

# Energy Production from biomass gasification by molten carbonate fuel cells: process simulation

Maurizio Fermeglia, Giulio De Simon, Giulio Donolo  
DICAMP, University of Trieste, Piazzale Europa 1, 34127 Trieste, Italy  
Dip. di ingegneria meccanica, Univ. of Trieste, Piazzale Europa 1, 34127 Trieste, Italy

This paper presents an integrated approach to the steady state simulation of biomass gasification, fuel cells and power generation processes. Attention was devoted to Molten Carbonate Fuel Cells (MCFC) due to the relative low cost, simpler construction and flexibility in the use of fuel. A steady state model simulating a global (MCFC) power plant is based on real plants data and the simulations are selected according to real operating conditions. The computer simulation is finally applied to a feasibility study of a MCFC coupled with a biomass gasification process.

The paper reports results of computer simulation for a realistic configuration of power generation system by MCFC, focusing on macroscopic quantities of interest such as stack efficiency, global process electrical efficiency, cogenerative efficiency.

The software developed allows to study 'in silico' the effect of variations of the process conditions as well as modification of the input fuel, thus providing a useful tool for supporting technical decisions and feasibility study on the use of fuel cells in developing countries.

**Keywords:** molten carbonate fuel cells, computer simulation, biomass gasification.

## 1. Introduction

Deregulation of the electric power industry and more stringent emission controls are stimulating investments into fuel-cell systems, which are virtually free from noxious emissions of nitrogen oxides normally associated with burning fossil fuels. They can convert chemical energy directly into electricity with greater efficiency than most other devices, thus conserving fuel resources and reducing CO<sub>2</sub> emissions.

The application of fuel cells is particularly attractive in the renewable energy arena: biomass could be used as fuel for the hydrogen production, thus addressing the problems of generation of carbon dioxide at the same time. This topic is also of interest to developing countries for off-grid power generation with low impact to the environment. It is therefore important to be able to make feasibility study and decide if a given process is suitable to a task.

Among the different fuel cells developed so far, molten carbonate fuel cells (MCFC), also referred to as "second generation" cells (Kraaij et al., 1998), have been deeply investigated in the last decade for several advantages with respect to other technologies. MCFC's simulation may be helpful in their further development before commercialisation (Bishoff et al., 2002, Joon, 1996).

In fuel cells, and in MCFC in particular, high global efficiency, with respect to other electrical energy production systems, can be reached in merit to many contributory causes (Hart et al., 1967, Kordesh et al., 1996):

- working temperatures are sufficiently high to enhance chemical and physical processes, but not so high to lower the free energy;
- construction materials for the cells are not very expensive and no costly catalysts are needed;
- discharged heat can be used either inside the cell or transferred to down stream systems;
- carbon monoxide tolerance, a pollutant in other technologies, can be ~~burned~~processed in MCFC;
- low emissions are reached since many pollutants are not present and exhaust gases are processed and partly recycled;
- power scalability can be achieved by simple addition of compact modules, transportable by rail or road;
- low pressures are involved and voltage can be improved by increased partial pressures of reactants, keeping in mind that mechanical resistance of materials requires less than 3.5 bars operating pressure.

A molten carbonate fuel cell plant integrates a stack with a pre treatment of fuel, conditioning and post treatments of residual energy recover. The former does essentially desulphurisation and reforming, the latter makes use of steam and gas micro-turbines. Thermal control is obtained by varying both the exhaust gas recycle and the inlet temperature. The stack is made up by a number of piled up cells, and soft joints, to comply with mechanical tolerances. Figure 1 shows the general process for energy production from biomass in which the process is spitted in three parts: (i) the biomass gasification, (ii) the fuel cell stack and (iii) the cogeneration.

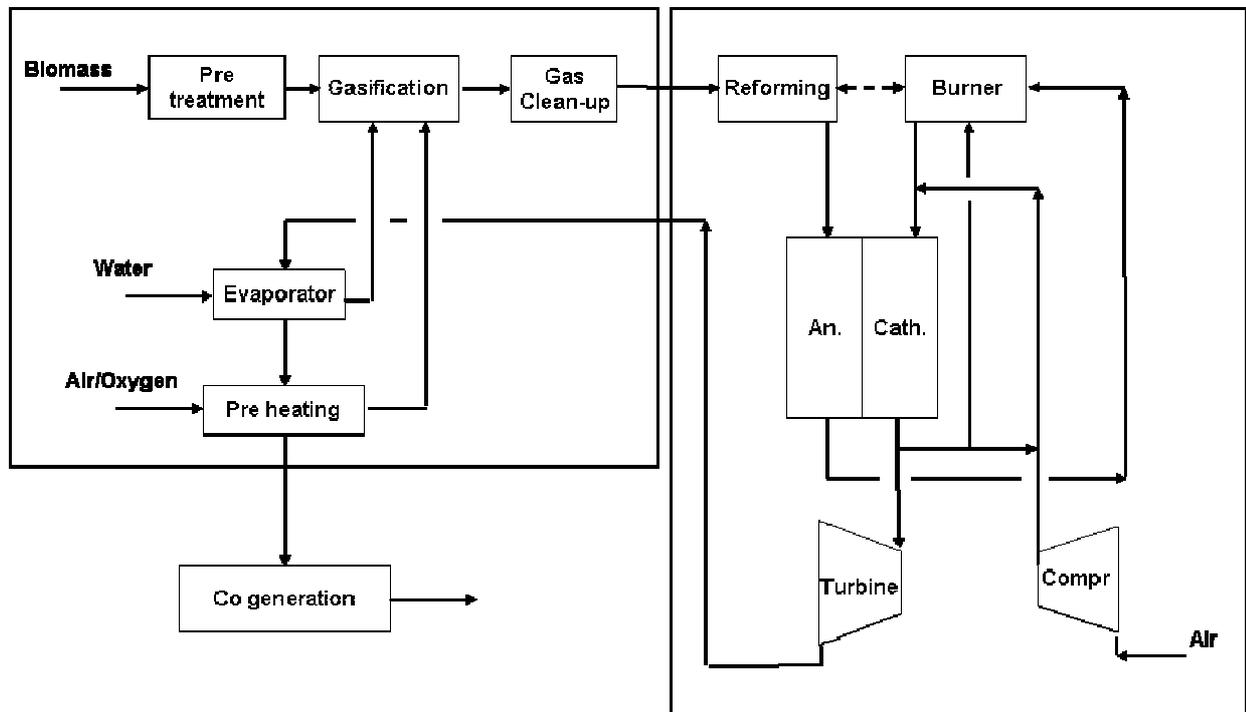


Figure 1: general schema of the process.

Natural gas has been considered the fuel for fuel cells in the development of the technology. There are many differences in the process for the feed change to biomass, due to the strong difference in the composition of the gas fed to the fuel cell. The main differences are (i) the external reforming is less important since the gas output from the gasifier contains hydrogen and carbon monoxide and only a few per cent of methane, (ii) the gas out from the gasifier needs to be cleaned from many impurities (ash, sulphur, alkaline metals and other impurities) and (iii) **more heat is produced in the gasification but at higher temperature (850-900°C), underlining the importance of a good heat integration and recovery.**

Many are the intervening parameters for defining the optimum process condition and its stability with respect to possible external perturbations. It is therefore important to simulate the process for different steady state conditions to determine the best process parameters and study the effect of process modifications with respect to efficiency and energy production.

In the past few years many authors have developed steady state models based on macro balances (Miyake et al., 1995) applied on both single cell and stack, or on differential equations (Yoshiba et al, 1998, Bosio et al., 1999, Koh et al., 2000, Arato et al., 2001, Kim et al., 2002, Park et al., 2002, Mangold et al., 2003) applied to both mean and distributed variables. An interesting review of steady state simulation of fuel cells is reported in (Koh et al., 2001). Many problems were solved in assumption of hypothesis,

in formulation of equations and in approximation of accessory devices (De Simon et al., 2003), but many others are still to be solved, as integration of the cell model in the plant and in the control strategies. Models for electrodes were developed assuming various structures for micro pores and internal meniscus (Fontes et al., 1995 and 1997, Fehribach et al., 2000) but not always such models are easily integrated in the macrostructure to be simulated.

This paper aims at presenting a steady state model for the simulation of a process that includes both the biomass gasification for the production of hydrogen and its utilization in molten carbonate fuel cells. The model is based on the exact solution of material and energy balances for all the units involved in the process and will be used for the energetic analysis of the process as a function of the biomass in the feed. The model presented in this work starts from the simulation of an Ansaldo Fuel Cell process modelled in a previous work (De Simon et al., 2003) and all the necessary modifications to adapt the model to the gasification of biomass are done.

## 2. Theory and Model Development

In comparison to other devices, fuel cells are complicated by the electrochemistry of the system. A fully distributed bi-dimensional open loop model was here implemented in a software application, to understand physical and chemical phenomena ruling MCFC. A steady state model of MCFC has developed in a previous work (De Simon et al., 2003) and has been recently extended to dynamic simulation of the single cell (Fermeglia et al., 2005). In both models, the chemical-physical fundamental equations are organized to give an easy-to-solve system which deeply integrates fluid dynamical, pressure drop, and reaction equations, thus avoiding 'off line' approach in the solution of the set of equations, but rather solving the system in an equation oriented approach. Equations are grouped together logically, but not analytically, in modules (duplicated variables are eliminated during the solution) thus allowing simple and fast modifications of the system for screening many different configurations. Chemical reactions are coupled with homogeneous and heterogeneous heat and mass transfer thus generating a system of non linear differential equations. The models account for heat transfer by convection and conduction and each solid phase is considered separately each with their own physical properties and characteristics. Furthermore the anode and cathode are modelled independently.

The input variables are velocities, temperatures and densities and the water gas shift reaction is considered at equilibrium and constrained by the continuity equation. The model is written in terms of dimensional variables and tested for a wide range of input variations: steps, linear ramps and sinusoidal ramps. è una frase restata dal modello dinamico

### 2.1 Fuel cell stack model

A molten carbonate fuel cell plant described in the introduction, and reported in figure 1, is the reference flow sheet for the development of the steady state simulation of the process. Figure 2 shows the essential geometry of the single cell as modeled in this paper. The main components of the MCFC are: (i) two metal current collectors, also active in distributing the gas streams across the electrodes surfaces; (ii) a NiO-based

porous cathode, where the reduction reaction occurs, resulting in the production of  $\text{CO}_3^{2-}$  ion, that must travel across (iii) an electrolyte tile (made up of molten K, Na and Li carbonates in a solid porous and inert matrix), and reach (iv) a Ni-based porous anode, where oxidation occurs.

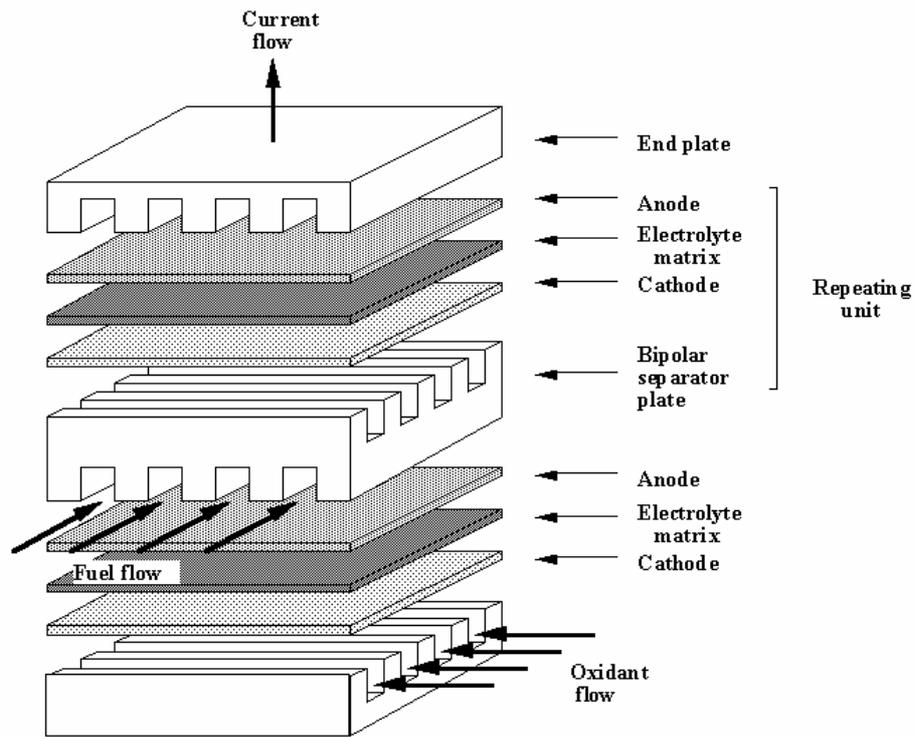


Figure 2: essential geometry of a fuel cell.

The cathode reaction is:



The anode reaction is:



The total reaction is essentially the hydrogen combustion reaction, combined with a  $\text{CO}_2$  transfer from cathode to anode:



The stack is made up by a number of piled up cells, separated by bipolar cooling plates, used to maintain a constant temperature, and soft joints, to comply with mechanical tolerances.

The steady state simulation model of the cells stack is based on the approach of Arato et al., (2001) as implemented by some of us in a previous paper (De Simon et al., 2003). The local behavior is described as a simple electrical circuit, series of an ideal voltage, determined by the Nernst equation, and an internal resistance, made up by the sum of the three contributions: (i) contact resistance ( $R_c$ ) between electrode and current collector, and electrolyte tile, (ii) Ohmic resistance ( $R_e$ ), and (iii) polarization contribution ( $R_p$ ). The first term is found to be constant, the second term is an exponential function of temperature, and the last one depends on both temperature and partial pressures of the species involved in the electrochemical reaction. All coefficients of this model are obtained by experimental data fittings (De Simon et al., 2003 and references therein).

The main assumptions considered in the model development are (i) steady state conditions; (ii) the anodic CO electrochemical reaction neglected due to its very low rate; (iii) non-limiting diffusion in macro-pores of the electrode and in gas stream; (iv) current collector as an ideal conductor (constant voltage on whole surface); (v) adiabatic conditions; (vi) water gas shift reaction considered at the equilibrium due to its high rate; (vii) ideal gas. It is important to note that diffusion phenomena occur at high reactants utilization, and reduce heavily the device efficiency. For this reason, they must be avoided by defining the cell working conditions in terms of low gas utilization. So, assumption (iii) is justified.

The model considers local temperature, pressure and composition changes along gas path in the ducts, because of reactions, heat transfer and pressure drop. To find overall cell behavior it is necessary to solve simultaneously four sets of equations: mass balance for each gas component, momentum balance for cathode and anode gas streams, energy balance, and local kinetics. The boundary conditions are input gas streams temperature, pressure and composition, and the assumption of adiabatic conditions. Physical and chemical properties are calculated from internal models available in the process simulator, or estimated from empirical equation (De Simon et al., 2003). Finite difference and relaxation methods have been employed to solve numerically the system of equations in an in-house Fortran 90 developed module.

## 2.2 Process description

The process flow diagram is show in figure 3 with an example of the process temperatures, taken directly from the simulator used in this work (Aspen+ 12.1 from Aspentech). The biomass is fed into a fluidised bed gasifier unit. From the bottom it receives a flow of steam and oxidant. The latter is air enriched in oxygen up to 95%. The use of oxidant instead of air is necessary for avoiding to dilute the producer gas with nitrogen and therefore to reduce its heating value. The solid separated in the cyclone is sent to a combustor where the unreacted char is burned and the heat produced is partially recycled into the system and partially used for cogeneration purposes.

The producer gas has a temperature about 870°C, so it has to be cooled in order to obtain a temperature suitable for the following units. It is then sent to a circulating fluidised bed tar cracker. The bed material, dolomite, acts as a catalyst for the cracking

process. The cracking reactor temperature is kept at 450°C by internal cooling with the air flow then used for the char combustion. The temperature reduction allows the alkali metals and residual uncracked tars to condense on the dolomite particles. The exiting gas is almost free of C<sub>2</sub>+ hydrocarbons and is composed primarily of CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O. Next it is further cleaned from sulphur in the desulphurisation unit and from fine entrained solid particles in the ceramic filters.

These units are not able to withstand temperature higher than 450°C, therefore the cracking low temperature is justified again, even if higher temperature gains higher tar conversion (Lopamudra et al, 2005). The gas is then heated again and sent to the reforming stage for converting part of the methane and water contained. This is accomplished in a compact reformer: it consists of a plates and frames heat exchanger with one side filled with reformer catalyst.

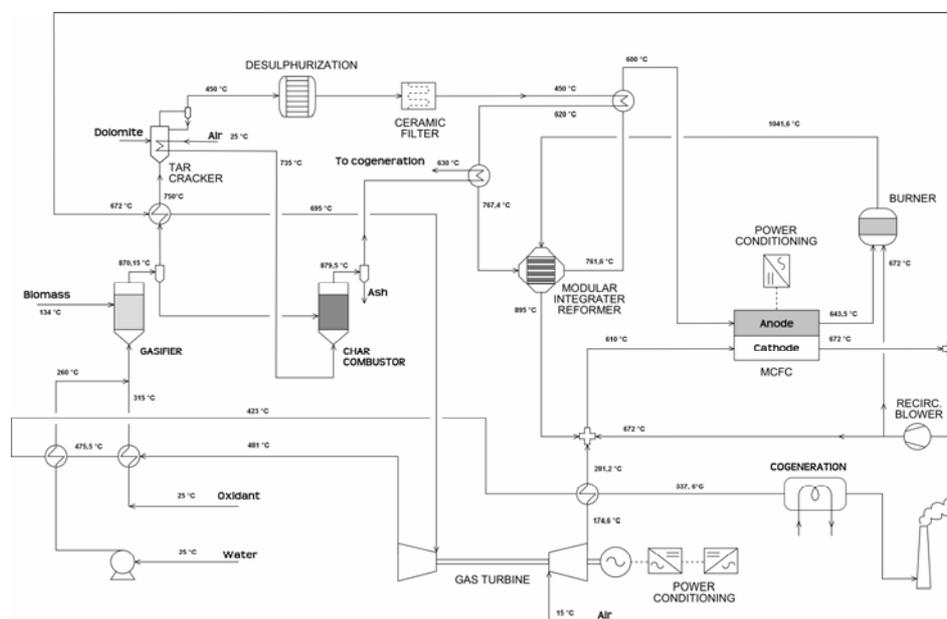


Figure 3: process flow diagram.

The heat required by the reaction is supplied by the gas flowing in the other side of the exchanger. The reformed gas is cooled down to 600°C and it's fed into the anode of the fuel cell stack where the following chemical reaction (4) and electrochemical reactions (2) take place:



Part of the fuel is not consumed in the anode to avoid diffusion controlled electrochemical reaction and because the stack is not able to process CH<sub>4</sub> (no internal reforming). Therefore it is burnt mixing it with part of the cathode exhaust recycle. The burned gas releases the heat necessary for the reformer and it is mixed with the fresh air

from the compressor and the other part of the cathode exhaust recycle before entering in the cathode. Here the other electrochemical reaction occurs (see equation (1)).

The cathode recycles (see figure 3) are needed for (i) keeping the fuel cell stack inlet temperature at about 600°C, (ii) keeping the flow at a rate suitable for the thermal management of the stack and (iii) supplying the carbon dioxide needed for the electrochemical reaction.

The exhaust not recycled gains heat exchanging with the producer gas and it's sent to the gas turbine for expansion and further power production. The flue gas heats the oxidant, evaporates the water for gasification and heats the compressed air in the regenerator. The residual heat is used for cogeneration purposes before the discharge in the stack.

### 2.3 Unit operation models

In the steady state simulation of the process, the in-house developed described above for the fuel cells stack has been introduced in a commercially available process simulator to take advantage of the available physical property calculations methods and data banks. The electricity production process around the MCFC has been modelled by using standard simulation modules. All the necessary pre-treatments, independent of process conditions, have not been considered, since they can be included in the input conditions. For the **gasifier** a simplified model was adopted. Once known as input the composition temperature of the producer gas and the proximate and ultimate analysis and HHV of the biomass, it performs the mass and heat balance of the unit. The input data were taken from (Lau et al. 2002).

The model developed for the simulation of the biomass gasification has never been presented before. It is based on experimental data of gasification behavior of specific biomasses. The model has been implemented in Aspen Plus™ by using two standard chemical reactor unit operation models: RYeld e RStoic.

The first reactor (RYeld) basically splits the biomass in its fundamental elements (H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, S, C, ASH and Cl<sub>2</sub>) based on the experimental ultimate analysis of the biomass. The necessary heat for the reaction is supplied by the next module (RStoic).

In the second reactor (RStoic) all the product formation reactions (CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub> ...) that are present in the real mixture of gas after gasification have been implemented. The flow rate of each component have been calculated from the experimental information through the conversion of each specie. The heat generated in this unit is partly transferred to the previous one (RYeld), partly is lost in heat losses and the rest is used to heat up the exit stream that leaves the second reactor at high temperature (around 870°C). Input to this unit is of course the output of the previous unit plus steam and oxygen.

The two couplet blocks allow calculating the material and energy balances, the composition of the gas at outlet, which matches the experimental data, if the ultimate analysis of the biomass is known.

The model of the **clean-up system** is here simply a unit that removes all the impurities to levels lower the permitted one for the reforming and the fuel cells. There's no energy related influence of this unit to the system.

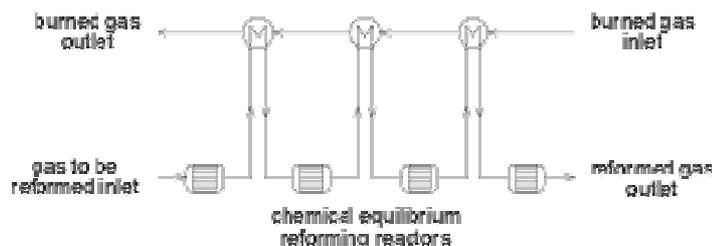
The gas produced by the reaction subsystem is then treated in the clean-up unit, which is made up by (i) a tar-cracker, (ii) an H<sub>2</sub>S sulphur removal system and (iii) a filter for

the removal of the fine particulate. The clean up section is needed because the gas outlet of the gasification reaction contains tars, **H<sub>2</sub>S sulphur compounds** (which is a poison for the reforming catalyst and for the anode fuel cell), alkali metals and particulate. The clean up section must work at a lower temperature in order to be efficient. For this reason the temperature is reduced to 400-450°C by means of an heat exchange with water in the catalytic cracking reactor (Lubachyov and Richter, 1998). The H<sub>2</sub>S is separated at 400°C by means of adsorbents (ZnO) (vv. Authors, 2001). Finally a ceramic filter for the removal of particulate is used at a temperature of around 500°C. **At the end of the treatment, the clean gas is sent at the reforming unit at about 400°C. All the reactors in the clean up section have been modelled by Aspen+ RGibbs units.**

Likewise the gasifier, also a **fuel cells** stack model wasn't available in the library of units of the simulator used. In this case the user model developed in (De Simon et al.) was employed, interfacing the Fortran 90 code with the process simulator. The parameters required by the simulation code are derived from ref. (Bosio et al. 1999) and are based on Ansaldo Fuel Cells experimental tests. Stacked cells are considered having the same behaviour as stand alone, so heat exchange between adjacent cells is neglected. Without this simplification the number of unknown variables to be solved for would be multiplied by the number of cells assembled in the stack, increasing exponentially the numerical complexity and computing time. This assumption doesn't introduce relevant approximation, as confirmed in (Bosio et al. 1998).

The number of cells in the stack are fixed and biomass feed rate is varied to keep the hydrogen and carbon monoxide utilization at about 75%; the cell surface and the stack current are fixed.

Also for the **reformer** no predefined unit was available in Aspen Plus™ libraries, so a well approximating scheme has been assembled using standard units. The model divides the unit alternating the reactions and heat exchanges, thus simulating the simultaneity of the two processes taking place. The reformer reactors (**bottom** side of **figure 4**) are in chemical equilibrium for methane reforming and gas-shift reactions.



**Figure 4: model of the compact reformer**

The **compressor, turbine and blower** units have been simulated by predefined blocks with fixed isentropic and mechanical efficiencies, employing typical values of existing units of similar size.

**The compressor, turbine and blower are assumed to work isentropically at a fixed mechanical efficiency, and the flow rate and/or pressure are fixed at the outlet conditions.** **è ripetuto** For the aims of this work **cogeneration** doesn't represent a

constraint: all residual heat of the effluent is exploited until exit temperature reaches about some tens of degrees over ambient conditions.

The heat exchangers, including the cogeneration heat exchanger, have fixed outlet temperatures. Heat losses and pressure drop (except those in the fuel cell) have been neglected. Another assumption for the simulation of the process is that the pressure drop of the various devices (except for the fuel cells) has been neglected. The main pressure drops are located at the stack and at the reformer: in the latter it has been estimated an order of magnitude of 1kPa per side (reformer and heating gas). The simulation considers an estimation of the total heat losses to 3% of the HHV of the biomass feed.

### 3. Thermal integration (Per ora la saltiamo )

Tabella con correnti da raffreddare e riscaldare, portate, potenze scambio necessarie e temperature

Motivo divisione flusso del ricircolo esausto catodo

Giustificazione scelte

In the all process scheme there are of course streams that has to be cooled and heated. Moreover some of them has to respect the temperature process bonds.

Referring to the Switchgrass process scheme main temperature bonds are:

- before entering in clean-up section, stream Gastocln has to be cooled to 750°C
- before entering in the stack's anode side stream 64 has to be cooled to 600°C
- before entering in the gasifier, oxygen and compressed water has to be heated to 315°C and 260°C respectively.

Moreover stream 15 that goes to the turbine has to be heated as much as possible as stream 9 which enter in the reforming section.

The entire thermal integration scheme can be summarized in table..

	Stream name	T in (°C)	T out (°C)	F*Cp (MMKcal/Kg°C)	H (MMKcal/h)	Block name
C	Gastocln	870,0	750,0	0,001099084	0,13189	B4
C	64	761,6	600,0	0,001070545	0,172946	B3
H	ox	25,0	315,0	0,000103448	-0,03	B12
H	24 (h2o)	25,0	260,0	0,001188245	-0,27924	B9
H	9 (in ref)	450,0	620,0	0,001017033	-0,17295	B3
H	35 (in ref)	620,0	767,4	0,001017033	-0,14986	B2
H	15 (in turb)	671,7	695,3	0,005550847	-0,131	B4
H	18 (u compr)	174,7	281,2	0,004169014	-0,444	excompr
C	22 (u turb)	481,2	475,5	0,005304183	0,03	B12
C	41	475,5	422,8	0,005304828	0,2798	B9
C	42	422,8	337,6	0,005199531	0,443	excompr
C	6 (u burn C)	879,5	630,0	0,000600761	0,14986	B2

The first four rows are the streams in which temperature bonds above are present. In the first column H and C indicate if the stream has to be Heated or Cooled.

It's interesting to note that last four rows represent stream which don't need to be cooled but they are very important and useful as a "heat recover streams"...

## 4. Process input conditions

### 4.1 Types of biomass considered

The model developed is used for the simulation of 3 different biomass feed conditions: (i) sugarcane bagasse (BG) which is a residue from sugar cane treatment, (ii) switchgrass (SW) and (iii) nut shells (NT) which is a mixture of 20% nut shell, 40% hazel nut shell and 40% wood. Table 1 reports the ultimate and proximate analysis of the three feeds, the humidity and the R ratio (Lau et al. 2002).

Table 1: biomass properties; data from Gas Technology Institute, 2002 (Lau et al. 2002).

	BG	SW	NT
<b>Proximate analysis</b>			
Ash	6.99	5.24	2.38
Volatile Subst.	80.06	80.09	76.28
C residual	12.95	14.67	21.34
HHV (MJ/kg)	17.77	18.62	19.80
<b>Ultimate analysis</b>			
C	46.46	47.73	48.51
H	5.4	5.56	5.65
N	0.18	0.67	0.77
S	0.06	0.01	0.01
Ash	8.5	4.6	3.07
O	39.36	40.68	41.98
Cl	0.04	0.11	0.01
<b>Other properties</b>			
$R = \frac{(kg_{H_2} + kg_{co})^{out}}{(kg_{biomassa})^{in}}$	0.24	0.34	0.38
Humidity	20%	12%	12.5%

Heating values express how much energy is released on combustion of a given quantity of fuel (J/kg). Two heating values are defined for a fuel: a "high heating value" includes the heat that can be obtained by condensing the water vapour produced by combustion and a "low heating value" does not include this heat. In this case HHV gives an energy released per kilogram of dry biomass.

The three different feeds are simulated with the process conditions reported in table 2 and 3.

Table 2: comparison of the gasifier performance of different biomass feeds for constant conversion in the cell.

	<b>BG</b>	<b>SW</b>	<b>NT</b>
T (°C)	870	870	870
P (bar)	3,5	3,5	3,5
Mass flow (Kg/h)	2722	2290	2095
<b>Mole fractions</b>			
H2	0,169	0,204	0,230
CO	0,119	0,178	0,198
CO2	0,249	0,231	0,210
CH4	0,080	0,086	0,086
H2O	0,365	0,275	0,250

Table 3: **general simulation input data**

<b>Gasifier input data</b>		<b>Stack input data</b>		<b>Input efficiency</b>	
T gasifier (°C)	870	Fuel utilization	75 %	Turbine isentropic efficiency	0,85
Pressure (bar)	3,5	T anode side (°C)	600	Turbine mechanical efficiency	0,97
Oxidant power consumption kWh/Nm <sup>3</sup> O <sub>2</sub>	0,4	T cathode side (°C)	600	Compressor isentropic efficiency	0,77
O <sub>2</sub> /C (mol/mol) (*)	0,28 for BG 0,18 for NT 0,23 for SW	Pressure (bar)	3,5	Compressor mechanical efficiency	0,97
H <sub>2</sub> O/ C (mol/mol) (*)	0,4 for all	Active surface (m <sup>2</sup> )	0,711		
T clean up (°C)	450	Current (A)	1100		
		Number of cells	2850		

(\*) O<sub>2</sub>/C it's a molar ratio between the oxygen fed to the gasifier and moles of carbon in the biomass

## 5. Results and discussion

### 5.1 Results

Table 4 shows the results obtained in the simulation of the process for different biomasses.

**Table 4: simulation results**

	<b>BG</b>	<b>SW</b>	<b>NT</b>
Biomass feed rate (kg/h)	1900	1550	1450
HHV (MJ/Kg dry)	17,77	18,62	19,8
MW	7,5	7,05	6,97
Oxygen feed rate(kg/h)	552	429	321
Water feed rate (Kg/h)	424	391	369
Gasifier cold efficiency <sup>(+)</sup>	76,5	82,8	84,5
Cracking power gain (MW) <sup>(+)</sup>	0,73	0,65	0,63
CH4 ref conversion (%)	86,8	85,5	84,5
Reforming power gain % <sup>(+)</sup>	14,8	14	13
<b>STACK RESULTS</b>			
T max single cell (°C)	686	681	682,5
T min single cell (°C)	625	622	624
Average solid T (°C)	654	648	651
I(A)	1100	1100	1100
V (V)	0,733	0,773	0,746
N cells	2850	2850	2850
Power (kW)	2299	2424	2341
Fuel utilization (%)	76,4	75,4	75,4
Efficiency (%) <sup>(+)</sup>	42,1	43,5	42
<b>POWER DATA</b>			
<b>Power production kW</b>			
Stack power	2299	2424	2341
Turbine power	1359	1322	1367
Total	3658	3736	3708
<b>Auxiliary power consumption kW</b>			
Air compressor	767	779	817
Blower	3,4	3,5	3,5
Pumps	0,1	0,09	0,09
O2 production	148	113	85
Total	918,5	895,6	905,6
<b>NET VALUES AND EFFICIENCIES</b>			
Net electrical power (MW)	2739,5	2841	2802,4
Net thermal power (MW)	2398,5	2035	2072
Electrical efficiency % <sup>(+)</sup>	36,5	40,3	40,2
Thermal efficiency % <sup>(+)</sup>	50,3	48,3	49,6
Cogenerative efficiency % <sup>(+)</sup>	68,4	69,1	69,85

(+) see the definitions hereafter listed

Several parameters were used in literature to characterize the results: for this reason it's important first of all to list which of them were employed in the following discussion and which are their definitions.

- Cracking power gain is the difference  $HHV_{out} - HHV_{in}$  in tar cracking unit (i are:  $CH_4, H_2, CO, C_2H_4, C_2H_6, C_6H_6$ ) the HHV of the tar in the producer gas that is recovered by cracking in form of  $CH_4, H_2$ .
- Reforming power gain represent the percentage gain calculated on a basis of HHV of the gas entering in reforming unit
- Gasifier cold efficiency is calculated as :  $HHV_{prod\ gas} / HHV_{bm}$  where bm is the type of biomass.
- Stack power efficiency is calculated as:  $\frac{Stack\ Power}{HHV_{H_2} + HHV_{CO}}$ .
- Electrical efficiency:  $\frac{Net\ Electric\ Power}{HHV_{bm}}$ ,
- Thermal efficiency:  $\frac{Thermal\ Power}{HHV_{bm} - Power_{stack}}$  l'ho tolto perché è un po' controverso e non ci sono termini di paragone
- Cogenerative efficiency is:  $\frac{Thermal + Electric\ Power}{HHV_{bm}}$

Finally a consumption of  $0,4\ kWh/Nm^3\ O_2$  (Ref. Techno economic Analysis for  $H_2$  prod. From gasification of bM) was used for oxygen production power estimation. messo tra i dati di ingresso

The results obtained for the gasifier are compared to experimental data of gasification of similar biomasses and there is a general good agreement between the experimental and the simulated data. Furthermore, the entire system converges to a solution that makes engineering sense and that is in line with literature results, thus allowing us to apply the model to the analysis of feed variations in the system.

## 5.2 Discussion

As shown in Table 4, the gasifier cold efficiency is in the range of 75-85%. It means that in the first step of the process about 20% of the chemical energy of the fuel becomes heat, underlining the importance of the thermal management of the subsequent part of the process. The best way to recover the above mentioned heat is at the reformer: the reactions are endothermic and therefore they convert heat into chemical energy of the hydrogen and carbon monoxide produced; this increased chemical availability is then converted to power in the fuel cell that is the most efficient energy conversion device of the plant. The higher heating value rise obtained for the reforming is about 14%, and this recovered energy in form of heat, becomes power in the fuel cell stack with the efficiency of about 42%. Consequently, the net electric power recovered for reforming is almost 6% of the producer gas, even if its methane content is not very high (8-9% mol/mol, see table 2).

Heat produced by gasification is also recovered by turbine expansion. The heat quality of the producer gas is the highest of the process (870°C), hence it is possible to exchange it with the gas to be expanded. The obtained temperature difference is only 20-25°C because the high heat capacity difference between the two fluids. The high flow rate of the turbine inlet fluid is necessary for the high flow rate at the cathode and the fixed temperature of the cathode inlet. High flow rate requires high gas recycle and this requires high fresh air input to keep the temperature at 600°C.

Another important energy related remark involves the cracking power gain (see table 4). It is the chemical energy recovered processing it in the cracking unit instead of managing it as a waste, so it's far higher heating value in the producer gas. It represents 4.5-5.5% about 10% of the HHV of the feed biomass and may be recovered efficiently only via cracking, able to add further hydrogen or methane to the gas. For these reasons it hasn't to be neglected in the energy considerations because the tar contains an important quantity of heating value.

Comparing the three feedstocks considered, the net electric efficiency is similar for switchgrass and nutshell (about 40%), not so for bagasse that reaches only 36,5%. From the chemical point of view the bagasse has a lower heating value and the gasification is conducted in a more difficult way. The gasification efficiency for bagasse is 76.5%, for switchgrass and nutshell it is 82.8% and 84.5% respectively. This means that for the same result in terms of hydrogen and carbon monoxide fed into the anode, in the bagasse case an higher biomass feed rate that is burned to thermally sustain the gasification, producing in this way a poorer gas. This can be noted in table 2, where the hydrogen, carbon monoxide and methane content in the producer gas is lowest for bagasse.

The cogenerative efficiency in all the cases is not very high (less than 70%). The reason has to be pointed out once again in the thermal dilution caused by the high fresh air flow rate: the gas exiting from the fuel cell system is in a degenerated form (temperature below 700°C) and its heat content can't be recovered in with good efficiency in the turbine before and in the cogeneration system next.

An analysis of table 4 shows clearly that, at almost constant conversion at anode and total electrical power, the electrical and cogeneration efficiency of the different biomasses are similar but a much lower flow rate is used in the case of nut shell biomass, which is directly related to the higher heating power of this biomass.

The electric efficiency is in the range of 36-40% depending on the type of biomass considered. In other studies (Kivisaari et al. 2002) similar results has been found. In (Kirill et al. 1998) an efficiency of 53% was calculated, for a hybrid system based on double fluidised bed reactor (gasifier-combustor), internal reforming MCFC and a complex steam turbine cycle.

## 6. Conclusions

This paper presented the development and the implementation of a model based on Aspen Plus<sup>TM</sup> for the steady state simulation of fuel cells and power generation processes coupled with the gasification of biomass. The fuel cell considered in the process is a Molten Carbonate Fuel Cells based on real plants data and the simulations

are selected according to real operating conditions. The paper presents also the details of a novel integrated gasification – fuel cell steady state model.

The paper reports results of computer simulation for a realistic configuration of power generation system by MCFC, focusing on macroscopic quantities of interest such as stack efficiency, global process electrical efficiency, cogenerative efficiency. The software developed allows to study ‘in silico’ the effect of variations of the process conditions such as modification of the input fuel, thus providing a useful tool for supporting technical decisions and feasibility study on the use of fuel cells. The model has been applied to three different biomasses allowing us to compare the performances of the different feeds and to understand the details of the entire process.

By means of the simulation presented it was possible to understand what described in the following remarks.

In the gasification process a lot of valued heat is produced (20% of the total input HHV at 870°C), underlining the importance of the thermal integration in the process.

The producer gas tar energy content is about 10% of the total biomass HHV. Therefore a good cracking processing is important in order to recover tar heating value.

The endothermic reforming is able to convert thermal energy into chemical one; at the same time it increases the hydrogen and carbon monoxide availability for the fuel cell stack. By means of the reforming, 6% of the biomass HHV becomes electricity.

Among the three biomass considered, the bagasse permit the lower electric efficiency because of its difficulties in being gasified, performing the worst gasification cold efficiency and then the lowest fuel content in the producer gas.

## 7. References

- Arato, E., B. Bosio, P. Costa, F. Parodi, Preliminary experimental and theoretical analysis of limit performance of molten carbonate fuel cells, *J. Power Sources*, **102**, (2001), 74-81.
- Bishoff, M., G. Huppman, Operating experience with a 250 kWel molten carbonate fuel cell (MCFC) power plant, *J. Power Sources*, **105**, (2002), 216-221.
- B. Bosio, P. Costamagna, F. Parodi, B. Passalacqua, Industrial Experience on the development of the molten carbonate fuel cell technology, *J. Power Sources* **74** (1998) 175–187.
- Bosio, B., P. Costamagna, F. Parodi, Modeling and experimentation of molten carbonate fuel cell reactors in a scale-up process, *Chemical Engineering Science*, **54**, (1999), 2907-2916.
- De Simon, G., F. Parodi, M. Fermeiglia, R. Taccani, Simulation of process for energy production based on molten carbonate fuel cells, *J. Power Sources*, **115**, (2003), 210-218.
- Fehribach, J. D., J. J. A. Prins, K. Hemmes, J. H. W. De Wit, F. W. Call, On modeling molten carbonate fuel-cell cathodes by electrochemical potentials, *J. of Applied Electrochemistry*, **30**, (2000), 1015-1021.

- Fermeglia M., A. Cudicio, G. De Simon, G. Longo, S. Priol, Process simulation for molten carbonate fuel cells, *Fuel Cells – From Fundamentals to Systems*, Topical Issue “Modeling of Fuel Cell Systems”, **5**, (2005), 66-79.
- Fontes, E., C. Lagergren, D. Siminsson, Mathematical modelling of the MCFC cathode – On the linear polarization of the NiO cathode, *J. of Electroanalytical Chemistry*, **432**, (1997), 121-128.
- Hart, A. B., G. J. Womack, *Fuel cells, theory and application*, Chapman and Hall LTD, London, 1967.
- He, W., Numerical analysis of molten carbonate fuel cell systems, *International Journal of Energy Research*, **21**, (1997), 69-76.
- He, W., Dynamic model for molten carbonate fuel-cell power-generation systems, *Energy Conversion and Management*, **39**, (1998), 775-783.
- He, W., Q. Chen, Three-dimensional simulation of a molten carbonate fuel cell stack using computational fluid dynamics technique, *J. Power Sources*, **55**, (1995), 25-32.
- Heidebrecht, P., K. Sundmacher, Molten Carbonate fuel cell (MCFC) with internal reforming: model-based analysis of cell dynamics, *Chemical Engineering Science*, **58**, (2003), 1029-1036.
- Joon, K., Critical issues and future prospects for molten carbonate fuel cells, *J. Power Sources*, **61**, (1996), 129-133.
- Kang, B. S., J.-H. Koh, H. C. Lim, Experimental study on the dynamic characteristic of kW-scale molten carbonate fuel cell systems, *J. Power Sources*, **94**, (2001), 51-62.
- Kim, M.-H., H.-K. Park, G.-Y. Chung, H.-C. Lim, S.-W. Nam, T.-H. Lim, S.-A. Hong, Effects of water-gas shift reaction on simulated performance of a molten carbonate fuel cell, *J. Power Sources*, **103**, (2002), 245-252.
- Kivisaari T., Björnbom P., Sylwan C., Studies of biomass fuelled MCFC systems, *J. of Power Sources*, **104**, (2002), 115-124
- Koh, J.-H., B. S. Kang, H. C. Lim, Effects of various stack parameters on temperature rise in molten carbonate fuel cell stack operation, *J. Power Sources*, **91**, (2000), 161-171.
- Koh, J.-H., B. S. Kang, H. C. Lim, Analysis of temperature and pressure fields in molten carbonate fuel cell stacks. *A.I.Ch.E. Journal*, **47**, (9), (2001), 1941-1956.
- Kordesh, K., G. Simander, *Fuel cells and their applications*, VCH, Weinheim 1996.
- Kraaij, G. J., G. Rietveld, R. C. Makkus, J. P. P. Huijsmans, Development of second generation direct internal reforming molten carbonate fuel cell stack technology for cogeneration application, *J. Power Sources*, **71**, (1998), 215-217.
- Lau F. S., Bowen D. A., Dihu R., Doong S., Hughes E. E., Remick R., Slimane R., Turn S. Q., Zabransky R., *Techno-Economic Analysis of Hydrogen Production by*

Gasification of Biomass, technical report of the DOE contract DE-FC36-01GO11089 (2002)

Lopamudra Devia, Krzysztof J. Ptasinska, Frans J.J.G. Janssen, Sander V.B. van Paasenb, Patrick C.A. Bergmanb, Jacob H.A. Kielb, Catalytic decomposition of biomass tars: use of dolomite and untreated olivine, *Renewable Energy*, **30**, (2005) 565-587.

Lubachyov K.V., H.J. Richter, An advanced integrated biomass gasification and MCFC power system, *Energy conv. Mgmt*, **39**, (1998), pg. 1931-1943.

Lukas, M. D., K. Y. Lee, A. H. Ghezal, An explicit dynamic model for direct reforming carbonate fuel cell stack, *IEEE Transaction on Energy Conversion*, **16**, (2001), 289-295.

Mangold M., M. Sheng, Nonlinear Model Reduction of a Dynamic Two-dimensional Molten Carbonate Fuel Cell Model, *AIChE's 2003 Annual Meeting 169a* (2003).

Miyake, Y., N. Nakanishi, T. Nakajima, Y. Ytoh, T. Saitoh, A. Saii, H. Yanaru, A study of heat and material balances in an internal-reforming molten carbonate fuel cell, *J. Power Sources*, **56**, (1995), 11-17.

Park, H.-K., Y.-R. Lee, M.-H. Kim, G.-Y. Chung, S.-W. Nam, S.-A. Hong, T.-H. Lim, H.-C. Lim, Studies of the effects of the reformer in an internal reforming molten carbonate fuel cell by mathematical modelling, *J. Power Sources*, **104**, (2002) 140-147.

Shinoki, T., M. Matsumura, A. Sasaki, Development of an internal reforming molten carbonate fuel cell stack, *IEEE Transaction on Energy Conversion*, **10**, (1995), 722-728.

vv. Authors, *Techno Economic Analysis of Hydrogen Production by Gasification of Biomass, Final Technical Report for the Period September 15, 2001 to September 14, 2002, GTI* messo sopra Lau et al.

Yoshida, F., N. Ono, Y. Izaky, T. Watanabe, T. Abe, Numerical analyses of the internal condition of molten carbonate fuel cell stack: comparison of stack performances for various gas flow types, *J. Power Sources*, **71**, (1998), 328-336.

### Ancora da farsi

- 1) togliere la numerazione automatica dei titoli
- 2) sistemazione della formattazione da 1.5 Equations in poi
- 3) sistemare figura 1
- 4) calcolare rendimento pila anche con LHV per avere riscontro con letteratura (inserire sia in tabella che nella lista delle definizioni)

5) verificare l'attendibilità del contenuto energetico del catrame  
(10%)