Simulations of a Plant with a Fluidized Bed

Gasifier WGS and PSA

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Abstract

Nowadays the renewable energy has an even more important role. In particular, among these, in the European countries the energetic valorisation of biomass is very important. In this way also waste biomass become an economic and environmental resource to produce both energy and energy vectors, as hydrogen.
The aim of this work has been the evaluation of the hydrogen production in a gasifier plant simulations. Using ChemCAD software simulations of a plant composed of a double bubbling fluidized bed combustor and steam gasifier with catalytic filters candles, HT/LT-WGSR and PSA have been carried out. In these tests the steam to biomass ratio and the operating gasifier temperature have been changed.

The simulation results show that to increase the hydrogen yield the optimal operating conditions should be characterized by high gasification temperature, high steam to biomass ratio and operation of the water gas shift reactors with an excess of steam. Therefore best results have been reached at 850°C with a steam to biomass ratio of 2.

Keywords: Gasification, Double bubbling fluidized bed gasifier, Simulation

1 Introduction

Text of section 1.Bioenergy can contribute to satisfy, in a sustainable way, the future energy request and it represents the most important renewable energy source in the world. It can have a significant development for the electric and thermal energy production, but also for biofuel and in this way for the transport sector. In the European countries really important is the energetic valorisation of biomass. Biomass include all the organic components like wood, wood waste, animal waste, etc. In particular an attractive opportunity is the waste biomass as agro-industrial sub-products or urban wastes. Biomass can be used to produce heat by combustion, mechanical energy by internal combustion engine or gas turbine [1, 33,34,35], electric energy directly by the fuel cells [2] or indirectly by mechanical energy (CE,ST, GT, CC) and a generator.

Table 1.Total consumption of solid biomass in the European Union in 2012 and 2013* (Mtoe)

Country	2012	2013
Germany	10.931	10.902
France	9.779	10.842
Sweden	9.563	9.211
Italy	8.383	8.837
Finland	7.963	8.146
Poland	6.988	6.497
Spain	4.964	5.443
Austria	5.021	4,971
Romania	3.655	4.233
United Kingdom	2.512	3.319
Denmark	2.473	2.523
Portugal	2.342	2.347
Czech Republic	2.057	2.173
Belgium	1.993	2,036
Hungary	1.330	1.407
Bulgaria	1.019	1.334

Table 2. (Continued): Total consumption of solid biomass in the European Union in 2012 and 2013* (Mtoe)

Latvia	**1.255**	**1.270**
Netherlands	1.350	1.125
Lithuania	1.003	1.026
Greece	1.136	0.928
Slovakia	0.786	0.813
Estonia	0.814	0.793
Slovenia	0.560	0.583
Croatia	0.497	0.500
Ireland	0,213	0.230
Luxembourg	0,043	0.049
Cyprus	0,009	0.009
Malta	0.001	0.001
European Union	88.639	91.459

* Estimate. Source: EurObserv'ER 2014

As can be seen in Table 1, every year the European Union increases its biomass consumption to produce electricity and heat. In 2013 the total energy consumption of the European Union has reached about 91.5 Mtoe which is a 3.3% increase on 2012 [3].

Any process produces different "energetic products" (as heat, electricity, fuels, etc.) and also bub-products and wastes.

As a function of the biomass characteristics, it can be converted with different processes. The biomass with high moisture and high carbon to nitrogen ratio (C/N) are more suitable for the biochemical processes [4–8], otherwise they are more suitable for the thermochemical processes[9–12].The thermochemical processes convert chemical energy in thermal and vice versa because they are made up of endothermic and exothermic reactions at high temperature. For these processes the biomass have to have a low moisture content (<50%). For this reason the more suitable biomass for the thermochemical processes are wood and its by-product, agricultural sub-product, urban and industrial dry wastes.

Gasification is a partial oxidation of a liquid or solid fuel in a fuel gas (syngas) that can be used to produce energy or utilized for the production of other biofuel or hydrogen. The gasification medium can be air, oxygen, steam or a mix of these, and the products of the reaction are syngas, composed of hydrogen, carbon monoxide, methane, carbon dioxide, steam and nitrogen, but also organic (TAR) and inorganic impurities and particulate. The technologies that use air as gasification medium produce a gas with low hydrogen content because the nitrogen in the medium dilutes the syngas. Another possibility is the gasification with oxygen or steam that produces a gas with high calorific value. However the cost of oxygen is still too high for a feasible application of this gasification technology in small scale plants[13–16]. Fluidized bed gasifier permits to keep the temperature constant and to have in this way greater efficiency than the fixed bed

technology. Steam blown indirect heated biomass gasification needs the use of two reactors, one for combustion and one for gasification, and the recirculation of the bed material to maintain the temperature level required by the gasification process. This kind of gasifier[17] produces a nitrogen-free gas with an high calorific value and a high content of hydrogen, but also with a high content of TAR and particulate. TAR are an undesirable and noxious by-product [12], whose yield can be reduced controlling the operating conditions, using an appropriate reactor design and a suitable gas conditioning system [18–20]. For this reason gasification is generally followed by a gas cleaning step, that can be done by different processes as a function of the end use of the syngas. The gas cleaning processes can be filtration, scrubbing, reforming and cracking. Among hot gas conditioning methods, catalytic cracking and steam reforming of TAR offer several advantages, such as thermal integration with gasification reactor, high TAR conversion and hydrogen rich syngas production. Among these there are different catalyser (dolomite, olivine, etc.) and the catalytic filter candles. Catalytic filter candles could be integrated directly in the freeboard of the fluidized bed reactor. This is the UNIQUE concept [21], consisting in a compact gasifier design integrating into a single reactor vessel both the fluidized bed steam gasification of biomass and the hot gas cleaning system, made of sorbents in the bed inventory to capture detrimental trace elements and a bundle of ceramic filter candles operating at high temperature in the gasifier freeboard. Such configuration produces a syngas free of TARs and Sulphur compounds and allows a remarkable plant simplification and reduction of costs [21–23].The coupling of UNIQUE technology with WGS and PSA aim at H_2 separation from residual gases, reaching a high hydrogen conversion efficiency. Generally WGS takes place in adiabatic converters where the effluent from the reformer system is converted in two steps with the second at lower temperature in order to shift the equilibrium towards the hydrogen production. The hydrogen rich gas at the outlet of WGS could be cooled down at ambient temperature to remove condensable and then compressed at relatively low pressure to feed PSA, obtaining pure hydrogen.

2 Materials and methods

The present paper deals with a specific plant configuration, based on the integration of a 100 kWth steam fluidized bed gasifier with HT and LT-WGSR and PSA to produce pure hydrogen. The gasifier is based on the UNIQUE concept and can operate at high temperature (750-850 °C). The analysis is based on a gasifier model that was developed by some of the authors in an earlier work[24] and then improved in a subsequent work[25] and validated for steam gasification[26]. In the latter work an enriched air gasifier was simulated and, thus, also the combustion reactions with oxygen were considered, differently from the model developed here which is used to simulate gasification only with steam.
The proposed gasification model was based on the following reactions, solved simultaneously:

$$C+H_2O \rightarrow CO+H_2 \qquad \text{R1}$$
$$C+CO_2 \rightarrow 2CO \qquad \text{R2}$$
$$C+2H_2 \rightarrow CH_4 \qquad \text{R3}$$
$$CH_4+H_2O \leftrightarrow CO+3H_2 \qquad \text{R4}$$
$$CO+H_2O \leftrightarrow CO_2+H_2 \qquad \text{R5}$$
$$C_6H_6+6H_2O \leftrightarrow 6CO+9H_2 \qquad \text{R6}$$
$$C_{10}H_8+10H_2O \leftrightarrow 10CO+14H_2 \qquad \text{R7}$$
$$C_7H_8+7H_2O \leftrightarrow 7CO+11H_2 \qquad \text{R8}$$
$$C_6H_5OH+5H_2O \leftrightarrow 6CO+8H_2 \qquad \text{R9}$$

Thermodynamic behaviour of the plant is analysed by means of the process simulator ChemCAD.
The simplified ChemCAD flowchart used for the simulations is reported in Fig. 2.

Fig. 2 - Flowchart (with thermal balance flows in red)

Biomass (stream 1) is fed into the gasification zone (Gasifier) and gasifier with steam (stream 2). The bed material, together with some charcoal (stream 3), circulates to the combustion zone (Burner Gas). This zone is fluidized with hot air (stream 4) and the charcoal is burned, heating the bed material to a temperature that is higher than the entrance one. The hot bed material from the combustor is circulated back to the gasifier (stream 5) supplying the thermal power needed for the gasification reactions. Off gas from PSA (stream 6) is also burned in the combustion zone to supply extra heat required by the gasification process.

Catalytic filter candles (Cat Candle) convert Tars in additional syngas and remove particulate directly in the freeboard of the gasifier. Injection of extra water/steam (stream 7) cools down the clean syngas (stream 8) and provides the necessary water content for HT-WGS and LT- WGS reactors to increase the H2 concentration in the gas. The steam required for this process is generated by a Steam Generator (SG1). The gas from LT-WGS (stream 9) is mainly composed of H2, CO2, residual steam and traces of CH4 and CO. The gas (stream 9), first preheats the air (stream 10) for the dual fluidized bed gasifier, and then passes through a condenser where residual steam is removed. The dry gas (stream 11) is compressed and cooled to ambient temperature to feed the PSA where pure H2 is obtained (stream 12). The heat released by the cool down of stream 11 is used to generate extra-steam (SG2) for the gasification process (stream 13). The off gas (stream 6) is utilized in the gas burner as previously described. Finally the sensible heat of the flue gas (stream 14) from the gas burner is used to enhance pre-heating of air (stream 4) and to produce superheated steam (stream 15) for the gasifier by a steam generator (SG3).

Finally focusing on the hydrogen production, a sensitivity study was carried out setting three parameters:

- steam to biomass ratio: 0.5 and 2;
- separation efficiency of the PSA: 80%;
- gasifier operating temperature: 750 and 850°C.

In the simulations biomass input flow have been fixed at 20 kg/h (100 kWth) and the moisture content at 20%.

During the simulation the following main assumptions have been done:

1.   The temperature difference between the gasifier and the combustor is set at 50 °C[27].

2.   The inlet temperature at the HT-WGS and LT-WGS are set to 400 °C and 200 °C, respectively.

3.   The candle filters and the WGS reactors were considered at thermodynamic equilibrium because they are catalytic reactors.

The hydrogen chemical efficiency has been calculated by the following equation:

$$\eta = \left(\frac{\dot{Q}_{H2} * LHV_{H2} * PM}{\dot{m}_{bio,daf} * LHV_{bio,daf}} \right)$$

Where $\dot{Q}$ is the volumetric hydrogen flow produced by the plant and $\dot{m}_{bio,daf}$ is the mass flow rate of biomass dry and ash free feeding the plant.

3 Results and discussion

The simulations show how the results depend on the steam to biomass ratio and the gasification temperature.

In Figure 1 is shown the chemical efficiency as a function of temperature and steam to biomass ratio at the output of the catalytic filter candle, because these are

inside the freeboard of the gasifier. As shown the chemical efficiency increases with the S/B and also with the temperature, reaching its maximum value of about 87% at 850°C and S/B=2. It is known from the literature [28–30] that the hydrogen yield increases with the gasification temperature and with the steam to biomass ratio. Is important to notice that these values are rather high because into the candles the methane steam reforming, tar steam reforming and the water gas shift reactions occur [31,32].Indeed as shown in Table 2, the methane at the output of the catalytic filter candles decreases at 850°C, and the temperature is reduced, because into the candles the endothermic reforming reactions occur. The carbon monoxide concentration increases even if less respect to the methane reacted, this because into the candles the water gas shift reaction also occurs.
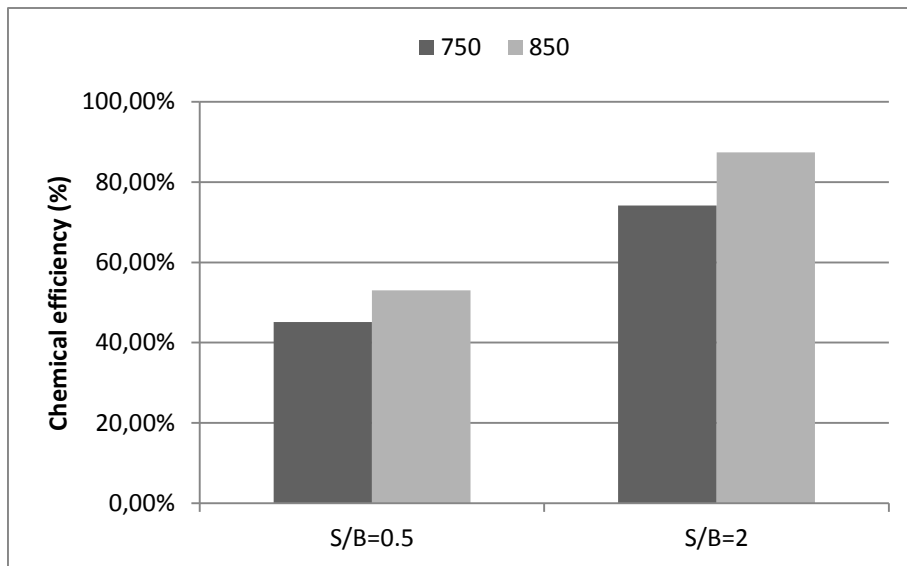
Figure 1 Hydrogen chemical efficiency at the output of the catalytic filter candle

TAR concentrations are not reported on Table 2, because they are totally reformed in each simulation.

T=750°C		
	S/B	
(mol/h)	0.5	2
CH4 out candle	123.23	58.17
CO out candle	226.74	90.67
CO2 out candle	245.63	462.54
Toutcand	612	559

T=850°C	S/B	
(mol/h)	0.5	2
CH4 out candle	80.98	12.91
CO out candle	323.82	183.75
CO2 out candle	220.54	479.64
Toutcand	650	634

In these simulations water has been added in the first water gas shift reactor in different concentrations in order to maximize the chemical efficiency. In Figure 2 it can be notice that at the output of the WGS reactors, the chemical efficiency at 850°C and S/B=2 from the value of 87% has reached 99%.
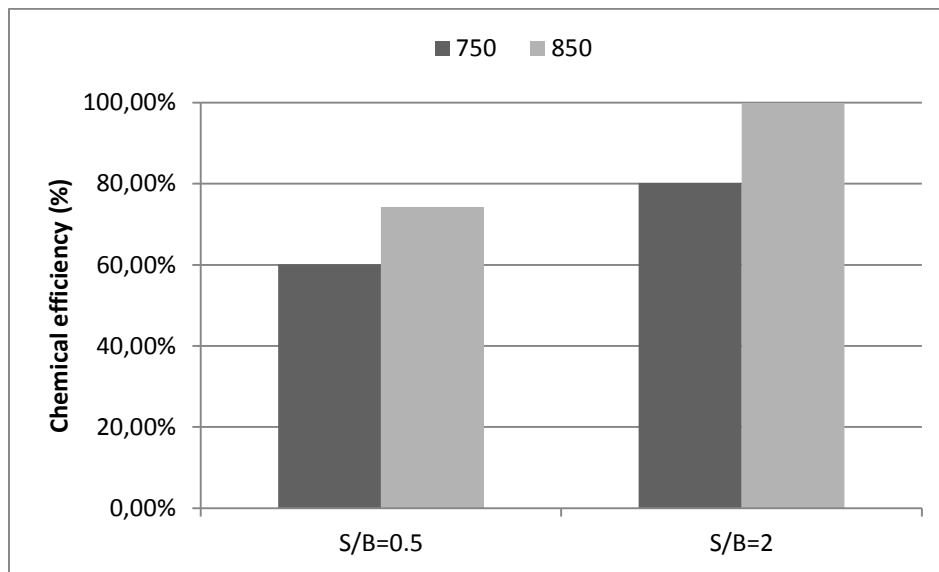

Figure 2 Chemical efficiency at the output of the WGS reactors

In Figure 3 is reported the chemical efficiency at the output of the whole plant after the PSA, in which the separation efficiency has been set at 80% and the pressure at 9 bar. Chemical efficiency increases with temperature and steam to biomass ratio because there is more steam that can react in the different reactions, producing more hydrogen. The maximum value has been reached for S/B=2 and T=850°C maintaining the trend seen above.
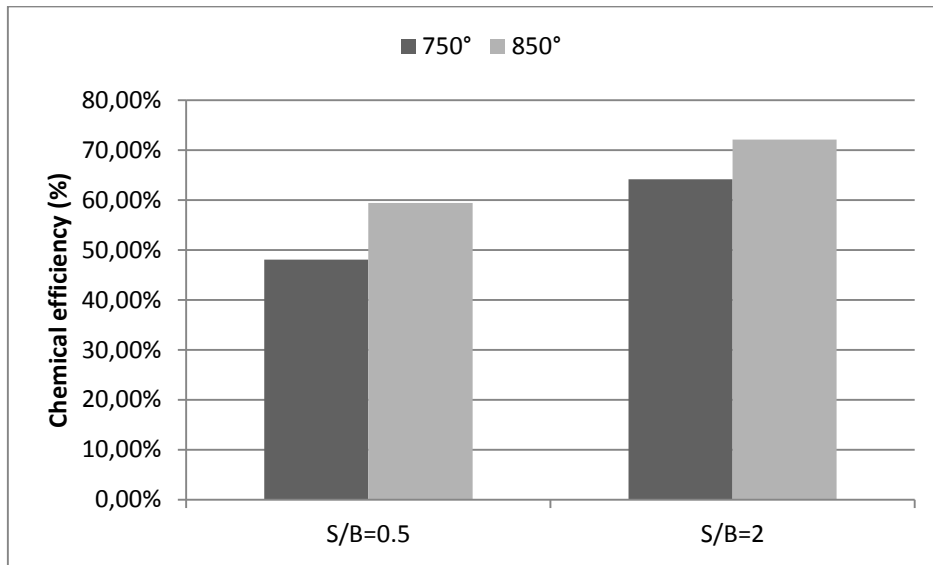
Figure 3 Chemical efficiency of the whole plant

The off gas that is used to maintain the set temperature is not always totally recirculated except in the case of S/B=2 and T=850°C in which 100% of the off gas has been recirculated and also an auxiliary fuel has been added from the outside. This auxiliary fuel is methane in concentration of 0.76 Kg/h.

4 Conclusions

In this study, simulations of a double bubbling fluidized bed gasifier with catalytic filter candles, WGS reactors and PSA have been carried out. The results show that methane steam reforming, tar steam reforming reactions and the water gas shift reaction occur in the catalytic filters candles. In the WGS reactors, the system efficiency has been always optimized by adding water as a function of gasification temperature and steam to biomass ratio. In this way, the trend of hydrogen chemical efficiency is similar to that at the output of the candles. Considering the whole plant, hydrogen chemical efficiency always increases with temperature and steam to biomass ratio.

The simulation results show that to increase the hydrogen yield the optimal operating conditions should be characterized by high gasification temperature, high steam to biomass ratio and operation of the water gas shift reactors with an excess of steam. In particular in these simulations the best conditions have been reached at 850°C with a steam to biomass ratio of 2 obtaining a chemical efficiency of about 72%. In this case however it is necessary to add auxiliary fuel by the outside to maintain in temperature the process. For this reason the best operating condition can be considered the test with S/B=2 at 750°C, in which the chemical efficiency is about 64%.

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