From biomass to electricity through integrated gasification/SOFC system-optimization and energy balance

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Received 7 December 2005; received in revised form 23 January 2006; accepted 1 June 2006

Abstract

In this paper the integrated process of biomass gasification and a solid oxide fuel cell (SOFC) was studied in terms of thermodynamics. The study is based on an ongoing project intending to develop an innovative sustainable technology with high efficiency. According to some assumptions, the energy balance revealed that the process can be auto-thermal. Furthermore, and due to the utilization of the hydrogen content of steam utilized in the reforming stage, the overall efficiencies to electrical power could reach very high levels.

Keywords: Biomass; Gasification; SOFC; Optimization; Thermodynamics

1. Introduction

The conjunction of biomass gasification with solid oxide fuel cells (SOFCs) seemed to be a promising and forthcoming possibility for electricity and heat cogeneration along with profound environmental and socioeconomic benefits. Biogas, despite attractive advantages of being indigenous, local, versatile and renewable, remains largely underexploited, while SOFC cogenerators, owing to their high efficiency and relative insensitivity to microcontaminants, could substantially upgrade the value of this fuel. Feeding these devices with reformed biogas, a readily suitable for SOFCs hydrogen rich fuel, seems to be a promising way for the production of “clean energy” from biomass, which, on the other hand can speed up the SOFC’s steps to market [1–4].

Jan Van Herle performed the energy balance analysis on an anaerobic digestion system, in order to assess conversion efficiencies of cold biogas (CH₄ + CO₂) by SOFCs, as a function of the variation of adjustable operating parameters such as reforming conditions, air excess rate and SOFC stack temperature [1] and reported a case study of a small SOFC cogenerator operated with agricultural cold biogas, the largest potential source [4]. For a fuel inlet of 60% CH₄ 40% CO₂ at 800 °C and 80% fuel conversion, a SOFC can deliver 3 kWel and 5 kWth from an input of almost 9 kW lower heating value (LHV) biogas, corresponding to approximate 34% and 58% electrical and thermal efficiencies, respectively [3]. Concerning anaerobic digestion, the possibility of direct biological hydrogen production [5] enhances the, yet unsearched, capability to connect these processes to SOFCs.

Along with anaerobic digestion, which leads to biogas at ambient temperature, biomass gasification seems to be thermally more compatible to SOFCs, since both procedures operate at the same temperature level. Thus depleted air at the appropriate temperature from SOFC’s cathode compartment can be directly fed to the gasifier and upgrade the heating value of the produced biogas [1]. Furthermore, superheated steam produced at the anode can also be fed to a steam gasifier (directly or after the total combustion of the residual fuel in an after burner) and cover (partially or totally) the heat demands of the latter. Steam gasification exhibits enhanced conversions to hydrogen, and it is considered to be superior to the conventional
one since it evolves steam’s hydrogen in the integrated process [1]. The conjunction of SOFCs with steam gasifiers can contribute significantly to overpass the endothermicity of the latest and bypass the capital costs of the intermediate biogas reforming stage. Very recently Acumentrics shipped a 5 kW SOFC to the DOE’s National Renewable Energy Lab to investigate the benefits of running a high-efficiency fuel cell system with various biogas-derived fuels along with thermal integration issues. In addition, the inherent ability of SOFCs system to keep the anode and cathode exhaust gases separate will allow to look at SOFC over-fueling (low utilization) and adding downstream operations for the anode exhaust gases, such as a gas turbine [6]. Omosun et al. explored the possibility of combining SOFC and biomass gasification, for the generation of power and heat using the gPROMS modelling tool, considering a hot gas cleanup process and a cold gas cleanup process. In their work, the electrical and overall efficiency for the hot process were found to be 23% and 60% and for the cold process the efficiencies were 21% and 34%, respectively due to the superior heat management of the first one [7]. Despite the recent work of Baron et al. concerning the impact of wood derived gasification gases in SOFCs [8], the research field seems to be quite unexploited and yet very promising.

In the present study, the thermodynamic analysis of the integrated gasifier—SOFC process was performed and the influence of several parameters on the energy performance was investigated. Gas clean up, i.e the removal of tars and particulates as well as alkali, chlorine and sulphur trace-compounds, from the produced gas, is typically based on physical separation and sorption processes, which, from a thermodynamic point of view, do not consume or produce significant amounts of energy. Therefore, despite the pressure drop or the heat losses these processes can cause, their effect on the energy balances was neglected, along with any other heat losses through out the integrated process.

2. The processes

A simplified flow diagram of the gasifier—SOFC integrated process, is depicted in Fig. 1. Along with the gasifier and the SOFC, the process involved a biogas reformer, a burner for the total combustion of both solid residue from the gasifier and the fuel excess from the cell, a steam turbine and the necessary heat exchangers.

The technology of biomass air gasification seems to have a feasible application and has been developed actively for industrial applications. However this technology produces a gas with a low heating value (4–6 MJ/m³) and an 8–14 vol.% H2 content only. Biomass oxygen-rich air gasification is one attractive way of producing medium heating value (MHV) gas, but it needs a large investment for oxygen production equipment and this disadvantage impedes its commercialization. Extensive experimental studies reported in the literature show that fluidized-bed, steam-gasification process are also capable of producing a MHV (10–16 MJ/Nm³) gas with 30–60 vol.% H2 content [9–11].

An intermediate stage in the conjunction of the thermochemical biomass processes with the fuel cells technology is the reforming of gaseous and liquid products in hydrogen rich mixtures. This stage can be omitted in the case of gasification from the direct feeding of the biogas in an internal reforming cell. The thermochemical conversion of biomass concerns mixtures of H2, CH4, CO, CO2 as well as light hydrocarbons [1]. Reforming, mainly of CH4, has been studied intensively in Rh,
Ni, Ru, Pt, Ir and Pd [12] catalysts while the reaction is being used for the 90% of the hydrogen production globally [13]. Despite this fact, the simultaneous reforming of hydrocarbon mixtures and the influence of the CO, CO2 concentration in the H2 production is a very good base for further research.

The solid oxide fuel cells are devices that convert the chemical energy of a reaction of a fuel with oxygen, directly into electrical, without the intermediate conversion into heat. In these set-ups the oxygen from the air is reduced in the cathode to O2 anions, which reach the anode through the oxygen carrier, where they react with the fuel (H2, CO, CH4 or CH3OH) into CO2 and H2O. Compared to the conventional thermal cycles, SOFCs appear to have significantly higher electrical yields and they can operate on a variety of different fuels (H2 mixtures, natural gas reformats, light hydrocarbons etc). The heat eluted in the exit can be used either in external thermal cycles, increasing the total yield, or to cover the thermal demands of the integrated process (reforming of the fuel, thermochemical treatment of biomass) [2].

During the 1990s, SOFC stacks have been developed in an industrial scale. Since 1999, Siemens–Westinghouse operates a trial SOFC, with a power output of 100kW and 46% efficiency, at 1000°C, while the investment cost was of the order of 1 million €. Mitsubishi established a SOFC system, 4 MW, at a temperature of 900°C. Smaller apparatuses already operate from the Japanese Chubu Electric Power, the Ceramic Fuel Cells in Australia, and the Sulzer Hexis in Switzerland, etc. In a pilot scale a significant number of cells have been tested successfully with an efficiency that exceeds 45%. SOFC of medium production (50 kW–1 MW) are an attractive solution for decentralised cogeneration (Cogeneration plus electric efficiency, at 1000°C), while in order to become competitive it will have to be reduced to 3000 €/kW [2].

Biomass of the typical elemental analyses was fed to the gasifier. It was assumed that 5% of the massive biomass inlet was removed from the gasifier as a residue (both char and tar). The typical elemental analysis of the biomass and the residue are given in Table 1, where the values used during the analysis, are presented in brackets. The Lower Heating Value of the biomass and the solid/liquid residue was determined by the following equation [14]:

\[
\text{LHV} = 4,186\{1 + 0.15[\text{O}]\}(7.837, 667[\text{C}]) + 33,888, 889[\text{H}] - [\text{O}]/8
\]

\[= 24.872 \text{ kJ/kg},\]

where, the brackets notify the % w/w of the corresponding element [14]. The specific heat of the biomass and the residue was assumed equal to that of the average wood and wood charcoal (2.3 and 1.01 kJ/kg·°C, respectively) [15].

The heat demand or generation of the gasifier was calculated, by taking into account the lower heating value LHV of the biomass feed. Thus, according to the composition of the produced biogas, the heat produced (+) or consumed (−), in the gasifier, can be calculated through the following general expressions:

\[
\text{biomass + air} \rightarrow \text{biogas} \times \text{H}_2 + \text{CO}_2 \times \text{biogas} \times \text{CO}_2
\]

\[+ \text{CO}_{biogas} \times \text{CO} + \text{CH}_4 \times \text{biogas} \times \text{CH}_4
\]

\[+ [\text{LHV} + (\text{H}_2 - \text{CO}_2)]
\]

\[\times \text{CO}_2 \times \text{biogas} \times \text{H}_2O + \text{CH}_4 \times \text{biogas} \times \text{CH}_4] \text{kJ},\]

where \(\xi\) denotes the extend of each reaction. The energy demands of the gasifier, which was assumed adiabatic, were balanced by adjusting its temperature as well as the temperature and the feed rate of the gasifying air supply.

Regarding the energy balances of each process of the integrated process:

\[
\sum_j \sum_i h_i = \sum_j \sum_i h_i + H_P,
\]

where \(j_{OUT}, j_{IN}\): the streams leaving or entering process \(P\), \(h_i\): the sensible of component \(i\) in stream \(j\), and \(H_P\): heat generated or consumed during the process \(P\) the calculation of \(h_i\) was based on the integration of \(c_P(T)\) expressions:

\[
h_i^j = n_{j,i} \int_{298}^{T_j} c_{P,i} dT,
\]

where \(c_{P,i}\) the heat capacity of component \(i\) in stream \(j\), and \(T_j\) the absolute temperature of stream \(j\), while \(H_P\) was calculated as the sum of the heat of the reactions in process \(P\):

\[
H_P = \sum_{Pr} n_{i} h_{0,i} - \sum_{Re} n_{i} h_{0,i},
\]

where \(h_{0,i}\) stands for the heat of formation of component \(i\) at 298 K and indicators \(Pr\) and \(Re\) denotes the products and the reactants of each reaction in process \(P\) (water evaporation was also taken into account in the gasification process and the steam generating heat exchanger).
Electrical efficiencies of the SOFC, the turbine and the overall process are defined as the percentage of the LHV of the biomass fed to the process, which is converted to electricity:

\[
\eta_{el}^{SOFC} = \frac{W_{el}^{SOFC}}{LHV} \quad \eta_{el}^{turbine} = \frac{W_{el}^{turbine}}{LHV} \quad \eta_{el}^{overall} = \eta_{el}^{SOFC} + \eta_{el}^{turbine}.
\]

The biogas consistency was calculated by assuming that the available hydrogen (elemental hydrogen in biomass — elemental hydrogen in residual char + tar) was converted to methane, while the remaining carbon was partially oxidized to carbon monoxide, due to the lack of oxygen at the depleted air inlet. The oxygen feed at the depleted air stream, was assumed to be adjusted in order that no carbon dioxide or gaseous oxygen was present at the outlet (fuel rich conditions). No reforming reactions were assumed to occur in the gasifier. So methane values, used for the analyses were adjusted to involve the amount of hydrogen at the outlet of the gasifier. This is not expected to affect the energy balance of the overall process, since reforming to adequate extent is assumed to occur in the reformer. The following reactions in the reformer were assumed to be at equilibrium, at the reformer’s temperature:

\[
\begin{align*}
CH_4 + H_2O & \leftrightarrow CO + 3H_2 \quad (1) \\
CO + H_2O & \leftrightarrow CO_2 + H_2 \quad (2) \\
CH_4 + 2H_2O & \leftrightarrow CO_2 + 4H_2. \quad (3)
\end{align*}
\]

Rich hydrogen (18.5%) and carbon monoxide (10.9%) mixture, from the reformer, was fed in the SOFC anode compartment, where 80% of hydrogen is oxidized, while the electrical yield of the cell was set down to 46% [2]. The air inlet to the cell was adjusted so that oxygen concentration at the outlet could be directly fed to the gastifier with the appropriate oxygen concentration, to maintain fuel rich conditions, that enhances the heating value of the produced biogas. Oxygen lean conditions result in a negative affect on the gastifiers autothermicity, which could be overcome by adjusting the temperature of the depleted air stream, at the inlet of the gasifier, at an appropriate value in the reformer’s steam preheater. In order to achieve the appropriate oxygen concentration at the outlet of the cathode compartment of the SOFC, the air inlet flowrate to the cell was kept low, resulting lean oxygen condition at the cathode. The effect of oxygen depletion on SOFC’s performance was not taken into account. Despite the low ambient air flowrate to the SOFC, the depleted air outlet of the cathode compartment was found to exceed the needs of the gastifier.

Depleted air excess as well as the un-burned fuel from the cell, were fed to the afterburner. The heat produced in the latter was found to be enough for preheating the air inlet to the process while a considerable amount of heat could be fed to the steam turbine for the production of additional electricity. The outlet streams of the gasifier, reformer, SOFC and the afterburner, were considered equal to operating temperature of the corresponding device. Finally the assumption that no reforming reactions occur in the gasifier, was not significantly affect the overall analysis, since these reactions were considered to occur in a separate reforming stage.

### 3. Results and discussion

According to the performed analysis, the mass flow rate, the composition and the temperature of each stream of Fig. 1, for the optimized process, is given in Table 2. It is worth to notice that no gaseous oxygen and/or carbon dioxide was calculated for the biogas exit flow of the gastifier (stream 3), in consistency with assumption that oxygen flowrate and concentration at stream 2 can be adjusted in the cell, in way that only partial oxidation of carbon would occur in the gasifier (hydrogen and carbon combustion to steam and carbon dioxide were considered negligible).

The thermal content of each stream, along with heat produced in the gasifier, the SOFC and the afterburner (AB), the heat consumed at the reformer and the electricity produced at the SOFC and the steam turbine (ST), are given at Table 3 (streams at 25 °C, are not mentioned). Adiabatic operation was assumed for the integrated process as well as each single part of the latest. The optimization procedure took into account the fact that it would be economic benefit of the process, to avoid heat removing or adding devices within its main components.

### Table 2

| Stream no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|------------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
| T (°C)     | 25 | 295 | 1300 | 1300 | 220 | 544 | 244 | 995 | 995 | 244 | 995 | 1282 | 995 | 25 | 220 | 220 | 25 | 1179 | 244 |
| M (kg/s)   | 1.00 | 3.00 | 3.95 | 0.05 | 1.32 | 5.27 | 6.22 | 6.19 | 5.30 | 3.08 | 2.30 | 13.6 | 3.00 | 3.43 | 3.43 | 2.11 | 9.30 | 11.6 | 9.30 |
| X_C        | 0.35 | 0.70 | 0.18 | 0.27 | 0.42 | 0.03 |
| X_O        | 0.19 | 0.04 |
| X_H        | 0.18 | 0.12 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| X_H2       | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 | 0.31 |
| X_CO       | 0.05 | 0.13 | 0.17 | 0.21 | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 |
| X_CH4      | 0.97 | 0.70 | 0.43 | 0.79 | 0.43 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 | 0.79 |
| X_H2O      | 0.05 | 0.04 | 1.00 | 0.23 | 0.38 | 0.24 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

...
Table 3
Energy balance of the integrated process

<table>
<thead>
<tr>
<th>Stream no.</th>
<th>Gasifier</th>
<th>SOFC</th>
<th>Reformer</th>
<th>After burner</th>
<th>Steam turbine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q (MJ/s)</td>
<td>4.3</td>
<td>8.1</td>
<td>-1.9</td>
<td>5.8</td>
<td>-16</td>
</tr>
<tr>
<td>W_{el} (MJ/s)</td>
<td>6.6</td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Overall electrical efficiency of the integrated gasification—SOFC—steam turbine process compared to the conventional gasification—steam turbine one.

Fig. 3. Overall electrical efficiency of the integrated gasification—SOFC—steam turbine process, for various hydrogen content, in biomass feedstock.

(SOFC, gasifier, reformer, burner), apart from the notified, in Fig. 1 heat exchangers. So the temperature at each stream in the process was calculated in a manner to remove or provide the appropriate heat to each component.

The production of electricity from the gasifier through a conventional steam turbine is compared to the integrated process of gasifier—SOFC—steam turbine, in Fig. 2, as percentage of the LHV of the biomass inlet. The thermodynamic analysis revealed that the generated electricity at the SOFC unit could, under ideal conditions, correspond to the 26.7% of the LHV of the biomass feed, while another 60.8% of the latest could still be fed to the steam turbine. Considering that the typical electrical yield of a steam turbine was about 25% [16], another 15% of the LHV of the initial biomass could be converted to electricity there, rising the overall electrical yield to 43.3%. It must be noted that, in the analyses it was assumed that along with hydrogen, carbon monoxide was also burned in the SOFC, at an equal extent, contributing almost 36% of the electrical power generation in the cell. Although carbon monoxide is a SOFC fuel, the extend of its combustion was mostly depending on the electrocatalyst, and in any case seemed to be a critical point of the overall procedure.

According to the present analysis, as the hydrogen content of the biomass rises, more steam is involved in the reforming stage. The result is a further increase of the amount of hydrogen involved in the integrated process. Fig. 3 depicts the amount of hydrogen, which enters the SOFC, as the elemental hydrogen in biomass increases from 5–10%. As it can be seen from the figure, the increase of the hydrogen content of biomass is accompanied by a proportional increase of steam’s hydrogen involved in the process. The electrical efficiency of the combined process exhibited a positive dependence on the hydrogen content of the biomass feedstock, as shown in Fig. 4.

4. Conclusions

The main parameter concerning the integration of fuel cells technology in thermochemical processes of biomass conversion is the sufficient heat energy production in the cell in order to cover the thermal requirements of the thermochemical conversion of biomass. Steam gasification is the most energy demanding process, but it facilitates the direct feed of the solid oxide fuel cell. From the thermodynamic analysis of the integrated process of biomass gasification of the solid oxide fuel cell, it becomes obvious that the overall heat generated can cover the heat demands of the reforming procedure and furthermore allow the production of extra electrical power at a conventional heat engine. The extra hydrogen introduced in the process, during the reforming stage, can enhance the electrical efficiency. Of course one must take into account the thermal losses in the several stages of the overall process, which were neglected in the present study. Furthermore, the most questionable assumption
is probably the one referring to 80% utilization of the carbon monoxide, under conditions of fuel dilution. CO utilization over the usual Ni-YSZ anodes of typical SOFC devices is usually much lower than H₂ utilization. Although the oxidation rate of CO is reported to be comparable to that of hydrogen over CeO₂ anodes, the subject needs further clarification [17].

The integrated process of biomass gasifier and a solid oxide fuel cell (SOFC) was studied in terms of thermodynamics. Since, both processes perform around 1000 °C, heat integration is one of the benefits of the proposed scheme, according to which, the cathode outlet of the cell can be directly fed to the gasifier. The thermodynamic analysis was based on the regulation of oxygen consumption in the cell, so that, the depleted air fed to the gasifier, led to the minimization of the total combustion reactions in the latest. According to the assumption, that the hydrogen content of the biomass feedstock is totally converted to hydrocarbons (methane for simplicity), during gasification under oxygen lean conditions, while the remaining carbon is only partially oxidized to carbon monoxide, as well as that both hydrogen and carbon monoxide were both oxidized in the SOFC, at the appropriate extent, the energy balance revealed that the process can be auto-thermal. Furthermore, and due to the utilization of the hydrogen content of steam utilized in the reforming stage, the overall efficiencies to electrical power could reach very high levels.

Acknowledgment

We thank the Ministry of Education and EC for supporting this research project under the program PYTHAGORAS II.

References