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# Investigation of a novel & integrated simulation model for hydrogen production from lignocellulosic biomass

A. Ersöz<sup>a,\*</sup>, Y. DurakÇetin<sup>a</sup>, A. Sarıoğlan<sup>a</sup>, A.Z. Turan<sup>a</sup>, M.S. Mert<sup>b</sup>,  
F. Yüksel<sup>b</sup>, H.E. Figen<sup>c</sup>, N.Ö. Güldal<sup>c</sup>, M. Karaismailoğlu<sup>c</sup>, S.Z. Baykara<sup>c</sup>

<sup>a</sup> TÜBİTAK Marmara Research Center, Energy Institute, P.O.21, 41470, Gebze, Kocaeli, Turkey

<sup>b</sup> Yalova University, Energy Systems Engineering Department, Central Campus, Cinarcik Road, Yalova, Turkey

<sup>c</sup> Yıldız Technical University, Chemical Engineering Department, Davutpaşa Campus, Topkapı, 34210, Istanbul, Turkey

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## ABSTRACT

Process simulation and modeling works are very important to determine novel design and operation conditions. In this study; hydrogen production from synthesis gas obtained by gasification of lignocellulosic biomass is investigated. The main motivation of this work is to understand how biomass is converted to hydrogen rich synthesis gas and its environmentally friendly impact. Hydrogen market development in several energy production units such as fuel cells is another motivation to realize these kinds of activities. The initial results can help to contribute to the literature and widen our experience on utilization of the CO<sub>2</sub> neutral biomass sources and gasification technology which can develop the design of hydrogen production processes. The raw syngas is obtained via staged gasification of biomass, using bubbling fluidized bed technology with secondary agents; then it is cleaned, its hydrocarbon content is reformed, CO content is shifted (WGS) and finally H<sub>2</sub> content is separated by the PSA (Pressure Swing Adsorption) unit. According to the preliminary results of the ASPEN HYSYS conceptual process simulation model; the composition of hydrogen rich gas (0.62% H<sub>2</sub>O, 38.83% H<sub>2</sub>, 1.65% CO, 26.13% CO<sub>2</sub>, 0.08% CH<sub>4</sub>, and 32.69% N<sub>2</sub>) has been determined. The first simulation results show that the hydrogen purity of the product gas after PSA unit is 99.999% approximately. The mass lower heating value (LHV<sub>mass</sub>) of the product gas before PSA unit is expected to be about 4500 kJ/kg and the overall fuel processor efficiency has been calculated as ~93%.

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\* Corresponding author.

E-mail address: [atilla.ersoz@tubitak.gov.tr](mailto:atilla.ersoz@tubitak.gov.tr) (A. Ersöz).

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### Nomenclature

#### Abbreviations

PSA	Pressure swing adsorption
WGS	Water gas shift
PFD	Process flow diagram
E	Heat exchanger
RQE	EQ-R Equilibrium reactor
STD	Standard
FP <sub>Eff</sub>	Fuel processor efficiency
CG <sub>Eff</sub>	Cold gas efficiency
LHV <sub>mass</sub>	Mass lower heating value
HHV	Higher Heating Value

#### Symbols

F	Feed
P	Pressure
T	Temperature
W	Water
$\Delta H^\circ$	Formation enthalpy
Q	Heat flow

## Introduction

Terrestrial biomass is a renewable, widespread and abundant energy source which captures carbon dioxide (CO<sub>2</sub>)<sub>g</sub> that leads to the green-house effect in the atmosphere, through photosynthesis and keeps it within the carbon cycle.

Finite nature of conventional fossil fuels, climatic concerns, and eco health issues related to their utilization render biomass an alternative route to hydrogen, a critical energy carrier [1–6]. As a renewable resource, contribution of biomass to the world energy demand is approximately 10–14% [4]. Gasification is the optimum and most economic approach for usefully eliminating biomass originating from forest and agricultural residues without environmental hazard [7]. Hydrogen can be obtained by thermal gasification of biomass. The hydrogen content of biomass is approximately 6–6.5% by weight and the average hydrogen yield is 63% [8]. Hydrogen produced via biomass gasification is presently more expensive than conventional hydrogen from steam methane reforming [9].

Lignocellulosic biomass wastes are defined as a renewable energy source. It is very important to evaluate the potential energy of these sources. There are some existing works done by several countries in the world. These sources have also been utilized as a fuel and energy material within some countrified areas of Turkey.

Solid biomass resources, a great majority of which are lignocellulosic, can be converted into gaseous fuels through thermochemical gasification processes. A gasification process involves successive drying, pyrolysis and gasification steps in the reactor. During the gasification step, many chain reactions take place. The resulting “product gas”, mainly contains hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrogen (N<sub>2</sub>). The product gas also

contains particulates, tar (Topping Atmosphere Residue), ammonia (NH<sub>3</sub>) and sulfur compounds in minor amounts depending on the operating conditions. After passing the product gas through cleaning, reforming and shift processes, “synthesis gas”, which is composed of CO and H<sub>2</sub> is obtained; and following separation stage, pure hydrogen gas is produced.

Basic gasification reactions are given in Table 1.

The “product gas” can be used only after processing and obtaining “synthesis gas” composed of CO, CO<sub>2</sub> and H<sub>2</sub>. Synthesis gas, in which H<sub>2</sub>/CO ratio can be regulated, is widely used in industrial applications such as the Fischer-Tropsch process, methanol synthesis and ammonia production [11]. Carbon monoxide is converted to carbon dioxide through the catalytic water gas shift (WGS) reaction (Table 1).

In most hydrocarbon processors, the water gas shift reactor is the biggest and heaviest component because the reaction is relatively slow compared to the other reactions and is inhibited at higher temperatures by thermodynamics [12].

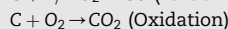
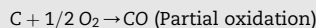
Water gas shift reaction is the intermediate step used for hydrogen enrichment and CO reduction in the synthesis gas. Water gas shift reaction is a moderately exothermic reversible reaction. The equilibrium constant of the reaction decreases with increasing temperature. The reaction is thermodynamically favored at low temperatures and kinetically favored at high temperatures. Since there is no change in the volume from reactants to products, the reaction is not affected by pressure. The WGSR can be catalyzed by both metals and metal oxides [13].

The WGS reaction is reversible and exothermic ( $\Delta H^\circ = -41.2$  kJ/mol). Due to its moderate exothermicity, the WGS reaction is thermodynamically unfavorable at elevated temperatures. This is illustrated by the continuous decline and eventual sign change in the Gibbs free energy as a function of temperature, and the corresponding decreasing equilibrium constant as temperature increases. The kinetics of the catalytic reaction is more favorable at higher temperatures [14].

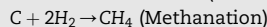
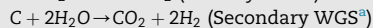
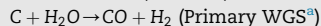
Catalysts containing oxides of iron, copper and nickel; and sulfides of cobalt and molybdenum are generally used in WGS. Hydrogen can be easily separated from mixtures with CH<sub>4</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> via adsorptive processes, owing to its low physical

**Table 1 – Basic gasification reactions [10].**

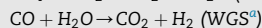
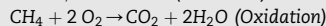
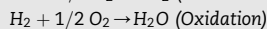
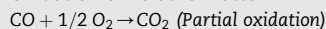
#### Char combustion



#### Char Gasification



#### Oxidation of volatile matter



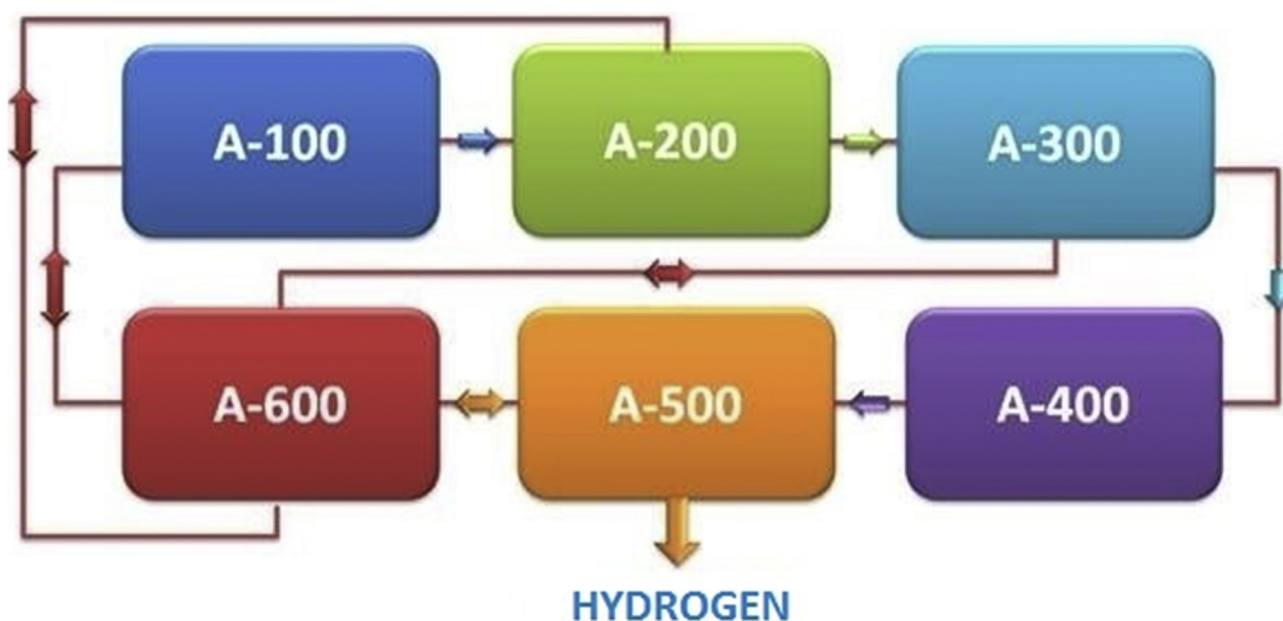
<sup>a</sup> Water Gas Shift reaction

bonding capability. Various types of gasification reactors are available for biomass gasification such as down draft fixed bed, bubbling fluidized bed and updraft fixed bed. While down draft fixed bed reactor produces the least amount of tar, updraft fixed bed reactor induces the most amount of tar production. Successful gasification of biomass is also possible in the fluidized bed gasifier [15–18]. Reports on studies related to gradual gasification in bubbling fluidized bed gasifiers are not common.

Various simulation studies on biomass-based hydrogen production have been carried out with the aim of assessment, improvement and optimization of the process. Saleme et al. [19] have studied solar assisted biomass gasification for pure hydrogen production to enhance the energy efficiency by using the commercial simulation software Aspen Plus®. Qiao et al. [20] performed a comparative analysis of hydrogen production systems from biomass based on different absorbent regeneration processes. Cohce et al. [21] investigated biomass-based hydrogen production from the oil palm shell, and they proposed a plant that uses a gasification process followed by steam methane reforming and shift reactions. In another study of Cohce et al. [22], the biomass-based hydrogen production process which also uses oil palm shell as a feedstock was simulated and analyzed thermodynamically. Ahmed et al. [23] have done the review of kinetic and equilibrium concepts for biomass tar modeling by using Aspen Plus. They have considered different tar models in which tar is represented as different components such as naphthalene, toluene and bulk tar. Moneti et al. have

investigated the main gasifier parameters on a real system for hydrogen production from biomass [24]. Tian et al. has also investigated the effects of temperature (in the range of 920–1220 °C) on the yield and chemical composition of syngas production by biomass gasification [25]. Kocer et al. have investigated the potential of hydrogen production from greenhouse tomato and pepper residues blending in different rates by air-steam gasification [26]. Kalinci et al. have also reviewed various processes for conversion of biomass into hydrogen gas in terms of two main groups, namely (i) thermochemical processes (pyrolysis, conventional gasification, supercritical water gasification (SCWG)), and (ii) biological conversions (fermentative hydrogen production, photosynthesis, biological water gas shift reactions (BWGS)) [27]. There are several other studies have been performed in the open literature which are related to hydrogen production using biomass gasification technology [28–44].

In this study, a process simulation of hydrogen production from synthesis gas obtained by gasification of lignocellulosic biomass is investigated in the scope of TUBITAK funded “Hydrogen Production from Biomass Gasification (BioH<sub>2</sub>)” project. An area scheme of this hydrogen production plant is given in Fig. 1. The chemical process simulation activities have been realized to determine pre-design conditions (Table 2) in line with the project PFD (Process flow diagram) (Fig. 2). The raw syngas is obtained via staged gasification of biomass, using bubbling fluidized bed technology with secondary agents; then it is cleaned, its hydrocarbon content is reformed, CO content is converted via water gas shift (WGS)



**A-100: Biomass storage, drying and feeding**

**A-200: Gasification and tar reforming**

**A-300: Gas cleaning**

**A-400: Water gas shift reactor (WGS)**

**A-500: Hydrogen purification (PSA) and PSA compressor**

**A-600: Steam, air, cooling water and auxiliary sub units (pumps, heat exchangers, technical gases, etc.)**

Fig. 1 – Area definition scheme of hydrogen production plant.

**Table 2 – Pre-design operational conditions for gasification unit - Gasifier Outlet Composition.**

Gasifier variable	Data		
Gasifier type	Bubbling bed		
Temperature (°C)	800–900		
Pressure (atm)	1–2		
Steam/Dry biomass feed	0.6–1.0		
Biomass feed (kg/h)	20		
Gasifier outlet composition (mol %)			
Cold gas efficiency (kmol dry gas/kg dry feed)	59		
	Mol % (wet)	ppm	
Water (H <sub>2</sub> O)	8.242	82418	
Oxygen (O <sub>2</sub> )	0.000	0.000	
Hydrogen (H <sub>2</sub> )	18.304	183039	
Carbon monoxide (CO)	14.185	141855	
Carbon dioxide CO <sub>2</sub>	15.284	152837	
Methane (CH <sub>4</sub> )	4.210	42099	
Nitrogen (N <sub>2</sub> )	39.536	395363	
Hydrogen sulfur (H <sub>2</sub> S)	0.040	400	
Benzene (C <sub>6</sub> H <sub>6</sub> )	0.154	1543	Tar components
Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	0.036	351	
Naphthalene (C <sub>10</sub> H <sub>8</sub> )	0.0357	357	
Pyrene (C <sub>6</sub> H <sub>10</sub> )	0.0029	29	
p-Xylene (C <sub>8</sub> H <sub>10</sub> )	0.0063	63	
Indene (C <sub>9</sub> H <sub>8</sub> )	0.00016	2	
E-Benzene (C <sub>8</sub> H <sub>10</sub> )	0.00007	1	
Anthracene (C <sub>14</sub> H <sub>10</sub> )	0.00021	2	
Acenaphthene (C <sub>12</sub> H <sub>10</sub> )	0.0039	39	
	Wet: HHV, LHV	Dry: HHV, LHV	
Gas heating value (kJ/kg)	5777	6002	
H <sub>2</sub> :CO molar ratio	1.29		
Biomass Heating Value in the Feed (HHV) (kJ/kg)	5777		

approach, and finally H<sub>2</sub> content is separated by the pressure swing adsorption (PSA) technique. Catalytic routes are used for reforming of hydrocarbons and for tar abatement.

An integrated chemical process simulation model has been developed for hydrogen production with required conditions. The chemical process units (reactors, columns etc.), heat exchangers and auxiliary sub units (pumps, compressors, etc.) can be simulated in steady state or dynamic modes by using thermodynamic fluid packages. Aspen HYSYS simulation software has been used to determine the outlet syngas composition for selected biomass source, gasifier conditions and gasifying agents at steady state conditions. The gasifier outlet stream has been connected to the process units which can increase the hydrogen production rates via tar reforming and water gas shift reactors. The hydrogen production rate should be maximized via choosing the appropriate operating conditions.

The proposed model is based on the Gibbs free energy minimization method for all reactor units such as gasifier, tar reformer and water gas shift reactor. These are accepted to be at equilibrium conditions. A reactor model is a single or simultaneous phase at chemical equilibrium stage. Chemical equilibrium is calculated by minimizing Gibbs free energy. This is a very user friendly method when the temperature and

the pressure levels are in hand and the stoichiometry of the reaction set is unpredicted.

Process simulation and modeling works are very important to determine novel design and operation conditions. It is very easy to say that several particular advantages can also be handled comparing to experimental throughput. Large number of data can be produced via less experimental ones using process simulation tools. The results of these works can help to improve the novelty of the gasifier and upstream units in terms optimization, design, and operation. This work can also contribute to reduce some industrial sector problems and to simplify the implementation of this kind of technology. In this respect, the objective of this work is to study the effect of parameters such as temperatures of the reactors on the concentrations of the syngas, reaction conversions, H<sub>2</sub>/CO ratio, fuel processing efficiency etc. Simulations were performed for a full scale 100 kW<sub>th</sub> process selected biomass (wood) gasifier outlet compositions. Besides this study, partial scale simulations have also been performed to reduce some of the overall system costs. Fig. 3 shows a simulation case realized for a full scale (100 kW<sub>th</sub>) system.

## Process description

Biomass is firstly gasified with a gasifying agent in a bubbling fluidized bed reactor. An outlet product composition of this gasifier is used as a basis feed stream (Stream 100) of the all other downstream simulation units. The product gas mainly consists of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, N<sub>2</sub>, char, ash and other substances impurities such as tars, NH<sub>3</sub>, H<sub>2</sub>S and HCl.

The main inlet stream (gasifier outlet) “Stream 100” is introduced to a reformer unit for conversion of the tar components inside of the raw syngas. The undesired components and other impurities in syngas (Stream 102) are cleaned by the gas cleaning units. The temperature of the tar reformer exit stream is then decreased by a heat exchanger (E–100) to maintain the inlet temperature of the WGS (water gas shift) reactor. The WGS reactor uses water to convert carbon monoxide to hydrogen and carbon dioxide. The resulting gas is then compressed and fed into a pressure swing adsorption (PSA) unit. The next step is the water gas shift reactor to increase the hydrogen contents of the syngas (Stream 104) stream. An additional superheated steam (Stream 113) is introduced to the raw syngas coming from tar reformer for the water gas shift reaction, because, there is not enough water to shift the CO content in the inlet stream of WGS reactor. The main goal is to find an appropriate H<sub>2</sub>/CO ratio for the last PSA (pressure swing adsorption) step. The tar reformer and water gas shift reactor units are operated at about 700 °C and 400 °C respectively. The operating pressures are about at atmospheric levels. The final stream (Stream 109) is fed to a PSA unit to purify hydrogen rich gas. A purified hydrogen (99.999%) is handled as an end product (Stream 110).

In this study, there are several assumptions for the process simulations:

1. Dry biomass feed rate: 20 kg/hr.
2. Biomass energy: 100 kW<sub>th</sub>
3. Steady state conditions are accepted.

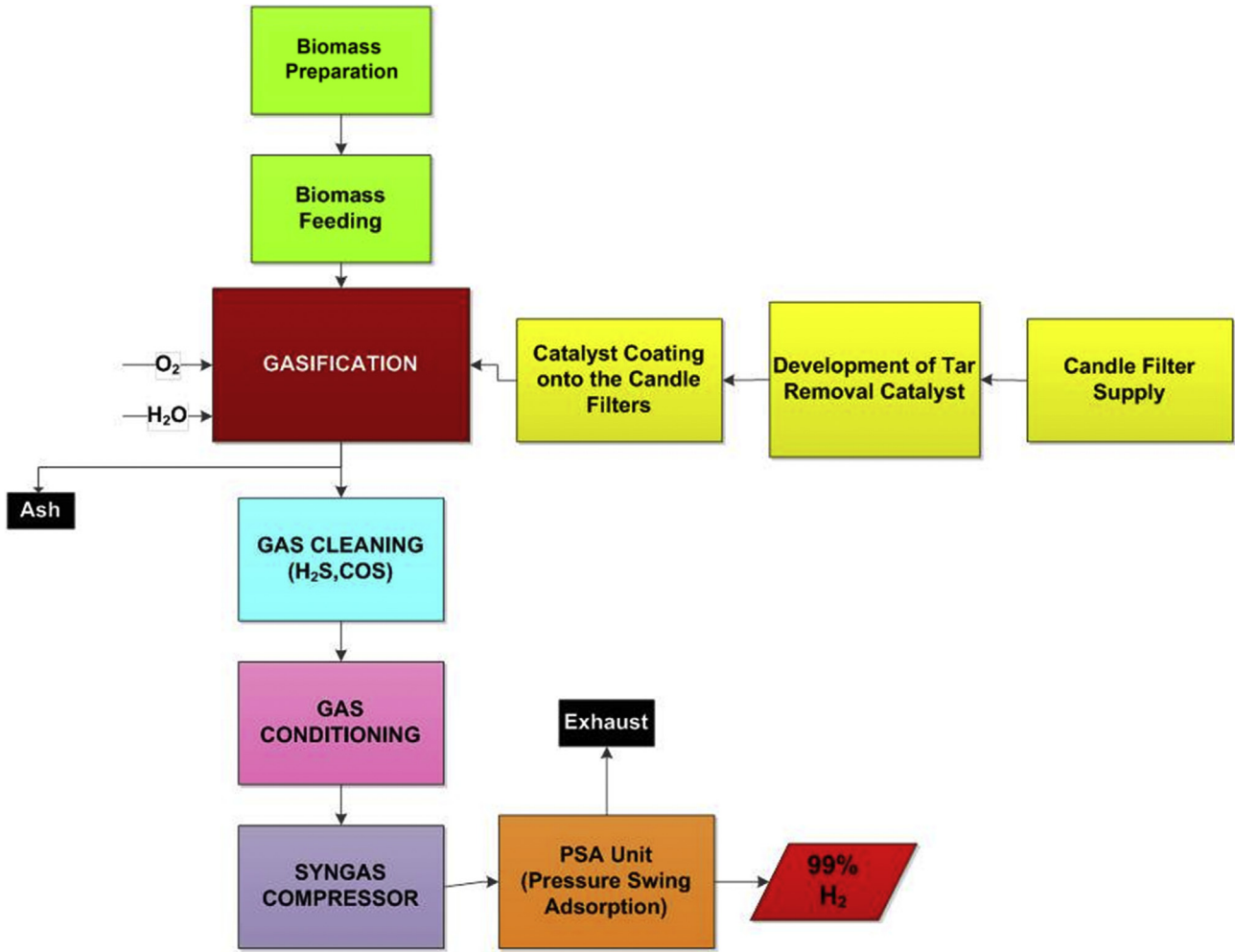


Fig. 2 – Process flow diagram (PFD).

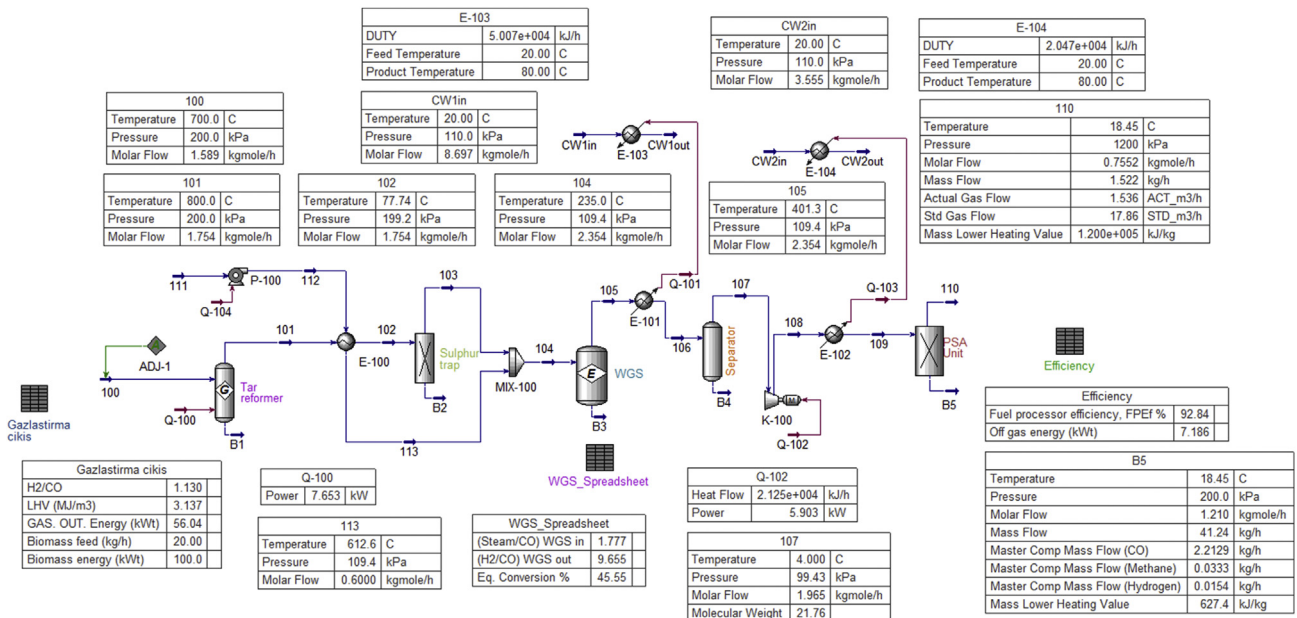


Fig. 3 – A Simulation flow sheet performed for a full scale (100 kW<sub>th</sub> capacity) hydrogen production system.

4. Pressures and temperatures are uniform inside the reactor units.
5. H<sub>2</sub>/CO ratio at gasifier outlet: 1.13
6. Isothermal conditions are assumed for the tar reformer unit (RGIBBS reactor model).
7. WGS (water gas shift) reactor is operated at adiabatic conditions and at thermodynamically equilibrium (An equilibrium reactor model (EQ-R)).
8. Tar reformer (RGIBBS) operating temperature: 800 °C
9. WGS (REQ) inlet temperature range: 200–400 °C
10. Steam/CO ratio at WGS inlet: 1.77
11. Full system except PSA units is operated at atmospheric pressure levels (~1 bara)
12. PSA Units are operated at about 12 bara and 25 °C.
13. Tar formation is considered and all sulfur (S) in biomass is converted to H<sub>2</sub>S in gasifier.
14. The product stream of gasifier consists of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S and tar components.
15. There is no carbon content in the product gas coming from the gasifier.
16. Peng-Robinson equation of state is used as a property fluid package method in the simulations.

**Results and discussion**

According to the preliminary results of process simulation PFD data, energy flows, composition values and process mass & energy balances are given for a full scale system approach in Tables 2–7.

The following main results have been obtained from the full scale simulation works:

- Hydrogen production rate (kg/h): 1.522
- Hydrogen production rate (Actual m<sup>3</sup>/h): 1.536
- Hydrogen production rate (STD m<sup>3</sup>/h): 17.85
- Fuel processor efficiency (FPEf) (%): 92.84
- Off-gas energy PSA downstream (kWth): 7.185
- Selected WGS (REQ) inlet temperature (°C): 235
- WGS (REQ) max. outlet temperature (°C): 401
- WGS eq. conversion (%): 45.55
- H<sub>2</sub>/CO molar ratio at WGS outlet (mol/mol): 9.665
- PSA efficiency (%): 98.9
- Operating conditions

**Table 3 – Tar reformer, WGS and PSA (off-gas) contents.**

Component	Tar reformer outlet gas mass flow (kg/h)	WGS outlet mass flow (kg/h)	PSA off gas mass flow (kg/h)	PSA outlet gas (Hydrogen) (kg/h)
H <sub>2</sub> O	0.371	0.430	0.029	–
H <sub>2</sub>	0.109	0.203	0.002	1.522
CO	1.428	0.120	0.120	–
CO <sub>2</sub>	0.926	2.983	2.983	–
CH <sub>4</sub>	0.003	0.003	0.003	–
N <sub>2</sub>	2.375	2.375	2.375	–

**Table 4 – Simulation PFD data: stream operating conditions.**

Stream name	100	102	112	113	103	B2	105	B3	108	110	B5	106
Vapour fraction	1.000	1.000	0.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	0.999	0.835
Temperature [C]	700.000	77.743	20.000	612.587	77.743	250.000	401.290	401.290	336.036	18.450	18.451	4.000
Pressure [kPa]	200.000	199.160	110.000	109.432	199.160	199.160	109.432	109.432	1200.000	1200.000	200.000	99.432
Molar flow [kgmole/h]	1.589	1.754	0.600	0.600	1.754	0.000	2.354	0.000	1.965	0.755	1.210	2.354
Mass flow [kg/h]	38.963	38.963	10.809	10.809	38.963	0.000	49.772	0.000	42.757	1.522	41.235	49.772
Std Ideal Liq Vol Flow [m <sup>3</sup> /h]	0.057	0.059	0.011	0.011	0.059	0.000	0.080	0.000	0.073	0.022	0.051	0.080
Heat flow [kJ/h]	-119485.606	-133528.441	-173820.705	-132225.348	-133528.442	0.001	-265753.900	0.000	-181191.584	-135.250	-201522.868	-315824.129
Molar enthalpy [kJ/kgmole]	-75202.467	-76116.506	-289701.176	-220375.581	-76116.506	67713.360	-112879.483	0.000	-92211.170	-179.103	-166573.907	-134146.910
Stream name	107	B4	109	104	101	B1	111	CW1in	CW1out	CW2in	CW2out	
Vapour fraction	1.000	0.000	0.996	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Temperature [C]	4.000	4.000	25.000	235.043	800.000	800.000	19.999	20.000	80.000	20.000	80.000	80.000
Pressure [kPa]	99.432	99.432	1200.000	109.432	200.000	200.000	100.000	110.000	110.000	110.000	110.000	110.000
Molar flow [kgmole/h]	1.965	0.389	1.965	2.354	1.754	0.000	0.600	8.697	8.697	3.555	3.555	3.555
Mass flow [kg/h]	42.757	7.014	42.757	49.772	38.963	0.000	10.809	156.679	156.679	64.043	64.043	64.043
Std Ideal Liq Vol Flow [m <sup>3</sup> /h]	0.073	0.007	0.073	0.070	0.059	0.000	0.011	0.157	0.157	0.064	0.064	0.064
Heat flow [kJ/h]	-202442.869	-113381.260	-201658.118	-265753.790	-91933.084	0.000	-173820.854	-2519550.456	-2469480.226	-1029882.751	-1009416.217	-1009416.217
Molar enthalpy [kJ/kgmole]	-103026.274	-291205.146	-102626.902	-112881.902	-52405.503	-69809.251	-289701.424	-289701.176	-283944.036	-289701.176	-283944.036	-283944.036

**Table 5 – Simulation results: energy flows.**

Unit name	Q-102	Q-101	Q-103	Q-100	Q-104
Heat flow [kJ/h]	21251.285	50070.229	20466.534	27552.521	0.149

**Table 6 – Simulation results: stream compositions.**

Stream name		100	102	112	113	103	B2	105	B3	108	110	B5	106
Comp Mole Frac	H <sub>2</sub> O	0.082	0.078	1.000	1.000	0.078	–	0.171	0.158	0.006	–	0.010	0.171
	O <sub>2</sub>	–	0.000	–	–	0.000	–	–	–	–	–	–	–
	H <sub>2</sub>	0.183	0.243	–	–	0.243	–	0.324	0.214	0.388	1.000	0.006	0.324
	CO	0.142	0.237	–	–	0.237	–	0.034	0.039	0.040	–	0.065	0.034
	CO <sub>2</sub>	0.153	0.083	–	–	0.083	–	0.204	0.280	0.245	–	0.397	0.204
	Methane	0.042	0.001	–	–	0.001	–	0.001	0.001	0.001	–	0.002	0.001
	Ethane	–	0.000	–	–	0.000	–	0.000	0.000	0.000	–	0.000	0.000
	Carbon	–	–	–	–	–	–	–	–	–	–	–	–
	H <sub>2</sub> S	–	0.000	–	–	–	0.000	–	–	–	–	–	–
	Nitrogen	0.395	0.358	–	–	0.358	–	0.267	0.308	0.320	–	0.519	0.267
	Acetylene	–	0.000	–	–	–	0.020	–	–	–	–	–	–
	Ethylene	–	0.000	–	–	–	0.980	–	–	–	–	–	–
	Benzene	0.002	0.000	–	–	–	0.000	–	–	–	–	–	–
	Stream name		107	B4	109	104	101	B1	111	CW1in	CW1out	CW2in	CW2out
Comp Mole Frac	H <sub>2</sub> O	0.006	1.000	0.006	0.313	0.078	0.065	1.000	1.000	1.000	1.000	1.000	
	O <sub>2</sub>	–	–	–	0.000	0.000	0.000	–	–	–	–	–	
	H <sub>2</sub>	0.388	0.000	0.388	0.181	0.243	0.162	–	–	–	–	–	
	CO	0.040	0.000	0.040	0.176	0.237	0.265	–	–	–	–	–	
	CO <sub>2</sub>	0.245	0.000	0.245	0.062	0.083	0.104	–	–	–	–	–	
	Methane	0.001	0.000	0.001	0.001	0.001	0.001	–	–	–	–	–	
	Ethane	0.000	0.000	0.000	0.000	0.000	0.000	–	–	–	–	–	
	Carbon	–	–	–	–	–	0.000	–	–	–	–	–	
	H <sub>2</sub> S	–	–	–	–	0.000	0.000	–	–	–	–	–	
	Nitrogen	0.320	0.000	0.320	0.267	0.358	0.402	–	–	–	–	–	
	Acetylene	–	–	–	–	–	–	–	–	–	–	–	
	Ethylene	–	–	–	–	–	–	–	–	–	–	–	
	Benzene	–	–	–	–	–	–	–	–	–	–	–	

**Table 7 – Mass and energy balance of the process.**

Mass balance			
Inlet material streams	Mass flow (kg/h)	Outlet material streams	Mass flow (kg/h)
100	38.963	B2	0,000
111	10.809	B3	–
CW1in	156.679	110	1.522
CW2in	64.043	B5	41.235
1	38.963	B4	7.014
5	10.809	B1	–
		CW1out	156.679
		CW2out	64.043
		3	–
		2	49.772
Total flow of inlet streams (kg/h)	320.265	Total flow of outlet streams (kg/h)	320.265
Energy balance			
Inlet streams	Energy flow (kJ/h)	Outlet streams	Energy flow (kJ/h)
Q-102	21251.267	B2	5.16E-04
100	–119485.606	B3	0
Q-100	27552.521	110	–135.250
111	–173820.854	B5	–201522.505
Q-104	0.149	B4	–113381.378
CW1in	–2519550.467	B1	0
CW2in	–1029881.849	CW1out	–2469480.237
		CW2out	–1009415.333
Total flow of inlet streams (kJ/h)	–3793934.839	Total flow of outlet streams (kJ/h)	–3793934.703

The hydrogen production process consists of an inlet stream from the gasifier, a tar reformer (steam reformer), high and low temperatures WGS (water gas shift) reactors, a gas booster and a PSA (Pressure swing adsorption) unit (Figs. 1 and 3). An efficient and novel fuel processing process can be designed and optimized using the appropriate *operating conditions* like flow rates, temperature, pressure, etc. In this study, steam reforming (tar reformer) and water gas shift reactions (HTS, LTS) are critical and our approach is that the reactors are at thermodynamic equilibrium conditions.

The inlet stream of the gasifier has been simulated at 700 °C and 2 bara pressure levels. The outlet composition of gasifier has been defined as a feedstock condition (8.24% H<sub>2</sub>O, 18.30% H<sub>2</sub>, 14.19% CO, 15.28% CO<sub>2</sub>, 4.21% CH<sub>4</sub>, 39.54% N<sub>2</sub>, 0.15% benzene, 0.04% toluene) (Fig. 3) (Table 3).

Steam reforming (SR) is a catalytic process. The reaction takes place in the tar refoe hydrocarbons from the gasifier outlet stream and steam. Hydrogen and carbon monoxide mixture has been formed during these reactions (Table 3). Tar reformer (Fig. 3) is operated at endothermic conditions. The reformer temperature and pressure have been selected as 800 °C and 2 bara respectively.

The inlet temperatures of the WGS reactors (HTS and LTS) are set to 350 °C and 200 °C. WGS reactors are operated at 450 °C and 260 °C respectively. The operation pressure has been selected around 1.1 bara. Steam/CO ratio (selected as 2.36) is also very critical operating condition for these reactors (Fig. 4). This ratio effects the conversion of CO during the WGS reactions to produce more hydrogen in the outlet streams. The LTS operating temperature is significantly lower than HTS reactor. This causes to shift the equilibrium towards more hydrogen product (Table 3).

The hydrogen rich syngas is cooled down to 4 °C at the outlet of LTS reactor and compressed as a feed stream to a PSA unit. The PSA unit is simulated as a component separator with a defined split ratio for hydrogen. This unit is assumed to operate at a pressure of 12 bar and a temperature of 25 °C. The fuel processor efficiency depends on the efficient PSA unit.

Two outlet streams (pure hydrogen, 99.99% and off-gas) have been found after PSA unit. The off gas stream (CO, CH<sub>4</sub> and H<sub>2</sub>) can be used to supply extra heat to the gasification process (Table 3). This action can provide improved energetic efficiency avoiding an auxiliary fuel for the gasifier.

The water gas shift step is an exothermic reaction used to produce hydrogen and carbon dioxide by reacting the carbon monoxide in the raw syngas with superheated steam. In this study, the following parametric case studies (Case study 1 and 2) have been performed for WGS operation as a hydrogen enrichment reaction. The results of these parametric works have been presented in Table 8 (Case 1) and Table 9 (Case 2).

**Case study 1:** The molar flow of steam (Stream 112 – WGS inlet) has been used as an independent variable. It was changed between 0.6 and 1.1 kgmole/h with an increment of 0.05 kgmole/h with 11 steps. The effect of this variable has been observed on the dependent variables such as temperature (Streams 103, 104, 105, 113), hydrogen mole fraction (Stream 109 – inlet of PSA), WGS reactor conversion, fuel processing efficiency, WGS inlet – Steam/CO ratio and WGS conversion.

**Case study 2:** For this case study, WGS inlet temperature has been selected as an independent variable. It was selected between 200 and 500 °C with an increment of 20 °C with 16 steps. The effect of this variable has been observed on the dependent variables such as mole fractions of the WGS outlet stream (H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>), WGS outlet temperature and WGS conversion.

The simulated water gas shift reactor (Fig. 4) reaction set (Eq. (1)) is reversible and exothermic which can favor formation of the inlet reactive components at high reactor operating temperatures. The water gas shift reaction is favored at lower temperature resulting in more hydrogen. The required high temperature steam injection shifts the equilibrium to the right side in water gas reaction to produce more hydrogen.

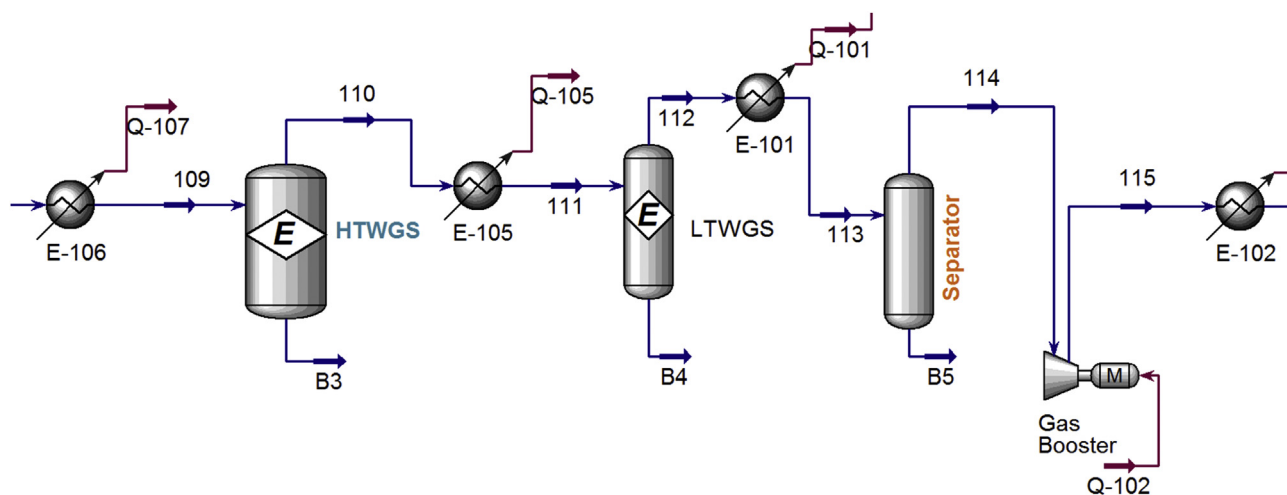


Fig. 4 – Simulation scheme of the WGS reactor.



**Table 8 – Results of a case study 1 for WGS reactor.**

State	State 1	State 2	State 3	State 4	State 5	State 6	State 7	State 8	State 9	State 10	State 11
112 – Molar flow	0.6	0.65	0.7	0.75	0.8	0.85	0.9	0.95	1	1.05	1.1
103 – Temperature	77.743	70.639	63.799	58.164	55.713	54.726	54.824	54.507	54.277	54.008	53.732
104 – Temperature	235.043	199.681	165.608	132.762	101.089	76.584	76.493	76.400	76.307	76.214	76.120
105 – Temperature	401.308	374.258	346.840	319.003	290.708	262.059	233.242	204.547	176.150	148.263	120.946
113 – Temperature	612.587	491.768	383.926	285.035	191.661	114.736	100.904	100.896	100.891	100.887	100.882
109 – Master Comp Mole Frac (Hydrogen)	0.388	0.394	0.399	0.403	0.406	0.409	0.410	0.411	0.411	0.412	0.412
109 – Master Comp Mass Flow (Hydrogen)	1.538	1.578	1.612	1.639	1.660	1.674	1.684	1.690	1.694	1.695	1.696
Fuel processing efficiency (%)	92.838	92.334	91.908	91.567	91.309	91.128	91.005	90.929	90.884	90.860	90.848
WGS inlet – steam/CO ratio	1.777	1.898	2.018	2.139	2.259	2.380	2.500	2.621	2.741	2.862	2.982
Existing biomass feed (kg/h)	20	20	20	20	20	20	20	20	20	20	20
Percent conversion (Equilibrium Reaction_1)	45.555	45.193	44.507	43.524	42.296	40.892	39.385	37.847	36.332	34.878	33.505

**Table 9 – Results of a case study 2 for WGS reactor.**

WGS inlet – Temperature °C	200	220	240	260	280	300	320	340	360	380	400
WGS out – Master Comp Mole Frac (H2O)	0.169	0.170	0.171	0.172	0.173	0.174	0.175	0.176	0.177	0.178	0.179
WGS out – Master Comp Mole Frac (Hydrogen)	0.326	0.325	0.324	0.323	0.322	0.321	0.320	0.319	0.318	0.317	0.316
WGS out – Master Comp Mole Frac (CO)	0.032	0.033	0.034	0.035	0.036	0.037	0.038	0.039	0.040	0.041	0.042
WGS out – Master Comp Mole Frac (CO2)	0.206	0.205	0.204	0.203	0.202	0.201	0.200	0.199	0.198	0.197	0.196
WGS out – Master Comp Mole Frac (Methane)	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
WGS out – Master Comp Mole Frac (Nitrogen)	0.267	0.267	0.267	0.267	0.267	0.267	0.267	0.267	0.267	0.267	0.267
WGS out – Temperature	393.792	397.937	402.063	406.204	410.361	414.536	418.730	422.944	427.180	431.438	435.719
Percent conversion (WGS Eq. reaction)	46.101	45.798	45.494	45.188	44.879	44.566	44.251	43.933	43.613	43.289	42.964
H <sub>2</sub> /CO ratio at WGS outlet	10.231	9.906	9.599	9.305	9.025	8.758	8.502	8.257	8.022	7.797	7.582

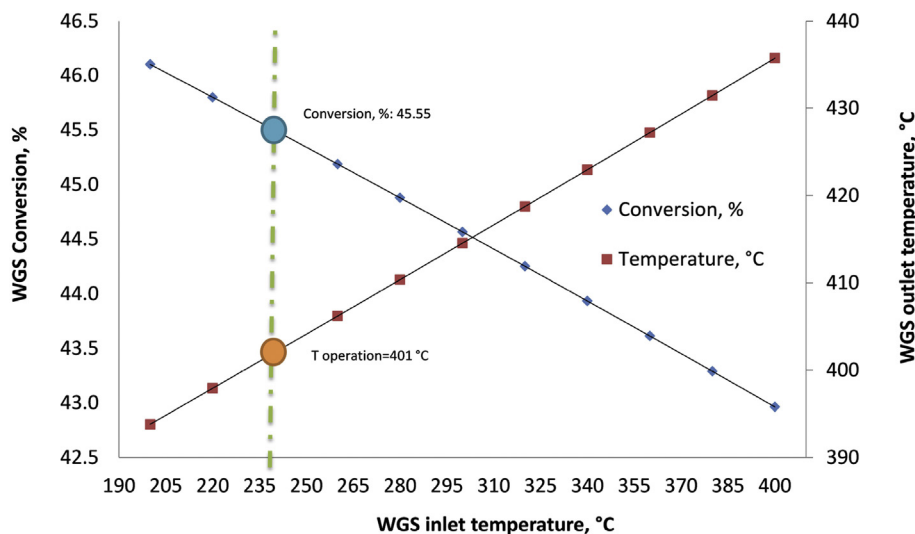
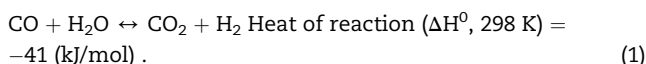


Fig. 5 – Effect of the WGS inlet/outlet temperature on the CO conversion.

Water gas shift reaction:



In line with the results of Case Study 2, the effect of the WGS temperatures on CO conversion has been presented in Fig. 5. It is seen that the thermodynamic equilibrium conversion of CO decreases with increasing WGS inlet temperature. CO conversion is decreased with increasing WGS outlet temperature.

The window of inlet temperatures 200 °C - 400 °C is much bigger than the window of outlet temperatures, 395 °C - 435 °C

in Fig. 5. It can be observed that the temperature difference in the WGS reactor (outlet minus inlet temperature) drops with increasing inlet temperature. This is also in agreement with the decreasing CO conversion, since the reaction is exothermal.

Fig. 6 shows the effect of the water gas shift reactor temperatures on the H<sub>2</sub>/CO ratio of the shift reactor outlet stream at a gasification outlet temperature of 700 °C. It is seen that H<sub>2</sub>/CO decreases with increasing WGS inlet temperature. This ratio is also increased with increasing WGS outlet temperature.

Fig. 7 shows the effect of the WGS inlet/outlet temperature on the outlet gas compositions. It is observed that the concentration of CO increases with increasing inlet temperatures whereas the H<sub>2</sub> and CO<sub>2</sub> concentrations decrease.

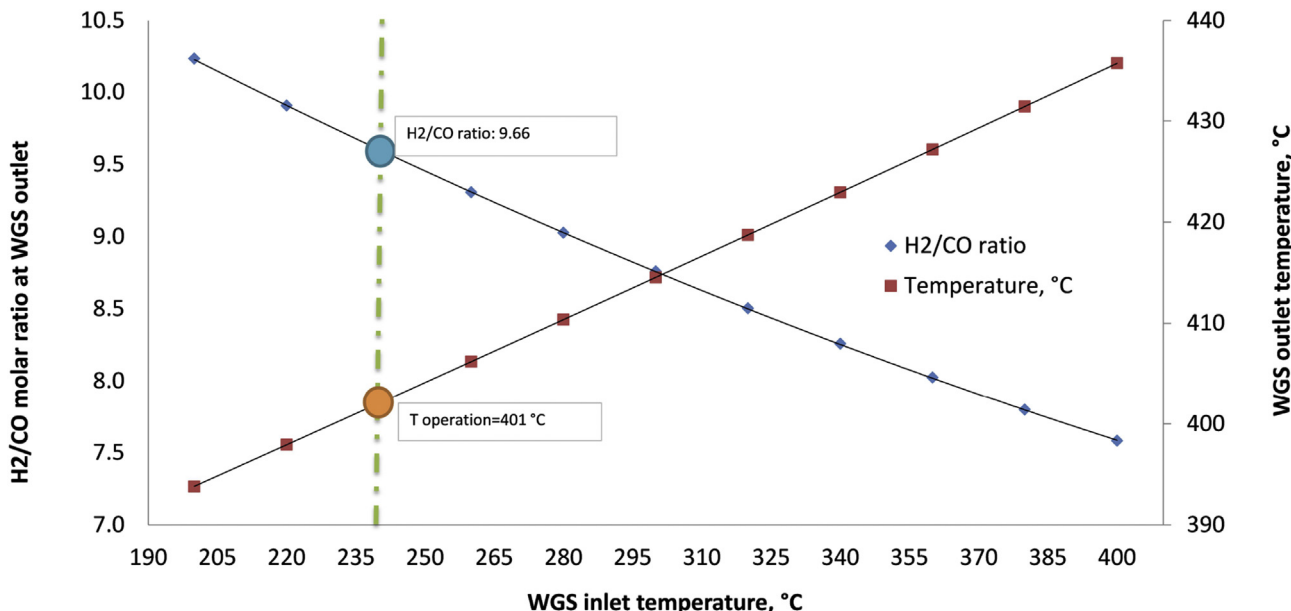


Fig. 6 – Effect of the WGS inlet/outlet temperature on the H<sub>2</sub>/CO molar ratio.

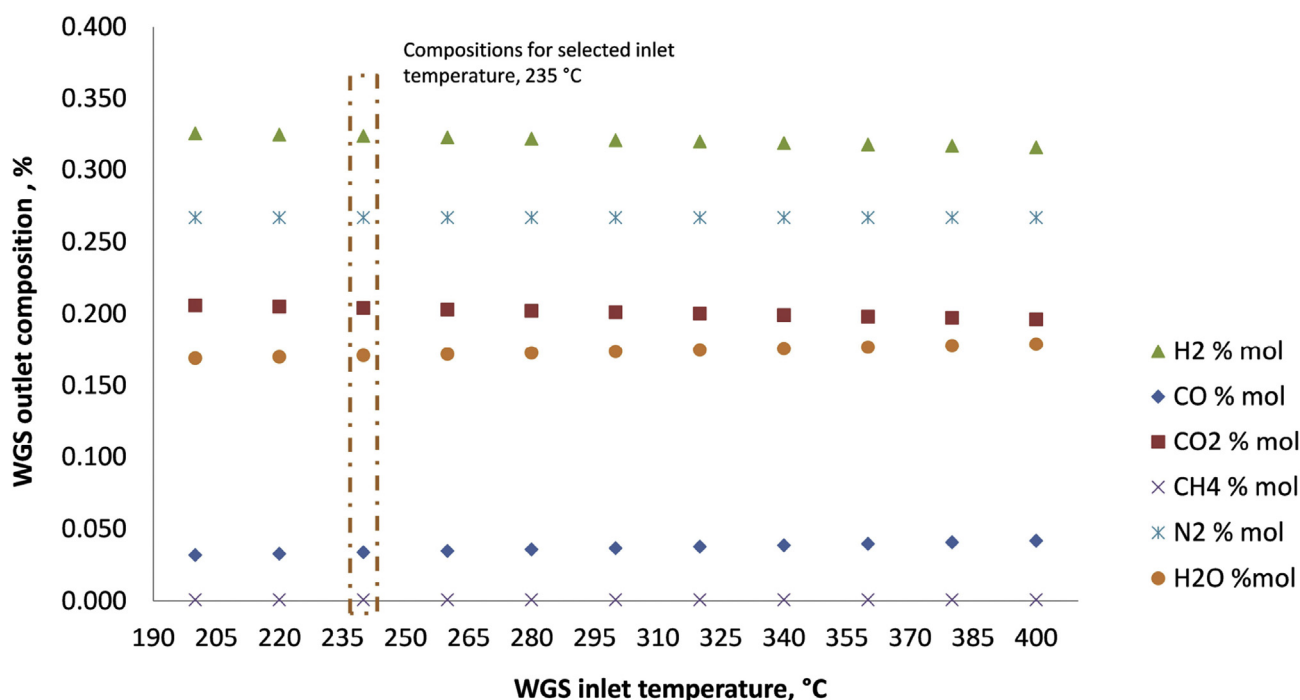


Fig. 7 – Effect of the WGS inlet temperature on the outlet composition.

The cold gas efficiency (Eq. (2)) represents how much hydrogen is generated per unit mass of biomass source. The cold gas efficiency ( $CG_{Eff}$ ) and the fuel processor efficiency ( $FP_{Eff}$ ) (Eq. (3)) are defined as follows. Hydrogen product is produced (g  $H_2$ /kg dry biomass) for wood at 76.1 (Eq. (4)).

The cold gas efficiency ( $CG_{Eff}$ ) % = 59.35.

[Product  $H_2$  mass flow (kg/h) × Hydrogen Heating Value in the product (HHV)]/[Biomass feed required (kg/h) × Biomass Heating Value in the Feed (HHV)] × 100 . (2)

HHV: Higher Heating Value (kJ/kg).

The fuel processor efficiency ( $FP_{Eff}$ ) % = 92.84.

(Net power ( $kW_{th}$ ))/(Feed energy ( $kW_{th}$ )) × 100 = (52.03/56.04) × 100 = 92.84 . (3)

Net power ( $kW_{th}$ ) = Product  $H_2$  Energy ( $kW_{th}$ ) + Net total BoP Power ( $kW_{th}$ ) = 50.75 + 1.283 = 52.03  $kW_{th}$

The hydrogen production rate.

[( $H_2$  product flow (kg/h) × 1000)/(Dry biomass)] (gr/kg) = ((1.522 × 1000)/20) = 76.1 g $H_2$ /kg dry biomass (4)

## Conclusion

Process simulation studies are very important to determine novel design and operation conditions. It is very easy to say that several particular advantages can also be handled

compared to experimental throughput. Large number of data can be produced via less experimental ones using process simulation tools. The results of these works can help to improve the novelty of the gasifier and upstream units in terms of optimization, design and operation. This work can also contribute to reduce some industrial sector problems and to simplify the implementation of this kind of technology.

In this study, an integrated chemical process simulation model for syngas and hydrogen production from lignocellulosic biomass source (here is a waste wood) with required conditions has been developed by using Aspen HYSYS software. The steady state conditions are accepted for all simulation cases. The syngas enrichment by means of hydrogen flow rates has been adjusted by using the shift reaction process. The proposed model is based on Gibbs free energy minimization for the all reactor units such as gasifier, tar reformer and water gas shift reactor. The operating temperatures have been determined for each reactor of the process. The Peng-Robinson equation of state is used as a property fluid package method in the simulations. Tar formation is considered and all sulfur (S) in biomass is converted to  $H_2S$  in gasifier. The effects of some selected parameters such as temperature of the WGS reactor on the concentrations of the hydrogen rich syngas compositions, reaction conversions,  $H_2/CO$  ratio, fuel processing efficiency etc. have been investigated.

The results show that the hydrogen content almost remains constant with increasing WGS temperature. The thermodynamic equilibrium conversion of CO decreases with increasing WGS inlet temperature between 200 and 400 °C. The CO conversion is increased with increasing WGS outlet temperature between 390 and 435 °C. The  $H_2/CO$  ratio at the outlet stream of WGS decreases with increasing WGS inlet

temperature between 200 and 400 °C. This ratio is also increased with increasing WGS outlet temperature between 390 and 435 °C.

According to the preliminary results of the ASPEN HYSYS conceptual process simulation model; the composition of hydrogen rich gas (0.62% H<sub>2</sub>O, 38.82% H<sub>2</sub>, 4.02% CO, 24.46% CO<sub>2</sub>, 0.11% CH<sub>4</sub>, and 31.97% N<sub>2</sub>) has been determined. The first simulation results show that the hydrogen purity of the product gas after PSA unit is 99.999% approximately. The mass lower heating value (LHV<sub>mass</sub>) of the product gas before PSA unit is expected to be about 4650 kJ/kg. The hydrogen production rate is found as 76.1 g H<sub>2</sub>/kg dry-biomass for selected biomass source. The cold gas efficiency (CG<sub>Eff</sub>) and the overall fuel processor efficiency (FP<sub>Eff</sub>) have been calculated as 59% and 93% respectively.

The overall “biomass to hydrogen production process” configuration and the preliminary results of the simulations are given in this study. As a main impact of this work, the simulation model calculation results show that hydrogen production reactions are realized in the tar reformer at high temperature (around 800 °C) and WGS reactor especially at lower temperature (around 400 °C). The overall fuel processor efficiency has been found as 93% which is greater than expected value (86%).

These first set of results can be used as a starting point for the basic design & engineering activities of a real hydrogen production plant in line with the objectives of BiOH<sub>2</sub> project. The detailed analysis will be performed within the work package activities of the project schedule.

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## REFERENCES

- [1] Meadows DH, Meadows DL, Randers J, Behrens WW. *The limits to growth*. New York: Universe Books; 1972.
- [2] Houghton JT, Jenkins GJ, Ephraums JJ. *Climate change: the IPCC scientific assessment*. Cambridge: Cambridge University Press; 1990.
- [3] Baykara SZ. *Ecohealth problems and climate change 1: anthropogenic climate change and ecohealth, worldwide environmental damage, IFSSH world congress, health challenges of the third millennium*. Istanbul: Book of Invited Background Papers; August 21-26, 2005. p. 295–313.
- [4] Boyle G. *Renewable energy*. New York: Oxford University Press; 2004.
- [5] Veziroglu TN, Barbir F. *Hydrogen energy technologies*. Vienna: UNIDO; 1998.
- [6] Baykara SZ. Hydrogen as fuel: a critical technology. *Int J Hydrogen Energy* 2005;30(5):545–53.
- [7] Energy Report 2011. World energy council Turkish national committee (in Turkish). 2011.
- [8] Adamson K. Hydrogen from renewable resources—the hundred year commitment. *Energy Policy* 2004;32:1231–42.
- [9] Cannon J. Clean hydrogen transportation: a market opportunity for renewable energy. REPP Issue Brief No 1997;7:20–1.
- [10] Basu P. *Combustion and gasification in fluidized beds*. Taylor and Francis; 2006.
- [11] Ay S, Atakul H, Ozyonum GN, Sarioglan A, Ersoz A, Akgun F, et al. Design studies for monolithic high temperature shift catalysts: effect of operational parameters. *Fuel Process Technol* 2013;116:175–81.
- [12] Choi Y, Stenger HG. Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen. *J Power Sources* 2003;124:432–9.
- [13] Smith RJB, Loganathany M, Shanthaz Murthy S. A review of the water gas shift reaction kinetics. *Int J Chem React Eng* 2010;8. Review R4.
- [14] Callaghan CA. *Kinetics and catalysis of the water-gas-shift reaction: a microkinetic and graph theoretic approach*. A dissertation. Worcester Polytechnic Institute; March 31, 2006.
- [15] Narvaez I, Orio A, Aznar MP, Corella J. Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas. *Ind Eng Chem Res* 1996;35:2110–20.
- [16] Kaewluan S, Pipatmanomai S. Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidized bed gasifier. *Energy Convers Manag* 2011;52:75–84.
- [17] Campoy M, Gomez-Barea A, Vidal FB, Ollero P. Air-steam gasification of biomass in a fluidized bed: process optimisation by enriched air. *Fuel Process Technol* 2009;90:677–85.
- [18] Hanping C, Bin L, Haiping Y, Guolai Y, Shihong Z. Experimental investigation of biomass gasification in a fluidized bed reactor. *Energy Fuels* 2008;22:3493–8.
- [19] Salemme L, Simeone M, Chirone R, Salatino P. Analysis of the energy efficiency of solar aided biomass gasification for pure hydrogen production. *Int J Hydrogen Energy* 2014;39:14622–32.
- [20] Qiao C, Xiao Y, Xu X, Zhao L, Tian W. Comparative analysis of hydrogen production systems from biomass based on different absorbent regeneration processes. *Int J Hydrogen Energy* 2007;32:80–5.
- [21] Cohce MK, Rosen MA, Dincer I. Efficiency evaluation of a biomass gasification-based hydrogen production. *Int J Hydrogen Energy* 2011;36:11388–98.
- [22] Cohce MK, Dincer I, Rosen MA. Energy and exergy analyses of a biomass-based hydrogen production system. *Bioresour Technol* 2011;102:8466–74.
- [23] Ahmed AMA, Salmiaton A, Choong TSY, Wan Azlina WAKG. Review of kinetic and equilibrium concepts for biomass tar modeling by using Aspen Plus. *Renew Sustain Energy Rev* 2015;52:1623–44.
- [24] Moneti M, Carlo A, Bocci E, Foscolo PU, Villarini M, et al. Influence of the main gasifier parameters on a real system for hydrogen production from biomass. *Int J Hydrogen Energy* 2016;41:11965–73.
- [25] Tian T, Qinghai L, Rong H, Zhongchao T, Yanguo Z. Effects of biochemical composition on hydrogen production by biomass gasification. *Int J Hydrogen Energy* 2017;42:19723–32.
- [26] Kocer A, Yaka IF, Gungor A. Evaluation of greenhouse residues gasification performance in hydrogen production. *Int J Hydrogen Energy* 2017;42:23244–9.
- [27] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: a review and analysis. *Int J Hydrogen Energy* 2009;34:8799–817.
- [28] Chang A, Chang H, Lin F, Lin K, Chen C. Biomass gasification for hydrogen production. *Int J Hydrogen Energy* 2011;36:14252–60.

- [29] Molino A, Chianese S, Musmarra D. Biomass gasification technology: the state of the art overview. *J Energy Chem* 2016;25:10–25.
- [30] Abuadala A, Dincer I. Efficiency evaluation of dry hydrogen production from biomass gasification. *Thermochim Acta* 2010;507–508:127–34.
- [31] Iribarren D, Susmozas A, Petrakopoulou F, Dufour J. Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification. *J Clean Prod* 2014;69:165–75.
- [32] Kalinci Y, Hepbasli A, Dincer I. Exergoeconomic analysis of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 2012;37:16402–11.
- [33] Abuadala A, Dincer I, Naterer GF. Exergy analysis of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 2010;35:4981–90.
- [34] Doranehgard MH, Samadyar H, Mesbah M, Haratipour P, Samiezade S. High-purity hydrogen production with in situ CO<sub>2</sub> capture based on biomass gasification. *Fuel* 2017;202:29–35.
- [35] Peng WX, Wang LS, Mirzaee M, Ahmadi H, Esfahani MJ, Fremaux S. Hydrogen and syngas production by catalytic biomass gasification. *Energy Convers Manag* 2017;135:270–3.
- [36] Zhao L, Lu Y. Hydrogen production by biomass gasification in a supercritical water fluidized bed reactor: a CFD-DEM study. *J Supercrit Fluids* 2018;131:26–36.
- [37] Al-Rahbi AS, Williams P. Hydrogen-rich syngas production and tar removal from biomass gasification using sacrificial tyre pyrolysis char. *Appl Energy* 2017;190:501–9.
- [38] Sansaniwal S, Pal K, Rosen MA, Tyagi SK. Recent advances in the development of biomass gasification technology: a comprehensive review. *Renew Sustain Energy Rev* 2017;72:363–84.
- [39] Shen L, Gao Y, Xiao J. Simulation of hydrogen production from biomass gasification in interconnected fluidized beds. *Biomass Bioenergy* 2008;32:120–7.
- [40] George J, Arun P, Muraleedharan C. Stoichiometric equilibrium model based assessment of hydrogen generation through biomass gasification. *Procedia Technol* 2016;25:982–9.
- [41] Sara HR, Bocci E, Villarini M, Di Carlo A, Naso V. Techno-economic analysis of hydrogen production using biomass gasification -a small scale power plant study. *Energy Procedia* 2016;101:806–13.
- [42] Wang S, Bi X, Wang S. Thermodynamic analysis of biomass gasification for biomethane production. *Energy* 2015;90:1207–18.
- [43] Vivanpatarakij S, Assabumrungrat S. Thermodynamic analysis of combined unit of biomass gasifier and tar steam reformer for hydrogen production and tar removal. *Int J Hydrogen Energy* 2013;38:3930–6.
- [44] Cohce MK, Dincer I, Rosen MA. Thermodynamic analysis of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 2010;35:4970–80.