

# Process model of the hydrogen production system integrated with biomass gasification.

Natalia Malgorzata Szymus  
natalia.szymus@tecnico.ulisboa.pt

Instituto Superior Tecnico, Lisboa, Portugal

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## Abstract

Sustainable energy resources have become a critical in energy transition, not only due do depletion of the resources, but negative impact on the environment as well. The emissions of carbon dioxide are drastically rising in the energy/heat and transportation sector, forcing international organization and national governments to implement more stricter rules. Hydrogen is a key element in the energy transition considering its versatility in applications, and growing interest in its consumption for short-range transportation and electricity generation.

The thesis attempted to explore the fields of end-to-end process of hydrogen production from biomass focusing on biomass gasification and synthesis gas processing. Based on the most feasible and proven technologies, production process model was composed and described. To validate the model, ChemCAD simulation was performed to study the hydrogen production efficiency based on process parameters documented at the industrial applications. Additionally, the influence of steam to biomass ratio was studied to draft conclusions on the most promising gasification parameters to ensure efficient hydrogen production.

**Keywords:** Biomass gasification, hydrogen, syngas cleaning, ChemCAD

## 1. Introduction

In the past decades interest around the global warming and climate change has been growing as the negative impact is already visible. The International Energy Agency have estimated that fossil fuels reservoir will be depleted by 2050. Moreover, energy production is predicted to rise in order to meet global demand and without deployment of new ways of electricity and fuel production the impact on environment will advance exponentially. The need of sustainable alternative to fossil fuels has become a urgent matter and concern for most countries and business sectors.

Countries, governments, as well as EU are financially supporting sustainable solutions to boost the innovation and energy transition in sector of transportation and

energy. This have brought interest to hydrogen and biofuels production from renewable resource. A clean hydrogen production processes are using either syngas sourced from biomass feedstock or renewable energy in electrolyzers to generate fully sustainable hydrogen.

*Table 1. GHG emissions in gigatons of CO<sub>2</sub> equivalent per sector over the years (Climate Watch, 2021)*

Sector	1990	2000	2010	2018
Agriculture	4.998	5.094	5.515	5.818
Industrial Processes	1.010	1.388	2.223	2.903
Waste	1.364	1.467	1.465	1.607
Electricity/Heat	8.596	10.553	14.151	15.591
Transportation	4.609	5.770	7.012	8.258

A clean hydrogen, or green hydrogen production processes are using either syngas sourced from biomass feedstock or renewable

energy in electrolyzers to generate fully sustainable hydrogen. Disadvantage of the electrolysis-based technologies lies in high energy requirement which needs to be provided from a sustainable resource (solar, wind, hydro) to meet the clean hydrogen goal. On the other hand, biomass gasification is technologically proven process, which relies on abundant feedstock. In order to utilize the potential of biomass gasification to hydrogen production, there is a need of creation a baseline process model for such facility together with analysis of the most influential factors and techno-economic study to promote further development.

The aim of the study is to present the current state of art of bio-hydrogen production focusing on gasification and raw gas processing to pure hydrogen stream. Based on the review, model for production was proposed and simulation of the process was conducted in the ChemCAD software.

## 2. Hydrogen

As the first chemical element in periodic table, hydrogen is odorless, colorless highly combustible gas which is fundamental building block for most elements in nature. Summary of main hydrogen properties is presented in Table 1.

When compared with currently widely used fuels, pure hydrogen in both gaseous and liquid phase has low energy per unit of volume (11.9 MJ/l in liquid state for hydrogen, while it is 23.0 MJ/l for LNG). Therefore, it should not be considered as a fuel, but rather as versatile energy carrier that has universal applications across the transport, chemicals and iron and steel production. There are various difficulties in handling, production and storage of hydrogen, mainly related to flammability, therefore extensive research is ongoing to overcome those challenges (Mazza, 2005).

According to IEA report, global hydrogen demand in 2019 was 75 Mt of H<sub>2</sub>, where in Sustainable Development Scenario, provided also by IEA, it is estimated to grow up to 520Mt by 2070. On the production side,

currently the hydrogen production routes are based on fossil feedstock. In 2019 pure hydrogen was obtained in three quarters from natural gas and a next quarter from coal, the rest mainly from oil. Only 4% of world hydrogen production is coming from renewable sources. Due to that, thought hydrogen production 800 Mt of CO<sub>2</sub> was emitted, accounting for approximately 2% of global CO<sub>2</sub> emissions from energy sector (International Energy Agency, 2021)

*Table 1. Main properties of hydrogen.*

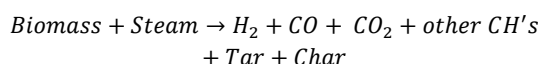
Property Description	Value	Unit
Molecular formula	-	H <sub>2</sub>
Molecular weight	g/mole	2.016
Density in standard conditions	kg/m <sup>3</sup>	0.0838
Density (liquid state)	kg/m <sup>3</sup>	70.8
HHV and LHV (liquid)	MJ/kg	141.9/120
Boiling Point	°C	-252.74
Freezing point	°C	259.18

This limitation is mainly caused by the cost of mature technologies for hydrogen production. As indicated by IEA, currently there are only two early adoption technologies for production: electrolysis and natural gas reforming. Situation on hydrogen use is better, due to mature ammonia production technology but over 60% of stated ways of use are either in demonstration or prototype phase. Therefore, meeting the sustainability goals is highly dependent on development rate of both production and use technologies.

### 2.1. Production routes and raw materials

Currently, 96 % of world's consumed hydrogen is derived from fossil fuels through hydrocarbon reforming as the primary production mechanism. Other production routes based on renewable resources include water splitting and hydrogen production based on biomass, which can be classified to thermochemical or biological routes. Thermochemical processes of hydrogen production are the most effective and fast. Water splitting and biological routes are difficult to scale up and provide limited amounts of hydrogen, therefore gasification and pyrolysis are gaining popularity

(Barbuzza, et al., 2019). The main principle in both processes is conversion of the biomass feedstock into gaseous biofuel or liquid biofuels which can be processed to pure hydrogen, but the conditions and process requirements are different (Balat & Kirtay, 2019). In gasification biomass conversion happens through four primary processes, (i) drying, (ii) pyrolysis, (iii) partial combustion and (iv) gasification of volatile products.



*Equation 1. Steam gasification biomass decomposition reaction*

During those steps, feedstock undergoes a series of physical and chemical changes that result in carbon monoxide CO and hydrogen H<sub>2</sub> mixture (syngas) and accompaniment gases, carbon dioxide CO<sub>2</sub>, and nitrogen. In gasification, the quality of produced hydrogen depends on biomass properties, used catalyst, working parameters and technology chosen for the process.

There are different types of gasification and pyrolysis, but three main routes specifically oriented for hydrogen production can be distinguished: steam gasification, supercritical water gasification and fast pyrolysis. Based on gathered data related to efficiency and advantages of the process, steam gasification was chosen for the purpose of this study.



*Figure 1. Reaction phases in gasification process*

### 3. Biomass

Biomass is defined as organic matter derived from plant or animals, and it is mostly composed of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and trace amounts of sulfur (S). It can be referred as sustainable and carbon-neutral resource as plant biomass growth is driven by photosynthesis process which uses ambient CO<sub>2</sub>. It is then released back into the atmosphere through combustion or wood degradation. Depending on the source, biomass can be divided into two

categories – primary and waste biomass. Primary biomass is obtained directly from botanical resources such as plants, wood and crops. Waste biomass consists of all type of waste with high organic content which includes municipal solid waste, agricultural waste and industrial wastes (sawdust).

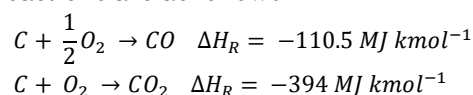
Based on the research made by A. Sharma et al over agricultural waste and virgin biomass the highest H<sub>2</sub> content (18 vol%) in produced gas was found pine gasification and at the same it had the highest content of CO. Another sample with high hydrogen content was cypress mulch, which content of H<sub>2</sub> in produces gas reached 16 vol% and had low CO content of only 6 vol%. Those two were also characterized with the higher HHV of 18.5 MJ/kg and 16.8 MJ/kg respectively. (Sharma, et al., 2017)

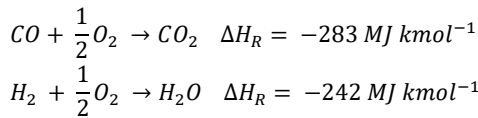
### 4. Gasification technology

In general, gasification follows four main steps as mentioned in chapter 3, which are:

- Drying: reduction of the moisture content in biomass under high temperature
- Pyrolysis: separation of the biomass compounds into volatiles and char
- Oxidation/Combustion: by which the heat needed for entire process is provided is provided through oxidation of gasifying medium,
- Gasification/Reduction: where syngas production takes place under reduced of oxygen provided (less than theoretical stoichiometric value) through series of chemical reactions

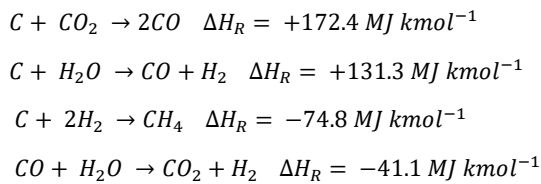
Oxidation and gasification reactions have a direct influence of the syngas composition. In oxidation zone at temperature range from 600 to 900 °C partial oxidation occurs. Complete oxidation reactions are taking place under 800 °C to 1400 °C. During reactions, heat is released in the process together with main products of CO<sub>2</sub> and H<sub>2</sub>O. Few of specific to oxidation reactions are as follows:





*Equation 2,3,4,5 (from the top) : Oxidation reaction occurring in gasification*

Gasification reactions include mainly CO, H<sub>2</sub>, and CH<sub>4</sub> production. Several other unfavorable gases that contribute to tar formation are being reduced in this zone. Desirable temperature should remain around 1000 °C range. The following reactions occur in reduction zone:



*Equation 6,7,8,9 (from the top): Oxidation reaction occurring in gasification*

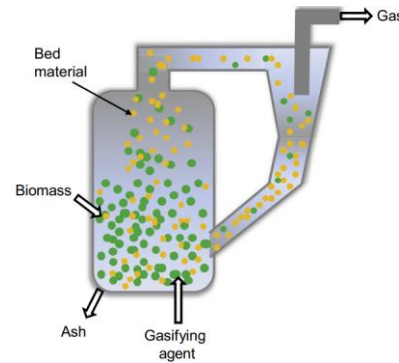
The type of oxidizing agent chosen for gasification influences the main reactions, giving different results of products. For hydrogen thermochemical production steam gasification is preferred as it water vapor shifts the water-gas shift equilibrium to the right side promoting H<sub>2</sub> production.

Depending on the working principles, gasifiers can be divided into three groups:

- Fixed bed technologies: updraft, downdraft, cross draft gasifiers,
- Fluidized bed technologies: bubbling bed, circulating fluidized bed and dual stage gasifiers,
- Entrained flow gasifier.

For biomass gasification circulating fluidized bed gasifier is preferred, as it can provide longer gas residence time. In this type of reactor, solids of bed and fuel are distributed along the tall riser, providing longer residence time for gas and particles and therefore conversion rate. The feedstock then can be of low-quality and have board particle size. Fluidization velocity of the bed is higher (3.5-5.5 m/s) compared to bubbling bed (0.5-1.0 m/s). Due to above characteristics, large portion of particles are carried out of the gasifier with product gas. They are captures in cyclones and returned back to the base of

the riser. The rate at which particles are returned to reactor and the fluidization velocity are high enough for the parties in the riser to reach unique hydrodynamic conditions called fast-fluidized bed.



*Figure 2. Schematic draft of circulating fluidized bed reactor. (Bermudez & Fidalgo, 2016)*

## 5. Hydrogen production from syngas

In order to use syngas and achieve pure hydrogen product, product gas from gasification needs to go through number of processes aiming removal of corrosive agents, pollutants and impurities. First particulate matter contained in gas (ash particles, unreacted carbon, soot and bed particles) needs to be separated to prevent fouling issues in downstream infrastructure. Currently, cyclone separation or scrubbers are the most common technologies used in the industrial field.

Following that, water-gas shift reaction is used to raise the yield of hydrogen in syngas (equation 9). The equilibrium constant of the reaction is constantly decreasing with temperature. The lower the temperature, the higher the conversion in WGS reaction (Liu, et al., 2010). For an industrial application of hydrogen production, water-gas shift unit includes one high and one low temperature reactor. For pure hydrogen production, conversion rate to H<sub>2</sub> can be raised by implementing a catalyst into WGS process. For high temperature step (300 to 500 °C), iron based alpha-Fe<sub>2</sub>O<sub>3</sub> catalyst is mostly used, and for low temperature step (200 to 300 °C) copper based catalyst as CuO are used. When using catalyst, it is important to note difficulties that can be met during the process. The high temperature catalyst is sensitive for thermal sintering of iron, which

causes deactivation. Secondly, most of the catalysts are paired with promoters as  $\text{Cr}_2\text{O}_3$ , which is highly toxic oxide. Therefore catalyst implementation to WGS needs to be done under strict supervision of process parameters, and with use of novel catalyst preparation methods. (Lang, et al., 2016). An advantage of using catalyst is that it allows to process gas with content of sulfur, also known as sour gas. Sour WGS is preferable as it does not require sulfur removal beforehand and presence of catalyst is promoting COS and HCN hydrolysis. It is worth to note here, that sour gas shift is not a feasible for direct application of syngas of a low steam concentration (eg. After Shell GSP). In this case, high amounts of steam are added to the gas before the process to achieve at 1.75 steam to  $\text{CO}_2$  ratio in syngas. (Liu, et al., 2015).

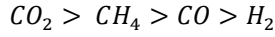
Following WGS, sulfur contaminants removal processes are applied. There are three categories of separations methods: chemical, physical and biological in which several technologies can be distinguished. Chemical methods are preferred over biological and sometimes over physical due to higher removal efficiency. They are also favorable if the partial pressure of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  gases is low. In case of high pressure, physical methods perform more efficiently (Hermann, et al., 2007). The most proven technology based on chemical absorption is the amine scrubbing using monoethanolamine (MEA) or methyldiethanolamine (MDEA). Optimal concentration of MDEA for its best efficiency in  $\text{H}_2\text{S}$  removal is around 15% at a temperature of 40 °C. In this case 98.7% of  $\text{H}_2\text{S}$  is removed, with co-adsorption of  $\text{CO}_2$  at 9.50% (Zhi, et al., 2010). Using amines for absorption processes is in general thought to be energy intensive due to their degradable nature. Certain zeolites and metal oxides including  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  are potential catalyst that would low higher operating temperatures. From physical methods of sulfur compounds removal two most common processes are used: Selexol process and Rectisol. The former is first choice in the

industry due to ambient temperature operating conditions, while the latter is more effective in hydrogen sulfide removal but requires cryogenic temperatures from  $-25^\circ\text{C}$  to  $-60^\circ\text{C}$  or lower, which results in high investment and operation cost. Selexol technology is using a mixture of dimethyl ethers of polyethylene glycols, which act as physical absorber of high selectivity for  $\text{H}_2\text{S}$  and COS. For syngas clean up to hydrogen two-stage process is usually required with two absorption and regeneration columns. In the first column,  $\text{H}_2\text{S}$  is removed with the lean solvent with little content of  $\text{CO}_2$ . After leaving the absorber column, rich in  $\text{H}_2\text{S}$  solvent is heated and stripped off in desorber column. Acid gas can be directed to Claus plant for sulfur production, while regenerated solvent goes to  $\text{CO}_2$  absorption column. Afterwards, the product gas is free of  $\text{H}_2\text{S}$  and has considerably lower  $\text{CO}_2$  content. Typically, Selexol unit can ensure the  $\text{H}_2\text{S}$  removal level at over 99% and 97% for  $\text{CO}_2$ .

The final stage is hydrogen purification at which all other chemicals contained in as needs to be separated. The processes used in the industrial applications are: pressure swing adsorption (PSA), absorption on chemical solvents, membrane separation, cryogenic separation and biological methods (Luis, 2016). They can separate impurities at different rate and the level of required purification depends on further application of hydrogen. Fuel cells require hydrogen to be purified to 99.97%, which can only be achieved by using PSA.

PSA is based on the principle of physical binding of the gas molecules to adsorbent material. It takes advantage of adsorbing properties of high surface area materials such as activated carbon, zeolites and mesoporous silica. The reaction between the inlet gas and the adsorbent is primarily determined by gas composition, its temperature, and its partial pressure. Taking into consideration the main gas components, the strength of adsorption for activated carbon follows below sequence presented on equation 10.





*Equation 10. Sorption selectivity of activated carbon in PSA.*

The PSA technology with activated carbon can recover from 60% to over 90% of hydrogen from gas stream where initial content of H<sub>2</sub> was around 50 vol.%. In case of low content of impurities in the gas stream, temperature swing adsorption (TSA) might be cost efficient way for hydrogen separation.

#### 6. Design of production process in ChemCAD and simulation parameters

Based on literature review, theoretical production flow chart was drafted as a backbone for the simulation model. The ChemCAD software was chosen for production process simulation as it can handle equilibrium calculations and allows to export data for mass and energy balance analysis. ChemCAD starts from gasification to downstream processes including initial scrubber cleaning, water gas shift station (WGS) and hydrolysis reactor, two stage Selexol process for H<sub>2</sub>S and CO<sub>2</sub> removal and pressure swing adsorption (PSA) unit for complete purification of hydrogen.

The model for biomass gasification is based on the circulating fluidized-bed gasifier, where the technology itself as well as operating parameters for gasification were verified with SES Gasification Technology (SGT). (Ściażko, et al., 2018) The gasifier is designed to handle low rank coals, biomass and municipal solid wastes (MSW) using oxygen, oxygen-rich air or air for the gasification reaction. In case fluidized bed reactor, gasification system should be equipped with tar reforming which includes thermal cracking to support conversion of higher carbon compounds such as aromatics contained in raw gas. At this analysis, the tar reforming unit was not included, and contentment of tar in the raw gas is assumed to be zero. Simulation assumes that gasification process is isothermal and in steady state. ChemCAD thermodynamic calculations are based on Soave Redlich Kwong equation. Solid components include

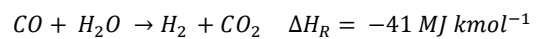
carbon, silicon dioxide, sulfur and calcium carbonate, other solid components are neglected. Gas cleaning from a particulate matter is neglected.

Gasification of a pine biomass presented best results in terms of volumetric production of both H<sub>2</sub> and CO, therefore it was chosen as a biomass for this study. Exact parameters of the feedstock are an average parameter presented for wood stem, branches and needles from the research made on Portuguese Maritime Pine woods. (Viana, et al., 2018). A detailed proximate and ultimate analysis of the sample is presented in below Table 3 and Table 4. As the raw wood biomass, the moisture content can vary from 30 up to 45%, it is usually dried to about 10 to 20% based on the technological requirements of gasifiers. In this study, the moisture content in biomass was adjusted to 16.66 % based on values available in reseach papers and operating requirement of gasifier.

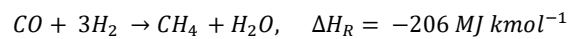
*Table 2. Proximate analysis of used biomass feedstock (Maritime Pine)*

Proximate Analysis	With Moisture [%]	Dry Basis [%]
Moisture	16.66	0.00
Ash	0.72	0.86
Volatile Matter	68.77	82.52
Fixed Carbon	13.85	16.62
Total	100.00	100.00

In order to simulate gasification process is equipped with series of two following reactors. First one is a Gibbs reactor, which used the equilibrium model for all possible reactions minimizing the Gibbs free energy on the products to obtain output conditions (pressure, temperature, heat of reaction). Second is a stoichiometric reactor, in which three additional reactions are added to model conversions of CO and N<sub>2</sub> (Equation 11,12,13)



$$CO \text{ fractional conversion} = 0.09,$$



$$CO \text{ fractional conversion} = 0.11$$



$$N_2 \text{ fractional conversion} = 0.008$$

*Equation 11,12,13 (from the top): gasification reactions used in modeling.*

*Table 3. Ultimate analysis of used biomass feedstock (Maritime Pine)*

Ultimate Analysis	With Moisture [%]	Dry Basis [%]
Carbon	40.47	48.56
Hydrogen	5.75	6.9
Oxygen	36.62	43.95
Water	16.67	0.00
Sulfur	0.21	0.25
Nitrogen	0.28	0.34
Total	100.00	100.00

The operating pressure is 30 bar and operating temperature is at the level of 997 °C and a 95% carbon conversion. Biomass loading rate is defined as 90,000 kg/h. Heavy duty losses of 111.99 MW for gasification reactor were estimated as a sum of heat losses of 1% of chemical enthalpy of the fuel introduced to gasifier and thermodynamic enthalpy of fuel formation. Both parameters were calculated as indicated by Chmielniak et. all. (Chmielniak, et al., 2021).

Oxidating agent chosen for the gasification is steam and oxygen which enters the reactor together with N<sub>2</sub> as a fuel transportation gas. Additionally, the CaCO<sub>3</sub> is introduced to the reactor in ratio of 0.1% of biomass loading rate to promote both gasification and reforming reactions. (Gomez-Vasquez, et al., 2021). In the ChemCAD model, component separator is introduced before the Gibbs reactor which returns 5% of carbon to simulate unreacted carbon composition in the gas after devolatilization. After gasification, ash and all solid components are removed by ideal separator. Hot ash goes through heat exchanger to recycle the heat from quenching process and leaves in form of cooled ash and water. As ChemCAD software estimates only the gas composition based on reaction equilibrium, the product gas leaves reactor at a temperature equal to operating temperature of equilibrium reactor. From there, the product gas is directed to gas cooling which

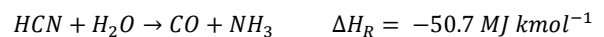
reduces the gas temperature from 997°C to 216°C with total pressure drop of 1 bar. (U.S. Department of Energy, 2011) Hot water vapor from the first heat exchanger is partially recycled as steam going into gasifier. Following the cooling apparatus, raw gas is treated with scrubber to simulate removal of particulate matter. The water for scrubbing is fed in ratio of 1 [m<sup>3</sup>] of water per 1 [Nm<sup>3</sup>] of gas, which is within the requirement of 1 – 4 [m<sup>3</sup>/Nm<sup>3</sup>].

In order to raise the ratio of hydrogen content in the product gas and enable carbon capturing by increasing the CO<sub>2</sub> concentration, high and low temperature WGS reactors are used. Assumption in the simulation is that an ideal catalyst are used in both reactors. For prevention of carbon deposition on the catalyst used in the reactor, a steam to carbon monoxide ratio is maintained above 1.75.

*Table 4. Sour WGS parameters for high and low temperature reactors*

Parameter	HT reactor	LT reactor
Inlet gas temp.	210.5 °C	200 °C
Inlet gas pressure	28.7 bar	27.4 bar
Pressure drop	0.7 bar	0.5 bar
Outlet gas temp.	336.1 °C	215.8 °C

After the second reactor, hydrogen concentration in the product gas is higher by 56% and the CO conversion is at the level of 97.6%. In presence of catalyst in WGS reactors, hydrolysis reactions are supported during the process. To simulate that in the ChemCAD model, stream from the low temperature reactor is directed to equilibrium reactor where two main hydrolysis reactions are simulated, namely COS and HCN hydrolysis according to the equation 14 and 15.



*Equation 14,15: Hydrolysis reactions.*

Conversion for COS hydrolysis is set at 99.5%, while for HCN it is 95% based on industrial standard. After hydrolysis, product gas at temperature of 186 °C and 26,5 bar

goes through series of heat exchanges to lower the gas temperature before the cleaning processes.

For H<sub>2</sub>S and CO<sub>2</sub> removal, dual stage Selexol was chosen. In ChemCAD model, Selexol process is simulated with ideal component separator with calibrated performance according to quality guidelines. Before entering the 1<sup>st</sup> column, process gas is significantly cooled down by series of three heat exchanges cooling the gas from 185 to 22 °C. The pressure drop on each heat exchanger is set as 2% of inlet gas pressure, giving on average 0.5 bar pressure drop on each heat exchange, which is within the measured range (0.3–0.7 bar) at industrial applications. First column selectively removes H<sub>2</sub>S together and partially CO<sub>2</sub>, while the second column removes remaining CO<sub>2</sub>. However, product gas requires compression before entering first absorption column due to pressure drop caused by cooling. According to process quality guidelines the product gas needs to meet requirements of at least 34 bar pressure and 34–35 °C temperature. Compressor and heat exchanger are applied to meet the specification. (U.S. Department of Energy, June 2019).

*Table 5. Dual stage Selexol parameters for first and second absorption columns*

Parameter	1st stage	2nd stage
Inlet gas temp.	39.6 °C	44 °C
Inlet gas pressure	31 bar	30 bar
Pressure drop	1 bar	1 bar
$\eta$ H <sub>2</sub> S	99.77%	-
$\eta$ CO <sub>2</sub>	20%	97.5%
H <sub>2</sub> loss	0.3%	0.3%
Outlet gas temp.	26.7 °C	18 °C

The CO<sub>2</sub> gas from the second column is received at two pressure levels. The high-pressure stream is at 10 bar. The low-pressure stream is at 1.2 bar and is around 40% of a total CO<sub>2</sub> stream output. It goes through the 3-stage compressor with intercooling to even out the pressure up to high pressure stream level. Compression ratio is 2.2 bar and efficiency is 86%. The last mile for CO<sub>2</sub> gas stream is multistage compressing up to 135 bar. Process

parameters for compression are applied based on industrial measurements. At a pressure of 135 bar and temperature of 49.4 °C, CO<sub>2</sub> is in the supercritical state, which allows for it to be applied further in enhanced oil recovery (EOR) or sequestered in depleted oil and gas fields or saline aquifers.

Lastly, product gas is directed to PSA for final hydrogen separation. The process is simulated with ideal components separator with calibrated performance to quality guidelines from NETL. After Selexol process, the product gas is at 30 bar and temperature of 18 °C and has 81.8 mol% of H<sub>2</sub> in composition, which is above required 60 mol% of H<sub>2</sub>. Hydrogen recovery is 95% and pressure drop 2.3 bar based on the research made over PSA specifically for hydrogen purification. (Zhu, et al., 2018) The mass flow of the outlet hydrogen stream of purity 99.99% is 5,9697 kg/h. Depending on the further application of hydrogen, it needs to undergo relevant processing of compression or heating. The tail gas from PSA unit is at lower pressure due to desorption pressure losses. Due to high mass flow of 17,945 kg/h and high content of methane it is burned to recover energy. For this purpose, ChemCAD model contains a Gibbs reactor to simulate combustion with exhaust gas cooling unit.

Based on built ChemCAD model with described parameters elemental mass and energy balances were performed to validate the model output.

## 7. Performance indicators

Selected performance indicators are used to compare the simulation results with industrial standard. Cold gas efficiency (CGE) is given by equation 16. and is evaluated based on product gas from gasification and biomass feed stream. Hydrogen production efficiency (HPE) is evaluated on hydrogen stream from PSA and biomass feed stream. Carbon conversion efficiency (CCE) is a comparing a molar flow of unreacted carbon residue with molar flow of carbon contained in biomass. Lastly, carbon monoxide conversion efficiency (CME)



aims to evaluate WGS process efficiency and is comparing mass flow of CO out of LT reactor with mass flow of CO in the stream entering HT reactor.

$$CGE = \frac{\Sigma(\dot{m}_p * LHV_p)}{\Sigma(\dot{m}_f * LHV_f)} \quad HPE = \frac{\Sigma(\dot{m}_h * LHV_h)}{\Sigma(\dot{m}_f * LHV_f)}$$

$$CCE = \left(1 - \frac{\dot{M}_r}{\dot{M}_f}\right) \quad CME = \left(1 - \frac{\dot{m}_{CO_{out}}}{\dot{m}_{CO_{in}}}\right)$$

Equation 16, 17, 18, 19: Mathematical representation of measured performance indicators.

## 8. Results and conclusions

Based on the ChemCAD model, four simulations were made for different steam to biomass ratio (SBR) to measure its influence on the hydrogen production. In order to isolate the influence of just SBR ratio on the process performance temperature, pressure and biomass loading ratio were kept the same. The same rule was applied to further processing units, unless achieved results required system adjustment (temperature of ash cooling etc.) All of the parameters and performance indications are included in Table 6.

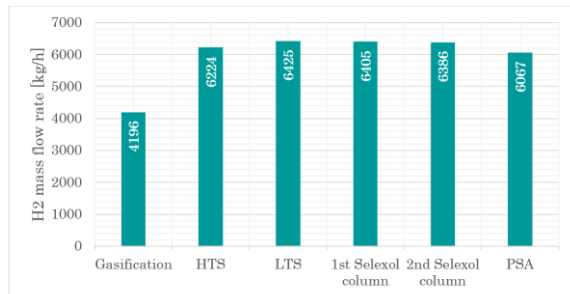


Figure 3. H<sub>2</sub> mass flow rate after each process step

Overall, the influence of the SBR within the range of 0.25 to 0.60 on the gas composition was rather weak, which is in line with published experimental observations for fluidized bed reactors. (Shen, et al., 2008) For all cases the mole% of each component in the syngas after gasification is declining, which is an effect of higher steam content in the gas. It is beneficial for hydrogen production as the steam to CO ratio is higher than required for WGS. Mass flow of CO has decreased by 12.1%, however H<sub>2</sub> formation has increased

by 16.8% in the raw gas. This can be explained by shifted equilibrium of water-gas shift reaction to the products already in the gasification reactor. The rising CO<sub>2</sub> mass flow may be a confirmation of the above conclusion. Looking at the CGE, it is falling by almost 3% as a result of lower yield of CO. At the same time H<sub>2</sub> production efficiency is rising by 3.8%, therefore the influence of the steam to biomass ratio is beneficial for biomass gasification if the desired product is hydrogen rich gas.

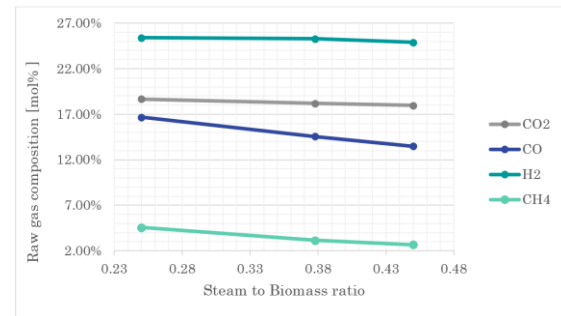


Figure 4. Effect of the SBR on raw gas components

According to the research work made by Shen et al. at around SBR of 0.70 and gasification temperature of 800 to 850 °C hydrogen yield is reaching its maximum. The influence of SBR is not as impactful in case of gasification over 850°, compared to low temperature gasification at temperatures of 650 to 850. (Shen, et al., 2008) Considering that, it can be concluded that the increase in production yield of H<sub>2</sub> goes in pair with raising SBR ratio up to a maximum point.

The HPE at 45.7% is the highest for SBR = 0.60. Hydrogen production with use of natural gas reforming has efficiency ranging around 80% and biogas reforming efficiency is between 55 to 60%. However, the first process is based on the fossil fuels, therefore it does not meet the requirement of sustainable production. The second is comparable, but not as scalable and versatile as biomass gasification. It can be concluded that hydrogen production with biomass gasification at a high SBR has a high potential for deployment.

Table 6. Results for hydrogen production simulation with biomass gasification.

Parameter	Unit	Case 1	Case 3	Case 2	Case 4
Steam to Biomass Ratio	%	0.25	0.38	0.45	0.60
Steam Flow Rate	kg/h	22,500	34,000	40,500	54,000
Oxygen Flow Rate	kg/h	31,850	34,350	35,500	37,720
Biomass Loading Rate	kg/h	90,000	90,000	90,000	90,000
Gasification Temperature	°C	997	997	996	996
Gasification Pressure	bar	30	30	30	30
Raw Gas Flow Rate	vol. m <sup>3</sup> /h	25,324	28,136	29,590	32,555
CO <sub>2</sub>	mol %	18.65%	18.19%	17.97%	17.48%
CO	mol %	16.68%	14.56%	13.48%	11.56%
H <sub>2</sub>	mol %	25.40%	25.27%	24.89%	23.72%
CH <sub>4</sub>	mol %	4.56%	3.15%	2.66%	1.96%
CO <sub>2</sub>	kg/h	58,690	63,597	66,126	70,733
CO	kg/h	33,398	32,396	31,575	29,785
H <sub>2</sub>	kg/h	3,661	4,047	4,196	4,398
CH <sub>4</sub>	kg/h	5,233	4,019	3,567	2,899
CGE	%	60.4%	59.2%	58.6%	57.3%
CCE	%	95.0%	95.0%	95.0%	95.0%
CME	%	95.9%	97.6%	98.1%	98.6%
Hydrogen Flow Rate	vol. m <sup>3</sup> /h	2,478	2,626	2,669	2,705
	kg/h	5,634	5,970	6,067	6,149
HPE	%	41.9%	44.4%	45.1%	45.7%

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