

An integrated process for hydrogen production from solid fuel gasification

¹**E. Biagini**, ¹**D. Brumini**, ¹**L. Masoni**, ²**L. Tognotti**

D. Energia Ambiente, Consorzio Pisa Ricerche, lungarno Mediceo 40, Pisa

D. Ingegneria Chimica, Università di Pisa, via Diotisalvi 2, Pisa - ITALY

e.biagini@cpr.it

INTRODUCTION

Biomass fuels represent a renewable energy source and can be considered as CO₂-neutral fuels, giving no contribution to the CO₂ level in the atmosphere when used to produce energy. This is especially the case of materials from energy crops with optimized harvesting cycles, e.g., poplar and miscanthus, as well as residues from agricultural and food industry, e.g., olive cake and pruning from vines. Tuscany, where this study is conceived, offers a variety of these biomasses and the intrinsic problem of the desultory availability of these fuels can be overcome by a programmed collection.

Further advantages of biomasses with respect to fossil fuels are the low content in sulfur and heavy metals with consequent lower emissions in combustion processes. As a matter of fact many drawbacks limit the use of these fuels, e.g., the low heating value (also diminished if considering the relatively high moisture content) and the fouling/slugging phenomena (due to tar formation and alkali compound deposition), which reduce the heat transfer and the energetic efficiency.

Most of these issues can be overcome in the gasification process, which transforms a solid fuel into a syngas (used as gas fuel or converted into chemicals, e.g., methanol or hydrogen). The process is more versatile as for fuel input and product output than combustion. If air is used as the gasifying agent, the syngas has a low heating value and conversion processes can be hardly applied. Pure oxygen should be used in the gasifier to produce a syngas without the nitrogen contained in the air and, thus, with a higher heating value (increasing the efficiency of the following combustion step) and indicated for production of chemicals. In particular, hydrogen is a valuable energy carrier giving no pollutant (including CO₂) emissions in distributed utilizations, e.g., vehicles and residential uses. Steam can be also added in the gasifier to increase the hydrogen yield. Moreover, the CCS (Carbon Capture and Sequestration) option can be considered in the gasification plant to eliminate the emissions of CO₂ in the atmosphere.

Gasification with oxygen is generally operated using coal and large plants, which justify the cost of the air separation unit. For biomass fuels, relatively small plants (100-500 kg/h of biomass) can be considered to avoid the economic penalty due to large distance transportation. On this scale, cryogenic air separation is not suitable and the economic feasibility of other solutions (e.g., storage of liquid oxygen) is arguable.

In this work, an integrated process for hydrogen production from the gasification of biomass fuels is studied. The idea is to associate two systems of hydrogen production of different purity and, thus, different uses. The first system, based on the electrolysis of water, produces high purity hydrogen for fuel cell applications. The second is based on the gasification of biomass fuels, using the oxygen produced in the previous system for producing hydrogen of a relatively lower purity for internal combustion engines. These applications are the scenarios of the project "Filiera Idrogeno" funded by Regione Toscana.

The study is on the technical feasibility of the integrated process, for quantifying the

energetic needs and the efficiency in different conditions and different configurations. A process model is developed with detailed descriptions of main units (syngas treatment and separation) to evaluate the size of the equipment (e.g., amount of catalyst in the water gas shift reactors and the area of membranes for hydrogen separation).

Different solutions are also considered as for the energy source of electricity production in the electrolysis plant: wind, geothermy and the same gasification/combustion scheme from biomass (as in the attached scheme). All these sources are available in the studied area.

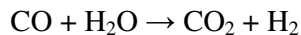
DESCRIPTION OF THE PROCESS

The entire process (Figure 1) is set to produce two streams of hydrogen with different purity: electrolysis way is used for producing hydrogen at high purity (for utilization in fuel cells) and gasification way for hydrogen at medium purity (for utilization in combustion systems). In this latter case, the separation of hydrogen (and then its purity) depends on the technological level considered (PSA or membranes), with an efficiency which can be supposed to increase in time. At present, a 99% pure hydrogen is supposed to be obtained. Also the scale of the plant can influence this parameter, advanced solutions being more conceivable in larger plants.

The gasifier adopted is a fixed bed downdraft reactor, operating under atmospheric pressure and handling relatively large particles of biomass (1-5 cm). Peak temperature of 1000-1200 °C are expected along the reactor, when air is used. In this case, oxygen (from the electrolysis unit) is fed so that steam should be added to limit the temperature inside the reactor.

The syngas produced is cleaned (from dust, tar and acid compounds) in a scrubber with a basic solution when a relatively clean biomass is used. Residues or grasses need a more onerous system (with recirculation of specific solvents) for purifying the syngas. In all cases, the syngas is assumed to leave this unit at a temperature of 40 °C and completely wet.

An engine is used to burn the syngas and produce electricity. Alternatively, the syngas is converted to hydrogen in the water gas shift reaction (WGSR) and separation units. The WGSR unit is formed by two catalytic reactors. The reaction is:



which is an equilibrium reaction, so steam is added to promote hydrogen production. The reaction is exothermic and an opportune heat recovery allows to get the inlet temperature of 350 °C in the first reactor (with Fe/Cr as catalyst) and 200 °C in the second one (with Cu/Zn as catalyst). These temperatures maximize the CO conversion.

Metallic (Pd) membranes are used to separate hydrogen. The syngas must be compressed and temperature close to 200 °C maintained for assuring a high efficiency of separation. Although this technology is at a developing level, it is considered here to study an innovative solution (with respect to conventional PSA units). The unpermeate contains some residual H₂, CO and CH₄ which can be burned. The exhaust gases contain mainly H₂O and CO₂. This latter can be sequestered after condensation.

Two configurations of the plant are compared, depending on the solution adopted to provide the steam necessary to the process (mainly the streams fed to the gasifier and the WGSR unit). In both cases, the entire process should be self-sufficient. In the first configuration (CONF1) the steam is produced subtracting heat from the cooling jacket of the gasifier. Considering the size of the reactor, more than 100 kWth can be recovered, even though important variations on the thermal profile inside the reactor should be expected.

In the second configuration (CONF2), the gasifier is not cooled but is assumed adiabatic (some dispersion are actually considered). The needs of steam are satisfied by an evaporator

burning the unpermeate stream at the end of the gasification process. This gas generally has a heating value high enough to produce the steam required. The comparison of these two configurations allows to assess the importance of the heat balance in the gasifier, and the differences reported in the results section will motivate the choice of a detailed model of the gasifier (described in the next section).

As for the electrolysis unit, a commercial alkaline electrolyzer is used. It is fed with water and an electrolyte, consumes electricity from the local electrical network and produces high purity hydrogen and oxygen which are separated and stocked. The electrolyzer is formed of several interconnected units to provide the amount of products needed. The outlet pressure is 3.8 atm.

Wind, geothermy and the same gasification/combustion scheme from biomass are the sources of electricity, directly conferred to the electrical network.

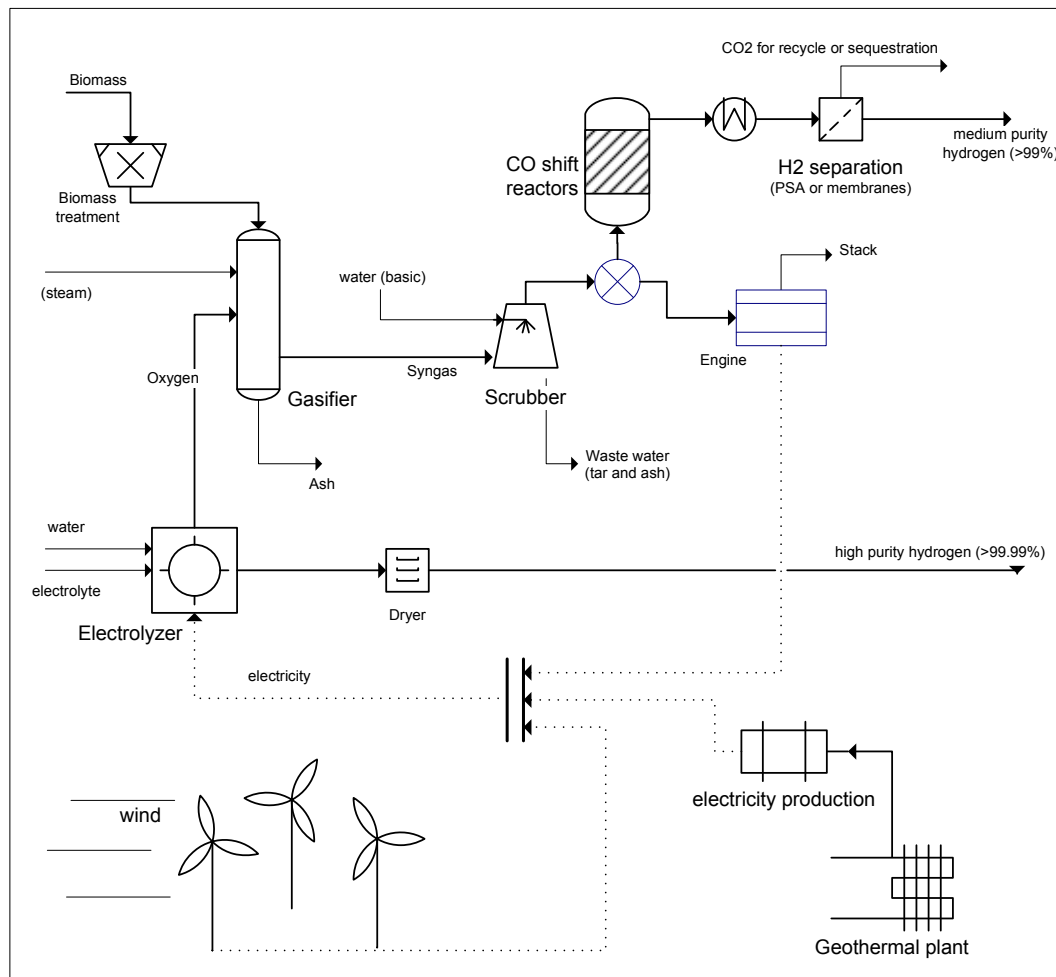


Figure 1. Scheme of the integrated process for hydrogen production

DEVELOPMENT OF THE PROCESS MODEL

The entire process is modeled in AspenPlus®, which is a commercial software for flowsheeting. Conventional blocks are adapted or dedicated sub-models implemented in the main code for each unit. The gasification unit is the most peculiar unit of the process because a detailed model is developed instead of an equilibrium reactor. This latter solution is usually adopted in many literature works but is hardly suitable for optimization procedure. The

choice of a detailed model instead of an equilibrium reactor is due to the following points:

- the thermal profile in the equilibrium reactor can be isothermal or adiabatic, so that heat recovery (for steam production) can not be modeled, while this contribution may be crucial for the global efficiency of the process; a detailed heat balance should be used, also for linking the operating parameters (fuel, oxygen and steam flow rates) to the reactor temperature;
- sub-products (CO₂, CH₄, hydrocarbons) are generally under estimated, as well as residual char and tar which give a loss in the global efficiency, while their quantification allows also to assess the syngas treatment units;
- different reactor configurations (downdraft, updraft, fluidized bed) can not be compared if every reactor is modeled as an equilibrium reactor.

Details of the gasifier model are given in the following sub-section. The other units are adapted from conventional blocks of AspenPlus®:

- the scrubber is modeled as an absorption column (RadFrac)
- the catalytic beds are modeled as plug flow (RPlug) reactors with kinetics from literature works [Keiski 1993] in the appropriate range of temperature.

A specific block is developed for the membranes by programming a multi-tube metal membrane customized library. Its User Subroutine considers a tube configuration for the membrane and the consequent variation of hydrogen partial pressure along it. The H₂ flux equation through the membrane that is considered is:

$$J_{H_2} = \phi_{H_2} (P_{H_{2,h}}^n - P_{H_{2,l}}^n)$$

where:

- J_{H₂} [Nm³/m²·hr] hydrogen flux;
- ϕ_{H_2} [Nm³/m²·hr·bar^{0.5}] hydrogen permeability;
- P_{H_{2,h}} [bar] hydrogen partial pressure in the feed side;
- P_{H_{2,l}} [bar] hydrogen partial pressure in the permeate side;
- n=0.5 .

The term ϕ_{H_2} is derived from the properties of the commercial Pd-based membrane produced by ATI Wah Chang.

Development of the gasifier model

A previously developed procedure for gasifier models is applied to a downdraft reactor, by adapting hypothesis and kinetics. The functional scheme of the reactor is composed by the main blocks, represented by sub-models, described in the following sub-sections. Conventional blocks of AspenPlus® or dedicated models, opportunely implemented in the main code of the gasifier model, are adopted. Each block is linked to the others (and in case, with other parts of the entire plant of hydrogen production) by material and heat streams. A combustion unit is modeled for the partial oxidation of the fuel or the syngas to provide the heat to the reactor. The reactor walls are used to recover heat for steam production. All heat streams are linked to find the reaction temperature by the iterative solution of the heat balance. The heat balance is formed by different terms: pre-heating (of fuel, air or oxygen, steam and nitrogen, for fuel transportation), reaction (devolatilization, combustion and

gasification) and heat recovery (for steam production). The heat balance is solved with a *Design Specification* that varies the reaction temperature to get zero dispersion of the entire system.

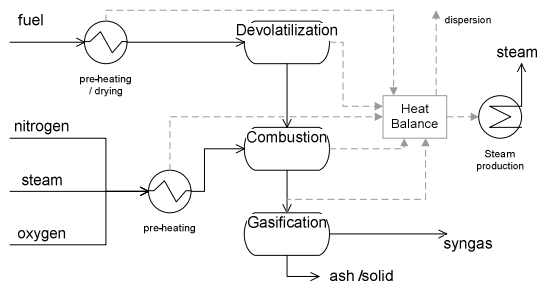


Figure 2. Functional scheme of the downdraft gasifier.

Devolatilization sub-model

After the pre-heating, the stream of the fuel enters the devolatilization sub-model. A thermal decomposition is modeled giving a solid residue (char), a condensable organic product (tar, here modeled as levoglucosane) and the main gaseous species (CO, CO₂, CH₄, H₂O, H₂, C₂H₂, N₂, NH₃, HCN, H₂S, COS). No conventional AspenPlus® block can represent this step. Therefore, the structural model ABCD (Advanced Biomass and Coal Devolatilization model) is used for the devolatilization in the form adapted by our group in previous works (Falcitelli et al. 2009). This model gives the yield of macro-products and the speciation of gases once the fuel composition and the operating conditions are known. The ABCD code can be hardly implemented in AspenPlus® because of the expensive computational cost. Therefore, a *User Routine* for the devolatilization step is developed, consisting of a database and a calculation function. The former is created with the results of off-line simulations of the ABCD model in a wide range of pressures and temperatures. The calculation function dialogues with the main AspenPlus® model by receiving the actual values of temperature and pressure, interpolating the results of the database and returning the balanced products.

Combustion sub-model

The combustion sub-model is represented as a *Plug-Flow Reactor*. Combustion reactions are modelled by assuming a first order kinetic model with parameters adapted from literature (Westbrook 1981). An isothermal configuration is adopted for this step.

Gasification sub-model

The gasification sub-model consists of a *Plug-Flow Reactor*. Homogeneous reactions are modelled by assuming a first order kinetic model, while the unreacted core-shrinking model of char gasification was actually adapted from Wen (1979). An adiabatic configuration is adopted for this step.

Table 1. Reaction sets used in the sub-model development

Combustion reactions	Gasification reactions
volatile combustion $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	char gasification $C(\text{char}) + H_2O \rightarrow CO + H_2$
$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$C(\text{char}) + CO_2 \rightarrow 2CO$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$C(\text{char}) + 2H_2 \rightarrow CH_4$
$C_2H_2 + 5/2 O_2 \rightarrow 2CO_2 + H_2O$	
char oxidation $C(\text{char}) + \frac{1}{2} O_2 \rightarrow CO$	methane reforming $CH_4 + H_2O \rightarrow CO + 3H_2$
	water gas shift $CO + H_2O \rightarrow CO_2 + H_2$

RESULTS AND DISCUSSION

A poplar wood (moisture 20.0, volatile matter 68.1, fixed carbon 10.4, ash 1.5 wt% on a as received basis; C 50.7, H 6.35, N 0.25, Cl 0.012, S 0.05 wt% on a dry basis) is used and its flow rate is maintained constant (250 kg/h) in all simulations, while variations of biomass and plant size will be studied in future works along with economical evaluations.

The results focus on the effects of the gasification conditions on the hydrogen production and process efficiency. The plant configurations described above are compared to evaluate the importance of heat recovery on the hydrogen production. Two ratios of the operating parameters are defined to compare different cases:

rO/C is the ratio (kg/kg) of the oxygen fed to the gasifier on the amount of C globally contained in the fuel;

rSt/C is the ratio (kg/kg) of the steam needs on the amount of C globally contained in the fuel.

The operating parameters are varied in wide ranges to study the optimal conditions. The efficiencies are defined as:

$$\eta_G = \frac{W_{H2,G} HV_{H2}}{W_{Biom} HV_{Biom}} \quad \text{net hydrogen efficiency of the gasifier}$$

$$\eta_P = \frac{W_{H2,P} HV_{H2}}{W_{Biom} HV_{Biom}} \quad \text{net hydrogen efficiency of the gasification process}$$

where W indicates the flow rate (kg/s) of hydrogen produced after the gasifier (subscript H2,G), at the exit of the gasification plant (H2,P), at the exit of the electrolysis plant (H2,E), or the flow rate of biomass (Biom); HV indicates the heating value of hydrogen or dry biomass.

Also, the needs of power in the process P_O (e.g., the power required by the compressors in the separation unit, the pumps and utilities) are quantified, as well as the electric power input to the electrolysis plant P_E.

The hypothesis and constraints of the plant are listed in Table 2.

Table 2. Hypothesis and reference conditions of the process

O2 purity from electrolysis plant	99.99	%mol
H2 purity from electrolysis plant	99.99	%mol
Electricity consumption of the electrolysis units	5.0	kWh/Nm ³ of H ₂
Outlet pressure of electrolysis plant	3.8	atm
Gasifier pressure	1	atm
Biomass flowrate	250	kg/h
Nitrogen feed/fuel	0.05	wt/wt
Maximum temperature in the gasifier	1000-1200	°C
Steam produced in the gasification plant	3	bar
Syngas temperature after scrubber	40	°C
H2O/CO inlet shift section	3	mol/mol
Syngas temperature inlet 1st WGS	350-400	°C
Syngas temperature inlet 2nd WGS	180-220	°C
Syngas temperature inlet membranes	200	°C
Syngas pressure inlet membranes	25	bar
Syngas pressure permeate membranes	1	atm

The first results are on the gasifier efficiency and the optimization of the operating conditions (mainly the ratio between fuel, oxygen and steam). The fuel flow rate is maintained constant for all simulations, while oxygen and steam flow rates are varied to guarantee a maximum temperature of the gasifier in the range 1000-1200 °C. This temperature is a constraint for the plant because of the refractory limitations. Three maximum temperatures are studied and the results of Figures 3 and 4 show the dependency of the oxygen and steam ratios and the efficiency obtained in configuration 1 and 2, respectively. In general, at fixed temperature, the higher the oxygen flow rate, the higher the steam flow rate required.

A higher flow rate of oxygen is required for configuration 1 (with rO/C in the range 0.84-0.94) than that required for configuration 2 (rO/C 0.59-0.69), with comparable flow rates of steam. The higher oxygen required is used to get a higher extent of the oxidation reactions in the gasifier. The generated heat is absorbed by the cooling jacket to produce steam at 3 bar (used in the plant). Correspondingly lower gasifier efficiencies can be observed in the graph of Figure 3 respect with those in Figure 4: 20-24% for configuration 1 and 25-30% for configuration 2, respectively. This is due the consumption of hydrogen produced (and other gasification products) for oxidation to generate heat.

The gasifier efficiencies of both configurations are directly compared in Figure 5, as function of the maximum temperature achieved in the gasifier and at different oxygen flow rates. It is worth reminding that in this graph also steam is varied (according to values reported in Figures 3 and 4) to limit the gasifier temperature. A maximum gasifier efficiency can be observed in this graph and this depends on the temperature (which favors the kinetics of reactions), the concentration of steam (promoting the gasification reactions and decreasing the temperature) and oxygen (promoting the oxidation reactions and increasing the temperature).

As a matter of fact, the syngas produced in the gasifier contains also CO which can be further converted to H₂ (in the water gas shift reaction unit). This section is a conventional system of two catalytic beds, which are optimized to globally convert more than 95% of the CO in the syngas. The optimal conditions are obtained varying the temperatures at the reactor inlet (obtained with appropriate heat recovery). Also steam is added at the first reactor to promote the conversion. A temperature of 350-375 °C at the first reactor allows a partial conversion of 70-75%, which is completed in the second reactor at an inlet temperature of 200 °C.

Also, the membrane unit is optimized and the conditions set to limit the hydrogen loss in the unpermeate stream. In all cases, 5-10% of hydrogen entering the separation unit is lost and can be burned (along with residual CO and CH₄) to produce steam in configuration 2. In both cases, this stream is burned and the exhaust gases (containing CO₂ and H₂O) can be used for heat recovery and condensate to sequestrate the CO₂.

The gasification plant efficiency is then reported as function of the gasifier conditions (the parameters for WGSR and membrane units being optimized in each case). The results are reported in Figures 6 and 7 for configurations 1 and 2, respectively. A maximum efficiency of 37% can be observed for configuration 1 at the highest temperature of 1200 °C. Higher values are obtained for configuration 2: 46% at the highest temperature studied. In general, at fixed oxygen flow rate, the higher the temperature, the higher the plant efficiency. At fixed temperature, a maximum efficiency can be achieved by varying the ratios of fuel, oxygen and steam. For instance, at 1100 °C the maximum efficiency of 0.64 is obtained for rO/C of 0.64 and rSt/C of 1.7 for configuration 2. It is worth noting that the rSt/C of the plant is the sum of steam fed to the gasifier and that added at the WGSR unit.

Finally, the performance of the entire system (gasification plant and electrolysis units) is evaluated. The production of hydrogen from both plants, the consumption of electricity in the gasification plant (for the compressors of syngas in the separation unit) and in the electrolysis units are quantified for all cases. These data will be the basis for further analysis (for energetic and cost demand of the system). An example is given in Figure 8, where the flow

rates of hydrogen of different purity is reported as function of the overall electricity needs (expressed as the sum of electricity consumption in the electrolysis units to give hydrogen of high purity and that in the separation unit to give hydrogen of medium purity). The analysis is performed by varying the oxygen produced in the electrolysis units and fed to the gasification plant and, thus, assuming that all oxygen is consumed. Consequently, the high purity hydrogen produced increases linearly with the electricity needs. The medium purity hydrogen exhibits a maximum which can be considered the optimal conditions of this case. Although reported in the graph of Figure 8, oxygen and steam consumptions are internal recycles of the system and do not require any input from external sources.

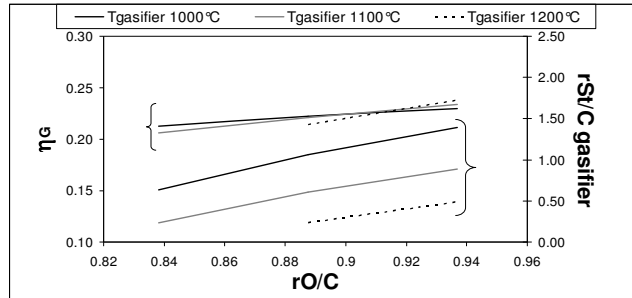


Figure 3. Gasifier efficiency and operating conditions at different temperatures (CONF1)

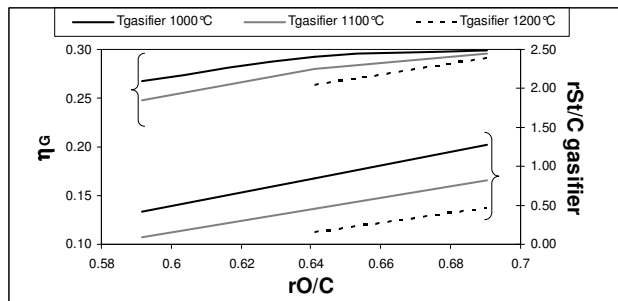


Figure 4. Gasifier efficiency and operating conditions at different temperatures (CONF2)

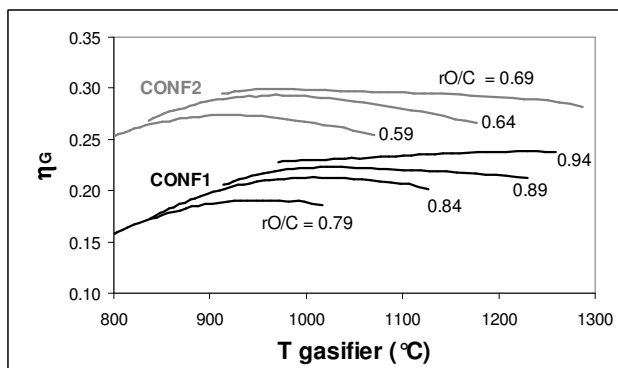


Figure 5. Comparison of the gasifier efficiency as function of the gasifier temperature and different cases of rO/C for both configurations.

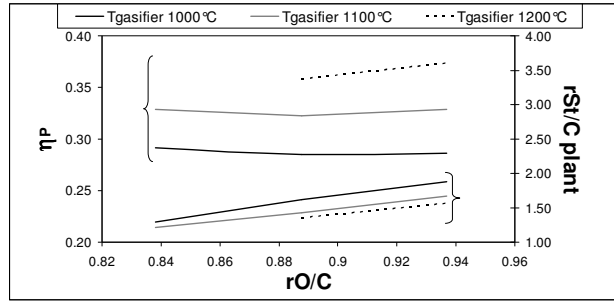


Figure 6. Plant efficiency and operating conditions at different temperatures (CONF1)

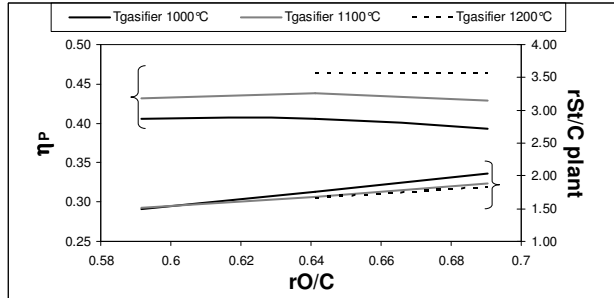
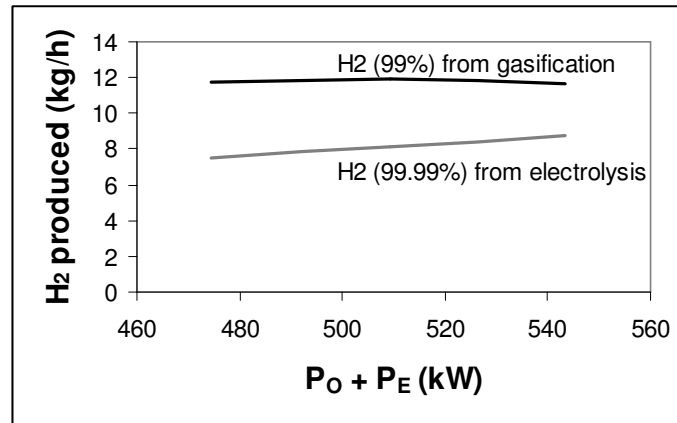


Figure 7. Plant efficiency and operating conditions at different temperatures (CONF2)



Electricity Electrolysis kW	Electricity Gasification kW	Oxygen consumed kg/h	Steam consumed kg/h	Hydrogen Electrolysis kg/h	Hydrogen Gasification kg/h
420	54.4	60	153.5	7.50	11.75
455	54.5	65	170.5	8.13	11.93
490	53.5	70	191.0	8.75	11.67

Figure 8. Hydrogen production from the entire system as function of the electricity consumption (Configuration 1, T gasifier 1100°C, biomass flow rate 250 kg/h).

CONCLUSIONS

- Hydrogen is a clean and valuable energy carrier which can be used successfully in distributed utilizations. Its production from renewable sources needs process studies for evaluating the technical and economical feasibility.
- An integrated process for biomass gasification is studied: two plant configurations are evaluated by modeling its units and interconnecting them. The detailed approach we

used for developing the process model allows to evaluate the suitability of the equipment and the feasibility of the process.

- The equipment of the plant is designed and preliminary optimization studies are conducted, focusing on oxygen and steam internal consumptions.
- A relatively small scale plant (250 kg/hr) fed with poplar wood is used in all simulations: variations of biomass and plant size will be studied in future works along with further optimization and economical evaluations.

REFERENCES

- ATI Wah Chang Allegheny Technologies – www.alleghenystechnologies.com , www.wahchang.com
Keiski, R.L., Desponds, O., Chang, Y.-F., Somorjai, G.A. 1993. Applied Catalysis A: General, 101, 317-338.
Ni, Q.; Williams, A. 1995. Fuel, 74, 102-110
Vizzini, G.; Bardi, A.; Biagini, E.; Falcitelli, M.; Tognotti, L. 2008. 31st Combustion Meeting of the Italian Section. Torino, 17-20 June, 2008.
Wen, C.Y.; Chaung, T.Z. 1979. Ind. Eng. Chem. Process Des., 18, 684.
Westbrook, C.K.; Dryer, F.L. 1981. Comb. Sci. Tech., 27, 31.
Xu, X.; Xiao, Y.; Qiao, C. 2007. Energy and Fuels, 21, 1688-1694.