Steady state simulation of energy production from biomass by molten carbonate fuel cells

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Received 26 August 2005; received in revised form 13 October 2005; accepted 15 October 2005

Abstract
This paper presents an integrated approach to the steady state simulation of biomass gasification, fuel cells and power generation processes. Attention is 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 based on real plants data is described and the simulations are selected according to real operating conditions. 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.

The paper reports results of computer simulation focusing on macroscopic quantities of interest such as stack efficiency, global process electrical efficiency, cogenerative efficiency. The computer simulation is applied to a feasibility study of a MCFC coupled with a biomass gasification module focusing on the energy consumption of the process and reporting comparison of the energy efficiency for three kinds of biomass.

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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 CO2 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 problem 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. Actually, in most developing countries there is a generally high availability of biomasses of different kind that could be easily used for the production of electrical energy in places where the grid is not available; a fuel cells based power generation systems of about 500 kW can be used for providing energy to small hospital and little villages. But the high range of quality of biomasses available in developing countries makes it difficult to design a process that may be directly applied to all the different cases. It is therefore important to be able to make feasibility studies on the energy generation process based on the biomass availability and the desired power to be generated and consequently 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 [1], 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 [2,3].

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 [4,5], which will be too long to discuss here in details.

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 desulphu-
sation 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. The general process for energy production from biomass is splitted in three parts: (i) the biomass gasification, (ii) the fuel cell stack and (iii) the cogeneration (see Fig. 1).

The typical fuel for MCFC is natural gas, which has been extensively used for the development of the technology. This paper addresses the issue of using biomasses as fuel for MCFC. There are many differences in the process if the feed is changed from natural gas 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 percent 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 [6] applied on both single cell and stack, or on differential equations [7–13] applied to both mean and distributed variables. An interesting review of steady state simulation of fuel cells is reported in [14]. Many problems were solved in assumption of hypothesis, in formulation of equations and in approximation of accessory devices [15], 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 menisci [16,17] 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 [15] and includes all the necessary modifications to adapt the model to the gasification of biomass.

2. Theory and model development

A fully distributed bi-dimensional open loop model was implemented in a software module, to describe physical and chemical phenomena involved in MCFC. A steady state model of MCFC was developed in a previous work [15] and has been recently extended to dynamic simulation of the single cell [18]. In both models, the chemical-physical fundamental equations are organized to give an easy-to-solve system of non linear algebraic and differential equations which deeply integrates fluid dynamical, pressure drop, chemical, electrochemical reaction and heat and mass transfer 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.

2.1. Fuel cell stack model

A molten carbonate fuel cell plant described in the introduction, and schematically represented in Fig. 1, is the reference flow sheet for the development of the steady state simulation of
the process. The steady state simulation model of the cells stack is based on the approach of [10] as implemented by some of us in a previous paper [15]. 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, (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. The electrochemical equation used and the value of the coefficients are the following.

$$R_{tot} = A e^{B/T} \prod_{i} \beta_i \gamma_i + C_i R + D_e F/T$$

$$\beta_i = 0 \text{ for } i \neq O_2, \quad \beta_{O_2} = 0.67, \quad A = 1.38 \times 10^{-7} \Omega m^2 Pa^{-0.67}, \quad B = 11,400 K, \quad C_i = 0.348 \times 10^{-4} \Omega m^2, \quad D = 4.8 \times 10^{-8} \Omega m^2, \quad F = 6596 K.$$  

All coefficients of this model are obtained by experimental data fittings ([15] 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. To find overall cell behavior it was 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.

### 2.2. Process description

The process flow diagram is shown in Fig. 2 with an example of the process temperatures. 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 units that follows. After cooling at 730 °C, it is sent to a circulating fluidised bed tar cracker [19] in which the bed material (dolomite) acts as a catalyst for the cracking process. The exiting gas ($T$ over 800 °C) is almost free of C$_2$+ hydrocarbons and is composed primarily of CH$_4$, H$_2$, CO, CO$_2$ and H$_2$O. This gas is cooled at 450 °C, by exchanging with the air feed. 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, thus justifying the temperature reduction. 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 plate and frame heat exchanger with one side filled with reformer catalyst.

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 and electrochemical reactions take place:

$$H_2O + CO \rightarrow H_2 + CO_2$$

(Part 2)

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 CH4 (no internal reforming): this gas is burnt together 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.

The cathode recycles 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 is heated by exchanging with the producer gas and it is sent to the gas turbine for expansion and further power production. The flue gas out of the turbine 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 fuel cell stack model described above has been used for the steady state simulation of the process. It is introduced in a commercial 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.

A simplified model was adopted for the gasifier. Starting from the composition, temperature of the producer gas (output of the gasifier) and the proximate, ultimate analysis and HHV of the biomass, it performs the mass and heat balance of the unit. The input data were taken from [20]. 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: RYield and Rstoic (see Fig. 3). The first reactor (RYield) basically splits the biomass in its fundamental elements (H2O, N2, O2, H2, S, C, ASH and Cl2). It is an hypothetical reactor whose task is to convert a non convectional stream, the biomass, to a conventional one, a gas mixture of elementary molecules. The inlet biomass composition is based on the experimental ultimate analysis, which must be available for the simulation. The necessary heat for the reaction is supplied by the next module (RStoic). The second reactor (RStoic) receives the hypothetical gas generated from the first reactor, the oxidant and the steam and generates all the reaction products (CH4, H2, CO, CO2, ... ) that are present in the real mixture of gas after gasification. The yield of the reactions involved were adjusted for obtaining the desired producer gas composition, that must be known form experimental data, and to satisfy the mass balance. The final heat generated in this reactor is partly transferred to the previous reactor (RYield), 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). The two coupled blocks allow Aspen Plus to calculate the material and energy balances and the composition of the gas at outlet is automatically matching the experimental data, thus obtaining all the component flowrates, if the ultimate analysis and flowrate of the biomass is known.

The model of the clean-up system is simply a unit that reduces all the impurity concentrations at the values allowed for the reforming and the fuel cells. This section is made up by (i) a tar-cracker, (ii) a 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, sulphur compounds (which is a poison for the reforming catalyst and for the anode fuel cell), alkali metals and particulate. The clean up section, except for the tar cracker, must work at a low temperature in order to be efficient. For this reason the temperature is reduced to 400–450 °C after the tar cracker by means of an heat exchanger [21]. The H2S is separated at 400 °C by means of adsorbents (ZnO) [24]. Finally a ceramic filter for the removal of particulate is used at a temperature of around 500 °C.

Likewise the gasifier, also a fuel cells stack model was not available in the library of units of the simulator used. In this case the user model developed in [15] was employed, interfacing the Fortran 90 code with the process simulator. The parameters required by the simulation code are derived from the literature [8] and are based on Ansaldo fuel cells experimental tests. Stacked cells are considered having the same behavior 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 does not introduce relevant approximation, as confirmed in [22]. The number of cells in the stack are fixed and biomass feed rate is varied to keep the temperature reaches about some tens of degrees over ambient conditions. The heat exchangers, including the cogeneration heat exchanger, have fixed outlet temperatures. 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 1 kPa 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. Process input conditions

3.1. Biomasses considered

The model developed is used for the simulation of three 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 moisture content and the R ratio [20].

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

4. Results and discussion

4.1. Results

Table 4 shows the results obtained in the simulation of the process for the different biomasses reported above. For sake of clearness, the definition of the parameters reported in Table 4 for characterizing the results is here reported. They are:

- Cracking power gain is the HHV of the tar in the producer gas that is recovered by cracking in form of CH4, H2 and CO.
- Reforming power gain represent the percentage gain calculated on a basis of HHV of the gas entering in reforming unit.
- Stack power efficiency HHV is calculated as: Stack Power/ (HHVCH4 + HHVC0).
- Stack power efficiency LHV is calculated as: Stack Power/ (LHVCH4 + LHVC0).
- Electrical efficiency: Net Electric Power/HHVbm.
The heat quality of the producer gas is the highest even if the methane content is not very high (8–9% mol mol$^{-1}$). The power recovered for reforming is almost 6% of the producer gas, with the efficiency of about 42%. Consequently, the net electric energy in form of heat, becomes power in the fuel cell stack. High flow rate obtained for the reforming is about 14%, and this recovered energy is converted to power in the fuel cell that is the most efficient energy conversion device of the plant. The higher heating value is then converted to power in the fuel cell allowing us to apply the model to the analysis of feed variations in the system.

5. Discussion

As shown in Table 4, the gasifier cold efficiency is in the range of 75–85%. This means that in the first step of the process about 20% of the chemical energy of the fuel is transformed in heat, underlining the importance of the thermal management of the subsequent part of the process. The best place to recover this heat is in the reformer: the reactions are endothermic and therefor the subsequent part of the process. The best place to recover this heat, underlining the importance of the thermal management of the process.

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.

In Fig. 4 a simplified Sankey diagram of the nutshell biomass case is presented as an example of the general heat balances of the process. It is interesting to comment on the cracking power gain (see Table 4), which is defined as the chemical energy recovered in the cracking unit and is directly related to the tar quantity. It represents about 10% of the HHV of the biomass feed and may be recovered efficiently only via cracking, thus adding more hydrogen or methane to the gas. Since the tar contains an important quantity of heating value it should not be neglected in the energy balance.

Comparing the three feedstocks considered in this work, the net electrical efficiency is similar for switchgrass and nutshell (about 40%), while for bagasse it reaches only 36.5%. This is explained by the lower heating value of the bagasse and by the higher difficulties in its gasification. In fact, the gasification efficiency for bagasse is 76.5%, while for switchgrass and nutshell it reaches only 82.8% and 84.5%, respectively.
it is 82.8 and 84.5%, respectively. This means that for an equal amount of hydrogen and carbon monoxide fed to the anode, an higher biomass feed rate is necessary in the bagasse case to thermally sustain the gasification, thus producing 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 cogeneration efficiency in all the cases is not very high (less than 70%). The reason is 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 cannot be recovered with good efficiency in the turbine and in the cogeneration system.

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 [23] similar results has been found. In [25] 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 presents the development and the implementation of a model based on Aspen Plus™ 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.

The calculations reported in this paper for the biomasses considered allow us to take some conclusions.

The efficiency obtained by coupling the biomass gasifier and the MCFC is around 36–40%, depending upon the biomass used: considering the low performances of the biomass as fuel the efficiency obtained indicates that the process of production energy by using fuel cells is feasible.

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 the tar heating value.

The endothermic reforming converts thermal energy into chemical energy and it increases the hydrogen and carbon monoxide availability for the fuel cell stack. It is calculated that
the reforming allows about 6% of the biomass HHV to become electricity.

Among the three biomass considered, the bagasse gives 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.

The model developed in this work could be used in developing countries for performing feasibility studies on the possibility of using fuel cells technology for producing electrical energy starting from available biomass, addressing at the same time the problem of off-grid energy production and of accumulation of biomass.

Acknowledgments

The authors thank Gennaro Longo and Sadesh Kumar for helpful discussions.

References


