed	1000	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	1287	1173	1	3.48
	leaving compressor	1269	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 <sub>2</sub> -rich gas:	leaving HT shift reactor	1955	623	30	3.44
	leaving LT shift reactor	1973	473	25	3.35
Steam produced from gas cooling 2		195	473	10	0.05
Wastewater		567	298	1	0
PSA products:	CO <sub>2</sub> -rich gas	1330	298	1	0.61
	hydrogen	76	298	19	2.54

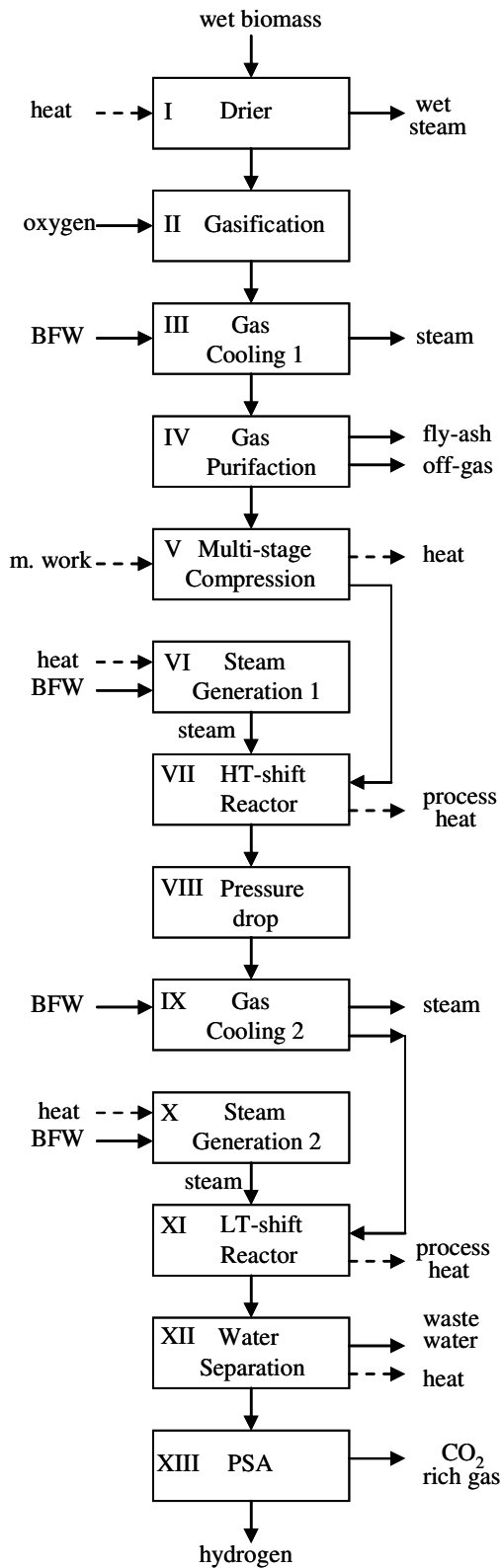


Figure 1. Flow sheet of the thermochemical process for hydrogen from wood.

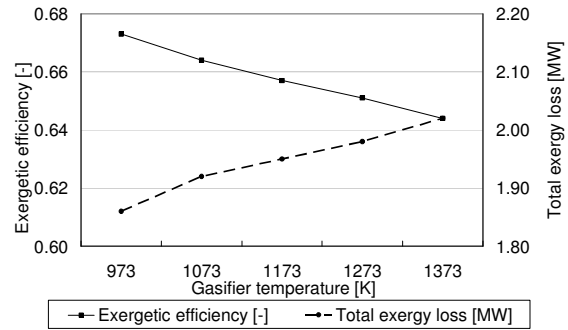


Figure 2. The influence of the gasifier temperature on the exergetic efficiency and exergy loss for the H<sub>2</sub>-from-wood process.

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<sub>2</sub>, CO<sub>2</sub>-rich gas and utilities (process heat from both shift reactors, steam from gas cooling 1 & 2, and drier) and the exergy of the process input: biomass, oxygen, utilities (compressor work, heat for steam generation 1 & 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 Fig. 3 for different gasifier temperatures and the standard value of the moisture content of biomass leaving the drier of 10 wt%.

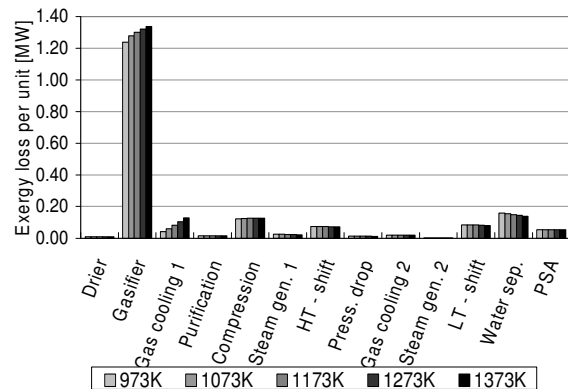


Figure 3. Exergy losses per unit for the hydrogen-from-wood process.

Table 4: Exergetic efficiency and amount of produced hydrogen for thermochemical processes (standard conditions).

Biomass	Exergetic efficiency	Amount produced H <sub>2</sub>
	%	kg/hr
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

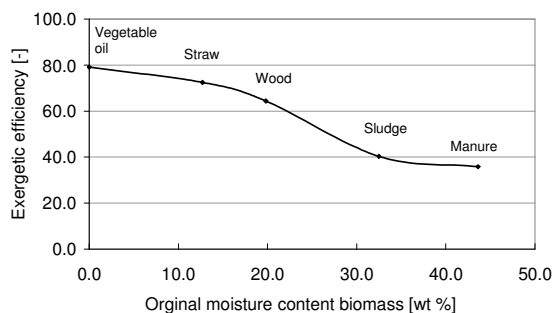


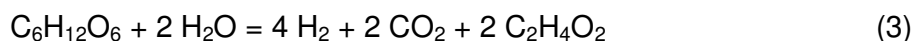
Figure 4. The influence of the original moisture content in biomass feed on the exergetic efficiency of thermochemical hydrogen production.

The principal exergy losses occur in the gasifier and these losses decrease with decreasing gasifier temperature what also influence the total exergy losses, as shown in Fig. 3. The exergy losses during water separation, gas compression, and both shift reactors are lower than that in the gasifier but still substantial. Table 4 summarizes the overall exergetic efficiency as well as amount of produced H<sub>2</sub> for all investigated biomass feedstocks. The results of exergy analysis for H<sub>2</sub> production from straw, sludge and manure are similar to those presented for wood in Figs. 2 & 3. On the other hand, the results of exergy analysis for H<sub>2</sub> from vegetable oil are different from those for other feedstocks. Table 4 shows that the highest amounts of H<sub>2</sub> are obtained from straw and wood, followed by vegetable oil, and much lower H<sub>2</sub> 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 Fig. 4.

#### 4. Comparison of Thermochemical H<sub>2</sub> with Alternative H<sub>2</sub> Production Processes

Biomass gasification, as previously discussed, is the most widely practiced process to produce bio-hydrogen. In this section the exergetic efficiency of H<sub>2</sub> from biomass gasification is compared to that of classical steam methane reforming (SMR) and biochemical processes. Today most H<sub>2</sub> (90%) is generated from fossil fuels mainly by SMR what is not a sustainable process route. The exergy analysis of SMR is presented by Rosen [7] 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<sub>2</sub> 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 [8].

The combination of dark and photo fermentation is shown in Fig. 5. In this process a high conversion of the (hemi) cellulosic part of biomass into H<sub>2</sub> and CO<sub>2</sub> is achieved. A wet biomass after pretreatment (hydrolysis) enters the dark fermentation reactor where at 70 °C and 0.5 bar H<sub>2</sub> and CO<sub>2</sub> are produced, in addition to organic acids, according to the chemical reaction:



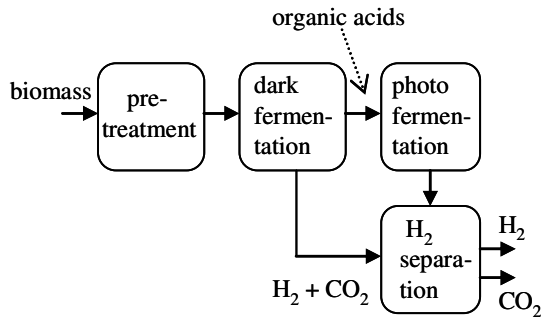


Figure 5. Schematics of the combination of dark and photo fermentation.

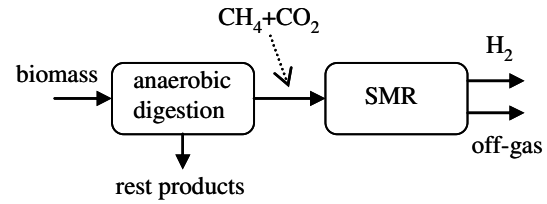
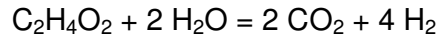


Figure 6. Schematics of the combination of anaerobic digestion and SMR.

The photo fermentation reactor is used to convert organic acids into  $H_2$  and  $CO_2$  at  $35\text{ }^\circ\text{C}$  and 2.5 bar according to the chemical reaction:



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  $CO_2$  [9]. The plant converts 793 kg/hr of potato peels (dry weight) into 57 kg  $H_2$ /hr of which 40 kg  $H_2$ /hr are produced in the photo-reactor. In the design study hydrogen gas can be used for a stationary PEM fuel cell and as transportation fuel.

Anaerobic digestion is the most well-know technology for biochemical conversion of biomass into biogas. In this process micro-organisms derive energy and grow by metabolizing 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, such as SMR, as shown in Fig. 6. 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 [10] have been analyzed. 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  $52\text{ }^\circ\text{C}$ . The specific gas production is  $0.26\text{ m}^3$  methane per kg of organic material. The other products of the plant are compost and wastewater.

Table 5 summarizes 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 5).

Table 5. Exergetic efficiency of SMR and biochemical processes for hydrogen production.

Process	Biomass feed	Exergetic efficiency (%)	
		biomass-to-biogas	biomass-to- $H_2$
Steam methane reforming SMR	natural gas	-	78.0
Dark & photo fermentation (UW)	potato peels	-	29.1
Anaerobic digestion (Vagron)	grey waste (organic fraction)	46.5	36.3

## 5. Conclusion

Hydrogen production from biomass can play a major role in future because it utilizes 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<sub>2</sub> 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<sub>2</sub> production from these feedstocks is lower both for gasification (35.8-40.3%) as well for biochemical processes (29.1-36.3%).

During H<sub>2</sub> production by gasification all solid biomass is converted into gas in which H<sub>2</sub> is the main exergetic output. On the other hand, during H<sub>2</sub> production by biochemical processes not only H<sub>2</sub> or H<sub>2</sub>-rich gas is produced but also some solid by-products are formed which could be eventually used, e.g. in agriculture (cattle feed, 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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