Assessment of innovative reforming procedures for biogas obtained from organic fraction of solid municipal waste

D. Borello, A. Calabriso, A. Marchegiani, F. Rispoli

Dipartimento di Ingegneria Meccanica e Aerospaziale, Sapienza University of Rome
Via Eudossiana, 18, Rome, I00184, Italy

domenico.borello@uniroma1.it
andrea.calabriso@uniroma1.it
andrea.marchegiani@uniroma1.it
franco.rispoli@uniroma1.it

Summary:

In the present paper reforming technologies for the treatment of biogas from municipal solid wastes are discussed. An approach based on the well-known ASPEN Plus software was adopted for the simulation of the whole process, assuming equilibrium conditions for the reactions development. The well-established steam-reforming, the dry reforming and an innovative two-steps reforming (including the basics of both models) were considered. A preliminary assessment was carried out comparing the predictions and experimental results of the steam-reforming procedure of diesel fuel. Then, the validated model was applied to the different schemes. The dry reforming (at 800 °C) showed better reforming efficiency if compared to steam reforming (at 600°C). However, carbon deposition occurs when dry reforming is in play. On the other hand, the two-steps technique demonstrated to be able to solve the problem of carbon deposition guaranteeing a very good efficiency.

Keywords:
OFMSW, Reforming, Aspen

1. INTRODUCTION

In the palette of the new, innovative concepts for the Combined Heat and Power (CHP) production, high temperature fuel cells represent the most promising technology due to its potential to use renewable sources reducing emissions (Farhad et Al., 2010; Kuchonthara et al., 2002). In particular, the Solid Oxide Fuel Cells (SOFC) are considered a suitable solution for CHP because they work at high temperatures (from 600°C to 1000°C) and then they are able to feed bottoming power cycles or district heating (Kimihiro et al., 2010). Furthermore SOFCs have high conversion efficiency and the capability to work with a large number of different fuel including biogas and (reformed) hydrocarbons (Shiratori Y. et al., 2010; Ahmed et al., 2002). Contrary to the PEMFCs, CO obtained by biomass, biogas or hydrocarbons reforming it is not a poison for the cell but it can be used as a fuel. On the other hand, unreformed fuel can hardly be treated performing internal reforming inside the cell. This is particularly relevant when biogas "dirty" gases are used such as biogas from wastes and/or heavy hydrocarbons. To this end, the reforming represents a very important research field, in the development of SOFC based power systems, aiming at minimizing of energy costs using "poor" fuel and maximizing of reforming efficiency. Several parameters influence reforming such as choice of proper catalysts, residence time, reforming mechanisms. Here we present and compare two different approaches: the well established steam reforming (SR) (Ming et al., 2002; Gallucci et al., 2004) and the dry reforming (DR) (Lau et Al., 2011; Nematollahi et al., 2011). The last approach can represent an interesting solution as it use CO_2 for fuel pre-treatment at high temperature (up to 800 °C) avoiding the production of high temperature steam (at 600°C). Furthermore, when treating biogas, the required CO_2 is present in the fuel itself and it will be available for the reforming without any additional costs (in terms of heating), provided that the CO_2 fraction in the biogas is at least stoichiometric. This aspect makes particularly interesting adoption of dry reforming. On the other hand, this approach is not well assessed yet as, for example, in dry reformers often carbon formation reactions occur, leading to a catalysts poisoning due to the deposition of solid carbon particles. Here we investigated the reforming of two kind of fuel: biogas produced by anaerobic digestion of Organic Fraction of Municipal Solid Waste (OFMSW) and a representative liquid hydrocarbons surrogate of diesel ($C_{16}H_{34}$). The second one is considered because of its very high hydrogen volumetric density, (100 kg_{H_2}/m^2), and gravimetric density (15% H_2). The other represents the best possible solution for disposal of a large part of municipal wastes. Biogas from municipal solid waste can represent a good solution for energy generation free from carbon dioxide emissions. The most common procedure to obtain biogas from municipal waste is the anaerobic digestion. This process consists in the accumulation of wastes in concrete storage tanks for an appropriate period (30-60 days) at appropriate temperature (20-50 °C) in order that fermentation occurs (Ferrer et al., 2008; Zupancic et al., 2003). The storage period and operative temperature depend on the bacteria activity and their nature. Mesophilic bacteria, for example, interact with the waste substrate in a temperature range around 35 °C and the needed period for total decomposition is roughly 30 days. The anaerobic digestion consists of three stages (Appels et al., 2008):

- Hydrolysis: here complex substrates are synthesized in fatty acids, ketones and alcohols.
- Acid fermentation: where formation of hydrogen, carbon dioxide, acetic and formic acid occur from fatty acids.
- Methanation: methane production from acetic and formic acids, CO_2 and H_2 reactions.

$$CH_3COOH \rightarrow CH_4 + CO_2$$
$$4\ H_2 + CO_2 \rightarrow 2\ H_2O + CH_4$$

$$4\ HCOOH \rightarrow 3\ CO_2 + CH_4 + 2\ H_2O$$

After obtaining biogas a reforming process is needed to produce clean and appropriate fuel to feed FCs. High Temperature Fuel Cells (HTFC) can be used in Combined Heat and Power (CHP) generation with high efficiency. The fuel adopted can be a mixture of hydrogen and light hydrocarbons. Hydrocarbons such as methane, ethane, propane and carbon monoxide, contrary to the Low Temperature Fuel Cells (LTFCs), do not poison the catalysts of the fuel cell. SOFCs (Solid Oxide Fuel Cells) that work at temperature of 1000°C can have an internal reforming due to its high operative temperature. In this work, reformed gas from diesel fuel and from biogas are compared. Experimental data of diesel fuel reforming are used as reference for assessing the reforming model developed in ASPEN PLUS®. The validated model will then applied to the analysis of biogas steam reforming to improve the efficiency of the process. Steam reforming process is coupled with a dry reforming reactor. The results of this two steps reforming will be analyzed and compared with the results obtained from biogas steam reforming. The present analysis was made by means of detailed model developed using Aspen Plus® chemical engineering software. A sensitivity study at the variation of operating conditions (temperature, pressure and S/C ratio) is carried out. Carbon deposition is also investigated.

2. REFORMING MODEL

Aspen is a commercially available simulator for the zero-dimensional analysis of energy systems, has strict thermodynamic functions and physical property database. It can be very useful for analyzing chemical processes by entering some parts of developed in-house routine in programming language, such as Fortran or C++. In the present computation ASPEN Plus did not consider the residence time and the catalyser influence on reforming. The simulations were performed in stationary conditions and the fluid properties were described on the basis of the Peng-Robinson state equation.

2.1. Steam reforming

Steam reforming process requires an amount of water in initial mixture. The molar ratio S/C (steam/carbon) is usually a value between 2 and 4 (Qimin Ming et al., 2002). Steam reforming is usually performed at 600°C (Sun et al., 2004). The chemical reactions that occur in the reformer are the following:

$$CH_4 + H_2O + 226\ KJ/mol \rightarrow 3H_2 + CO \qquad (1)$$
$$CH_4 + 2H_2O + 165\ KJ/mol \rightarrow 4H_2 + CO \qquad (2)$$

An amount of heat is required to allow to the reactions to shift their equilibrium to the right hand side. Here the needed heat is supplied from recirculation from exhaust gas. However in steam reforming process water gas shift (WGS) and the Boudouard reactions can occur (Dagle et al., 2008; Foo et al., 2012)

$$H_2O + CO \rightarrow H_2 + CO_2 + 41\ KJ/mol\ (WGS) \qquad (3)$$
$$2CO \rightarrow CO_2 + C + 173\ KJ/mol\ (Boudouard\ reaction) \qquad (4)$$

The equilibrium of the first one at high temperature change its verse, so it will occur the WGSR (Water Gas Shift Reverse), the hydrogen will be converted in water again. The second one is the cause of the carbon deposition (CD) and the poisoning of catalysts due to the solid particle carbon formation.

2.2. Dry reforming

Dry reforming process occurs without water. The reactions are the following:

$$CH_4 + CO_2 + 247{,}3\ \text{KJ/mol} \rightarrow 2H_2 + 2CO \qquad (5)$$
$$CO_2 + H_2 + 41{,}2\ \text{KJ/mol} \rightarrow H_2O + CO\ (\text{WGSR}) \qquad (6)$$

In this case the Boudouard reaction (4) can occurs easily due to the absence of water in the mixture. Consequently the catalysts used for this process will be different compared with steam reforming catalysts and should be appropriate to higher temperatures because the optimal temperature of the process is 1173 K. As shown, for one mole of methane two moles of hydrogen and two moles of carbon monoxide are generated. The CO can be used as a fuel as it’s an intermediate product of carbon oxidation reaction. Even if dry reforming is energetically more onerous than steam reforming it could be used when water supply would be difficult.

3. REFORMING ANALYSIS

3.1. Model assessment of diesel fuel

To validate the developed model we compared our results if diesel fuel reforming with results of a parallel analysis carried out in our laboratory of DIMA (Dipartimento di Ingegneria Meccanica e Aeronautica). The comparison showed a good agreement between experiments and computations.

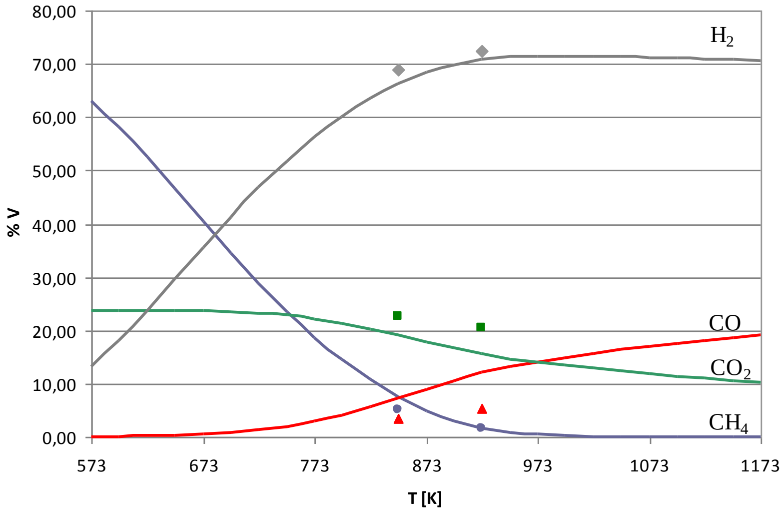

Figure 1 – Comparison between computational and experimental data from diesel fuel reforming (p = 1bar, S/C = 3)

Table 1 – Diesel fuel reforming experimental data

T [K]	H_2	CO	CO_2	CH_4
848	69	3.5	22.5	5
923	72.5	5.5	20.5	1.5

3.2. Analysis of reforming procedures of biogas from OFMSW

The reforming test is made through a box analysis with Aspen Plus features. Two mass streams are connected at the inlet and at the outlet of a Gibbs reactor.

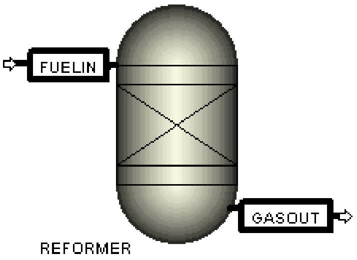

Figure 2 – Reforming scheme

At the inlet a mixture of gases is introduced in to the reactor. The biogas composition is reported in Table 2.

Table 2 – Biogas composition

Compound	% V
Hydrogen	8
Methane	60
Carbon dioxide	32

A certain amount of steam is added in order to facilitate reforming procedure. Usually the molar ratio S/C is kept in a range between 2 and 3 (Hardiman et al., 2004; Zou et al., 2010). In the following paragraphs the results of reforming simulations with ASPEN® software are shown.

3.2.1. Steam Reforming

The charts related to the steam reforming tests made with ASPEN PLUS are shown in Figure 3.

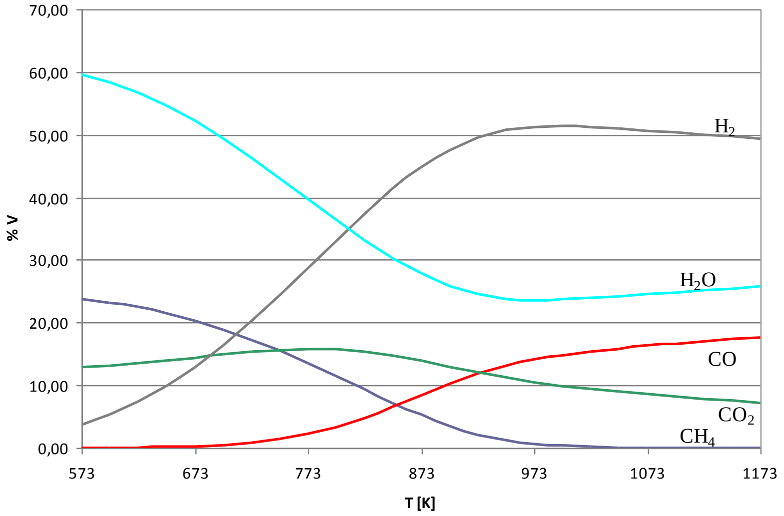

Figure 3 – Temperature sensitivity analysis at S/C = 2.5

Over 973 K (700 °C) the whole amount of methane is converted. When temperature increases WGSR (Water Gas Shift Reverse) begins to occur consuming the H2 produced producing water. So the optimal trade-off seems to be around 973 K where we obtained maximum H2 and minimum H2O content. Nevertheless operative temperature of reformer has been chosen as 873 K for three reasons:

- Energy consumption of the system;
- Lower amount of CO2 in the product mix and higher amount of H2O. The latter circumstance is useful as it can be used in recirculation flow to reach the imposed S/C ratio equal to 2.5.
- The small methane fraction in the product can be easily reformed in a SOFC due to the high operative temperature between 973 and 1273 K.

In the next chart the results of a sensitivity analysis on S/C ratio at constant temperature 873 K are shown.

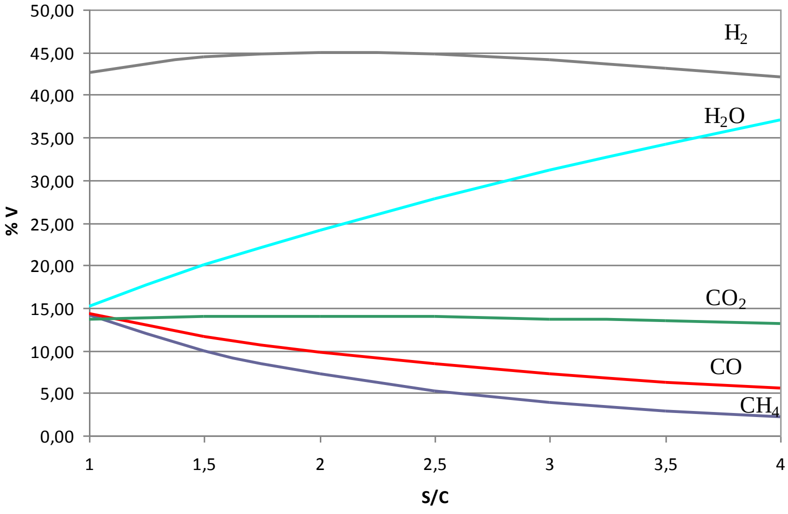

Figure 4 – S/C sensitivity analysis at T = 873 K

The choice of optimal S/C ratio is subordinate to the amount of energy needed to boil off a higher quantity of water, so it is important to keep S/C as low as possible. On the other hand low quantities of water could promote Boudouard reaction (4) leading to deposit of carbon particles that can be occlude the pores of catalyst active sites. The maximum amount of hydrogen is yielded between 2÷3 value of S/C ratio. In Figure 5 the relationship between S/C ratio and carbon particles quantities produced is shown.

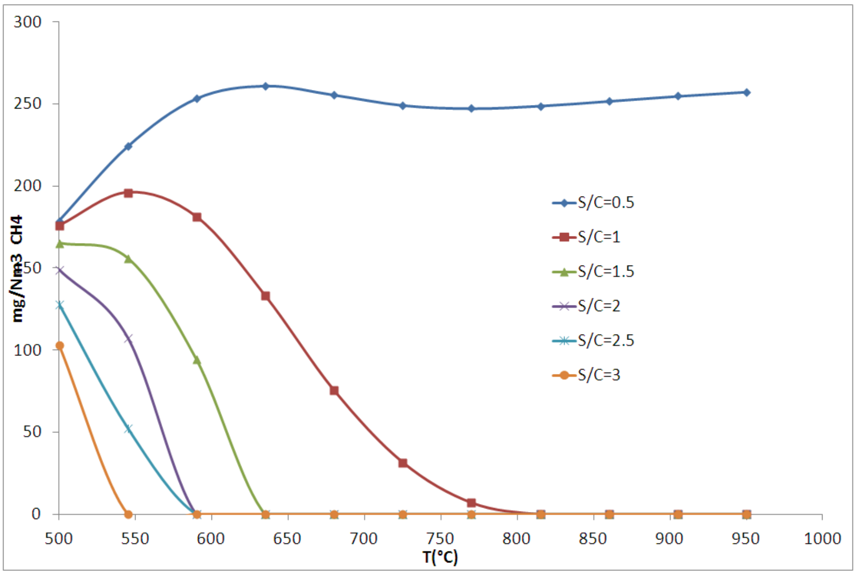

Figure 5 – Carbon deposition with temperature and S/C variation

The optimal choice is the S/C value is equal to 2.5 because as for S/C=3 the limiting temperature to avoid carbon deposition is lower than operating temperature. So it has been chosen a value of 2.5 that is less expensive (from energetic point of view) than S/C=3.

3.2.2 Dry Reforming

Dry reforming can be considered as a feasible alternative when water is not available and also when the quality of biogas is poor and a high CO_2 content is present. Temperature sensitivity analysis of dry reforming, at 1 bar pressure, is shown in the Figure 6. The composition of biogas from FORSU is the same used for steam reforming (Table 2).

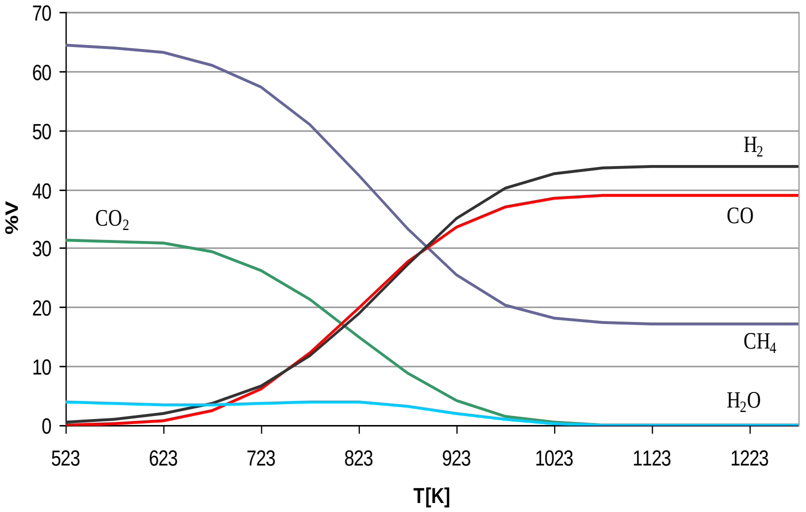

Figure 6 – Temperature sensitivity analysis of dry reforming

It is shown that in this chart operative temperature should be higher than in the steam reforming. The temperatures range of interest is 900÷1100 K. Over 1100 K the mole fraction of the species remains constant. The small quantity of water produced by WGSR at lower temperatures (i.e. 823 K) is consumed by steam reforming reactions at higher temperature. The effect is the neutralization of CO2 quantity and the increasing of CO amount in the resulting mixture.

$$CO_2 + H_2 + 41{,}2\ KJ/mol \rightarrow H_2O + CO\ (WGSR) \qquad (6)$$

$$CH_4 + H_2O + 226\ KJ/mol \rightarrow 3H_2 + CO \qquad (1)$$

$$CH_4 + 2H_2O + 165\ KJ/mol \rightarrow 4H_2 + CO \qquad (2)$$

Table 3 - Volume percentage of each species in products mix of steam (S/C=2.5, T=873K) and dry (T=1073K) reforming at 1 bar.

Species	*% v steam reforming*	*% v dry reforming*
H_2	*45*	*44*
H_2O	*28*	*0*
CH_4	*5*	*17*
CO_2	*14*	*0*
CO	*8*	*39*

Even though in the steam reforming process the whole amount of CH_4 is converted in H_2, at higher temperatures, the dry reforming is able to neutralize the presence of CO_2 and H_2O. However, in the dry reforming, the SOFC can be subject to catalysts poisoning because of carbon particles formation that is the main issue of dry reforming. In order to control the phenomena, the Carbon Deposition Diagram (CDD) can be used (Farhad, Hamdullahpur, 2009). It was derived from experimental data and it is shown in Figure. On the basis of the composition of mixture it’s possible to establish if the mixture is in the “carbon deposition” or in the “no-carbon deposition” zone. The curve that divides the two zones depends on the operative temperature of the process and it’s called Carbon Deposition Boundary (CDB). Lower are the H/C and O/C ratios of the reactant mixture and higher is the probability of carbon deposition (and viceversa). Three different fuel compositions are shown in the Figure 7.

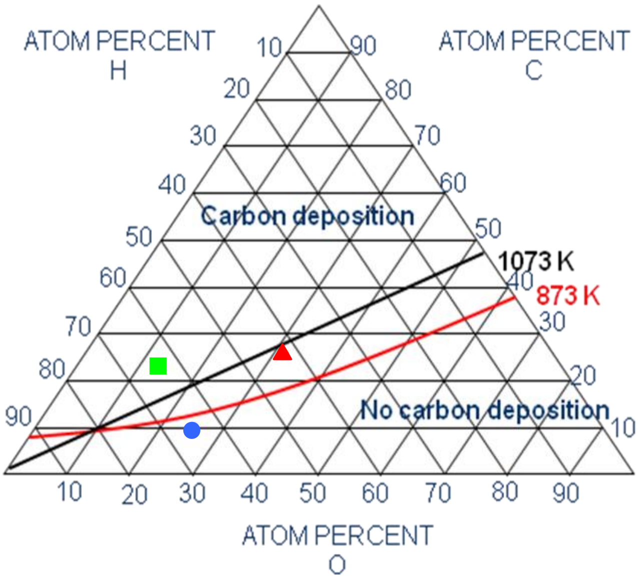

Figure 7 – Atomic percentage composition of inlet flow (steam reforming: blue dot; pure biogas: green square; biogas with CO_2 adding: red triangle) (Farhad, Hamdullahpur, 2009)

The green square represents the composition of pure free water biogas from OFMSW while the blue dot represents the atomic composition of biogas with S/C equal to 2.5.

From Figure 7 it can be seen that the first composition, represented by the green square, is in the carbon deposition zone. In order to lie in the no-carbon deposition zone a dilution with other species increasing the oxygen atoms content is needed. A possible route is to increase CO_2 in the inlet mixture. With a CO_2 content of 3.5 times higher than the initial CO_2 content in the OFMSW biogas composition, the molar percentage of the mixture would become the following:

1) CH_4 33.3%
2) CO_2 62.2%
3) H_2 4.5%

This atom composition (shown in the Figure 7 with the red triangle) allows avoiding carbon deposition for temperatures higher than 1073 K as can be seen by the CDD. On the other hand when operating at 873 K, carbon deposition will occur as the position relative to the actual mixture composition lies under the CDB curve.

3.2.3. Two Steps Reforming

To assess an optimized procedure for biogas reforming a two-step technique is here proposed. This system is capable to perform the reforming at very low volume percentage of water. The process is implemented by splitting the inlet biogas flow in two fluxes. The first one goes to the first reformer where a steam reforming is adopted with S/C ratio equal to 2 and operative temperature 873 K. The remaining biogas flows to the second reformer, operating at 1173 K, and it has mixed with reformed gas coming from the first reactor. This process has been called Two Steps Reforming (TSR) and its ASPEN PLUS® simulation scheme is shown in the figure 8.

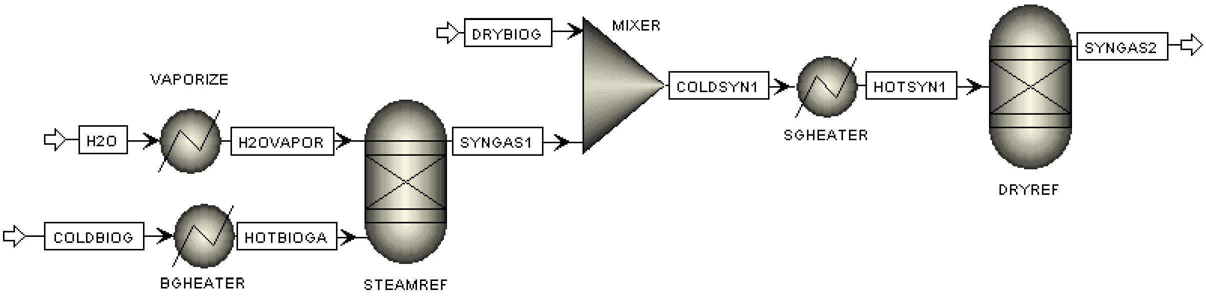

Figure 8 – TSR scheme

The results of the process are shown below (table 4). Molar flow of each species has been indicated in kmol/h and stream names are related at the Figure 8.

Table 4 – Molar flow of the streams of TSR in [mol/s]

Stream	Coldbiog	H_2O	Syngas1	Drybiog	Hotsyn1	Syngas2
CH_4	0.100	-	0.036	0.067	0.102	0.002
CO_2	0.053	-	0.069	0.036	0.105	0.041
CO	-	-	0.048	-	0.048	0.212
H_2	0.013	-	0.023	0.009	0.232	0.467
H_2O	-	0.200	0.119	-	0.119	0.084
Total Flow kmol/h	0.167	0.200	0.295	0.112	0.606	0.806

The fraction of splitted biogas was chosen in order to have, at the exit of the mixer (HOTSYN1), a mixture containing roughly a stoichiometric molar ratio between CH_4 and CO_2. This was made in order to minimize the CO_2 content in synthesized gas considering that the favored reactions at 1073 K are (5) and (6). Using this approach the amount of methane in the final mixture is almost zero while in the dry reforming there was a final amount of non-reacted methane of 17% in volume. Carbon deposition does not occur due to the presence of residual water from the previous reforming and the collocation of atomic composition of HOTSYN1 stream over CDB curve.

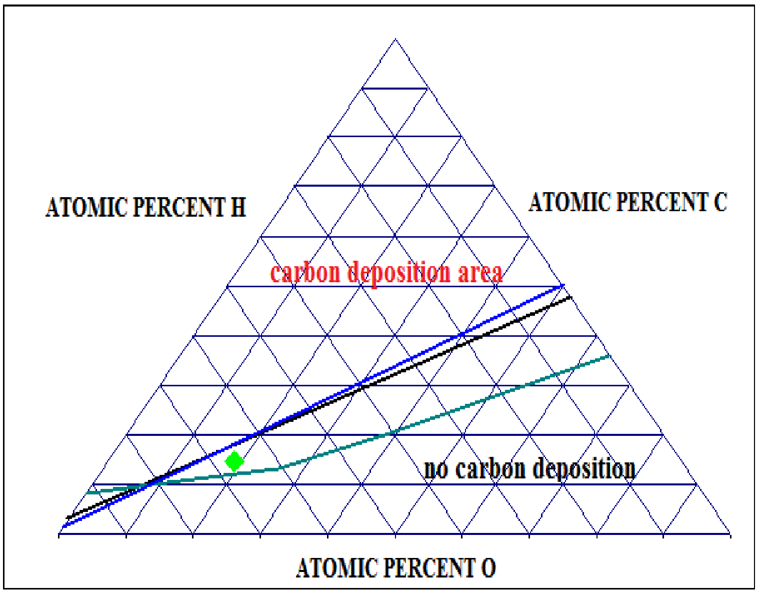

Figure 9 – C-H-O composition of HOTSYN1

The S/C ratio for each stage is:

Table 5 – S/C ratios in two-steps reforming

	Biogas carbon species [mol/s]	Water [mol/s]	Residual water [mol/s]	S/C
SR	0.100	0.200	-	2.00
DR	0.151	-	0.119	0.78
GLOBAL	0.167	0.200	-	1.20

The global content of saved water compared with steam reforming is 0.22 mol/s. Consequently the saved thermal power for not producing super heated steam is equal to 14 kW.

4. STEAM, DRY AND TWO-STEPS COMPARISON

In order to compare the efficiency of the three different processes, an energetic analysis will be carried out. Considering the reaction enthalpy of each component that is present in the final mixture of reformed gas (9-12) efficiency will be calculated by:

$$h_r = \sum h^0_{f,react} - \sum h^0_{f,prod} \qquad (9)$$

$H_2 + ½ O_2 \rightarrow H_2O$ (g) $\qquad h_{r,H_2} = 241.8 kJ/mol \qquad (10)$

$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ (g) $\qquad h_{r,CH_4} = -50.75 + 393.5 + 2 \cdot 241.8 = 826.35 kJ/mol \qquad (11)$

$CO + ½ O_2 \rightarrow CO_2 \qquad h_{r,CO} = -110.5 + 393.5 = 283 kJ/mol \qquad (12)$

The inlet biogas for each process has the same molar flow J = 0.28 mol/s. The initial and final temperatures of each flow entering in the reforming process are set equal to those temperatures of steam and dry reforming (T_{in} = 298 K and T_f = 1073 K).

4.1. Steam reforming

The steam reforming simulation was based on the following scheme:

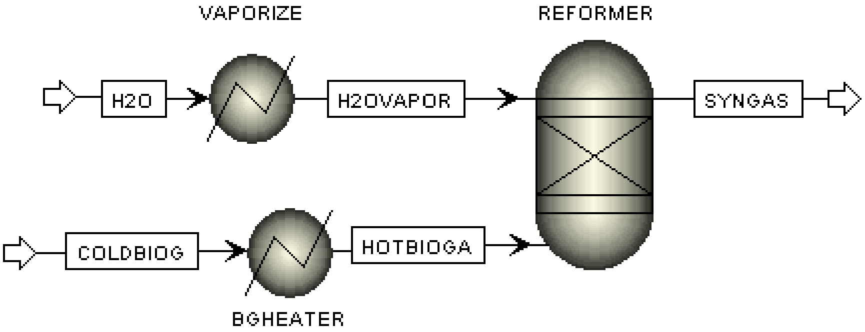

Figure 10 – Steam reforming scheme

Biogas and water are considered to be at ambient temperature (298 K) at the starting point. Each mass stream is heated up to the reforming operative temperature, before to convey it into the reactor, and the resulting gas mixture is heated up to 1073 K is close to a SOFC operative temperature. The operative temperature of the steam reforming is 873 K and the operative pressure is 1 atm. The molar flow of each species of the synthesized gas at 873 K is shown in Table 6. It shows also the Lower Heating Value (Hi) of the mixture of reformed gas that has been calculated with equation (13).

$$H_{i,sr} = \frac{\sum_i J_i h_{r,i}}{\sum_i J_i} \qquad (13)$$

Table 6 – Hi value of syngas from biogas steam reforming

	J [mol/s]	h_r [kJ/mol]
CH_4	0.050	826.35
CO	0.078	283.00
H_2	0.417	241.80
CO_2	0.129	
H_2O	0.259	
J_{tot}	0.933	
H_i		176.01

The Hi of biogas is calculated in the same way as shown above:

Table 7 - Hi value of biogas

Specie	J [mol/s]	h_r [kJ/mol]
metano	0.167	826.35
CO		283.00
H2	0.022	241.80
CO2	0.089	
J_{tot}	0.278	
Hi_{biogas}		515.15

In the table 8 the thermal power required by each heater is indicated (Figure 10) and then the global efficiency of the process has been calculated with the equation (14).

$$\eta = \frac{J_i H_i}{J_{biogas} H_{i,biogas} + \sum_i Q_i} \qquad (14)$$

Table 8 – Efficiency of biogas steam reforming

	J [mol/s]	H_i [J/mol]	Q [W]
$H_{i,syngas}$	0.93	176008	164079
$H_{i,biogas}$	0.28	515154	143098
Q_{vap}			27028
$Q_{bgheater}$			7672
Q_{ref}			24885
Q_{syngas}			7223
η_{dr}	0.78		

4.2. Dry reforming

In the dry reforming, water inlet flow is null. The scheme used for ASPEN PLUS® simulation is shown in figure 11. The biogas has heated up to 1073 K before to get inside the reformer. With the equations (13) and (14) Hi and efficiency have been calculated. The results are shown in Table 8 and Table 9.

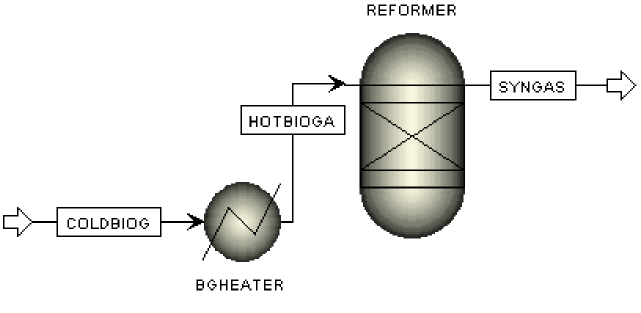

Figure 11 – Dry reforming scheme

Table 9 – Hi value of synthesized gas from dry reforming

	J [mol/s]	h_r [kJ/mol]
CH_4	0.078	826.35
CO	0.178	283.00
H_2	0.197	241.80
CO_2	0	
H_2O	0	
J_{tot}	0.453	
H_i		358.39

Table 10 – Efficiency of dry reforming

	J [mol/s]	H_i [J/mol]	Q [W]
$H_{i,syngas}$	0.45	358390	162271
$H_{i,biogas}$	0.28	515154	143098
Q_{vap}			0
$Q_{bgheater}$			11149
Q_{ref}			22847
η_{dr}	0.92		

The global results of the procedure are a clear improvement of the reforming efficiency. Dry reforming cannot be used due to the issue of carbon deposition that cause the degradation of the catalysts. Furthermore the reforming gas leaving the dry reformer has a higher temperature with respect to the steam reforming and the required heat for reaching SOFC operating temperature is lower. However, a third way has been followed.

4.3. Two-steps reforming

As shown before this process is composed by two reforming reactor connected in series. The first one is used for a steam reforming while the latter is used for a reforming at 1073 K in order to aid dry reforming reactions. The same quantity of biogas (0.28 mol/s) has processed, like in previous steam and dry reforming analysis. Here, the molar flow has been split in two. The first fraction is the 60% of total flow, the latter is the remaining 40% and it has been introduced in the second reactor. The nomenclature of the following Tables refer to the Figure 8.

The molar fraction of synthesized gas from TSR and its Hi is calculated in the Table 11.

Table 11 – Hi value of synthesized gas from two-steps reforming

	J [mol/s]	h_r [kJ/mol]
CH_4	-	826.35
CO	0.212	283.00
H_2	0.467	241.80
CO_2	0.041	
H_2O	0.084	
J_{tot}	0.804	
Hi		215.00

The efficiency of the whole process is shown in the Table 12.

Table 12 – Efficiency of two-steps reforming

	J [mol/s]	H_i [J/mol]	Q [W]
Hi_{syngas}	0.80	215149	172956
Hi_{biogas}	0.28	515154	143098
Q_{VAP}			12974
$Q_{BGHEATER}$			4603
$Q_{STEAMREF}$			13818
Q_{DRYREF}			24703
$Q_{SGHEATER}$			8354
η_{dr}	0.83		

4.4. Comparison

In the Table 13 are summarized the molar percentage of each component for the three cases and their relative efficiencies.

Table 13 – Comparison in composition and efficiency between steam, dry and two-steps reforming

Species	% v steam reforming	% v dry reforming	% v two steps
H_2	45	44	58
H_2O	28	0	10
CH_4	5	17	0
CO_2	14	0	5
CO	8	39	26
η	0.78	0.92	0.83

The higher efficiency is given by dry reforming even though the main issue (Carbon Deposition) of this process makes dry reforming unsuitable. With the two steps reforming the energy supply is lower than in steam reforming. From data in Figure 5 it can be seen that using the S/C ratio equal to 2 at the temperature of 873 K, carbon deposition can be avoided. Furthermore lower value of S/C ratio can be used because of methane conversion in H_2 will be completed in the next step where dry reforming is set. This is not possible when steam reforming is considered. The amount of heat needed to heat and vaporize water decreases from 27 kW to 13 kW. After the first step, the water quantity (cft Table 4) is not totally consumed. Then the S/C ratio in the second reforming at 1073 is quite close to 1. This value allows operating at 1073 K without carbon deposition, see Figure 5. Table 13 shows that with the TSR the amount of CO_2 and water in the final mixture is significantly lower, from 14 % (in the SR) to 5 %, while the CO and H_2 content is higher. No methane is present. This reduces the risk of carbon deposition as can be seen from C-H-O triangle. As a matter of fact with the decreasing of CH_4 and the increasing of CO content between the two-steps the location of fuel composition moves towards down-right in the C-H-O chart. Then it moves in the no-carbon deposition zone avoiding the damage of catalysts.

5. CONCLUSIONS

In this paper a comparison between steam and dry reforming of biogas from organic municipal waste was carried out. As a first step we validated the reforming of diesel fuel analyzed wirg Aspen Plus® against the experimental data obtained in our laboratory of DIMA. The computational data were considered valid and close to the experimental data. Then, using the model implemented with Aspen Plus®, steam and dry reforming techniques were examined. Sensitivity analysis on temperature for both reforming process and sensitivity analysis on S/C ratio for steam reforming are made. From sensitivity analysis optimal temperature and S/C ratio for steam reforming are chosen, respectively 2.5 for S/C ratio and 873 K for temperature. Dry reforming temperature was chosen as 1073 K. Energy analysis demonstrated that dry reforming is more efficient than steam reforming. The efficiency of the first one is equal to 0.92 while the efficiency of the latter equal to 0.78. Furthermore, in dry reforming, CO_2 and H_2O are totally annulled and only reacting species (CO, CH_4 and H_2) are present in the resulting mixture. The issues due to the carbon deposition, for dry reforming procedure, made it hard to realize. In order to minimize the energy consumption and to maximize the efficiency, eliminating carbon deposition issue, a third way for reforming process was realized. Two steps reforming procedure consisting in the coupling of a steam reforming, at 873 K and S/C ratio equal to 2, with a reforming, without adding of water at temperature of 1073 K, was analyzed. This procedure gives a global efficiency equal to 0.83. Methane is totally consumed and hydrogen production was maximized with a final molar fraction equal to 58 % against the 45 % of steam reforming. Resulting CO_2 and H_2O are minimized with respectively 5 % and 10 % of molar fraction content in the synthesized gas.

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Nomenclature

h enthalpy, kJ/mol

J molar flow, mol/s

$\dot{m}$ mass flow rate, kg/s

p pressure, Pa

P power output, W

Δp different of pressure, Pa

Q volume flow rate, m^3/s

H_i High heating value, kJ/mol

Greek symbols

ρ density

η efficiency

Subscripts and superscripts

f formation

0 standard

r reaction

react reactants

prod products

sr steam reforming

dr dry reforming

ts two steps reforming

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