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# Thermodynamic analysis and performance of a 1 kW bioethanol processor for a PEMFC operation $\stackrel{\text{tr}}{\sim}$

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# Abstract

A thermodynamic analysis of a bioethanol steam reforming processor for CO-free hydrogen production was performed. The stages selected to perform CO purification were water gas shift and CO preferential oxidation. In order to optimize the processor efficiency, several configurations were studied. A processor efficiency of 69% for a steam/carbon ratio (S/C) of 4.8 was achieved taking advantage of the heat released during the exothermic stages. An efficiency close to 28% at the same S/C ratio for a bioethanol processor-PEMFC system, which includes a heat recovery system for off-gas from the fuel cell anode, was obtained.

To produce a CO-free hydrogen rich stream, a 1 kW bioethanol processor was designed, built and operated, based on previous simulation studies. A new catalyst developed in the Institute of Catalysis and Petro-chemistry (ICP-CSIC) and tested for more than 500 h, that demonstrated excellent results at laboratory scale, was selected for the steam reforming stage. From bioethanol processor operation, a hydrogen rich stream, with CO composition as low as 3 ppmV was obtained, which is able to supply a PEMFC.

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Keywords: Bioethanol; Steam reforming; Fuel processor; Fuel cell; Hydrogen

# 1. Introduction

Towards the hydrogen economy, the development of more efficient processing systems has a special importance. Nowadays, hydrogen production is based on natural gas reforming by different technologies (steam reforming, auto-thermal reforming or partial oxidation), used largely for refinery processes and petro-chemistry industry. However, only a small quantity of this production is used for distribution [1]. The development of a fuel cell technology will increase the amount of high production reforming stationary plants and also small-distribution hydrogen plants. Upcoming studies performed in industrialized countries (USA, Japan, EU) show that, distributed power generation [2] based on fuel cells powered by renewable hydrogen and coupled to electricity distribution network, is the key to optimize power resources for a medium-term scenario [3]. Hydrogen produced for fuel cell applications, especially for PEMFC, needs very high purity levels (CO < 50 ppmV) to avoid electrocatalyst poisoning

from the anode. Several strategies to achieve this CO purity goal are possible: chemical purification processes based on water gas shift followed by CO preferential oxidation or, pressure swing adsorption (PSA) [4,5]. In this processor, a chemical purification process was chosen in order to reduce the pressure at which the reforming reaction operates. The ethanol reforming reaction is endothermic and thus favoured by low pressures. For this reason, the best solution is to choose a process which does not need a high feed pressure and thus allows a reduction in the operational reformer pressure. Additionally, comparative studies performed with ethanol and other fuels such as methanol, methane, gasoline and DME, demonstrate that the ethanol reforming option allows using an ethanol processor of intermediate size between those employed for methanol and methane where operation with the latter fuel requires the largest processor volumes for the same power production [6].

The aim of this work was to analyse the applicability of hydrogen CO-free production by bioethanol steam reforming, complemented with water gas shift (WGS) and CO preferential oxidation (COPROX) as hydrogen purification stages, for electricity production by PEMFC. In this sense, for the bioethanol processor-PEMFC system, it was designed a high efficient process capable of producing a process stream with a quality (<50 ppmV) able to supply a PEMFC. To achieve these

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goals, a thermodynamic analysis for different possible system configurations was performed. Finally, a 1 kW bioethanol processor was built and operated in order to analyse its performance in producing a CO-free hydrogen rich stream.

# 2. Experimental

#### 2.1. Thermodynamic analysis

In order to optimize the processor efficiency, energy and mass balances for three possible processor configurations were performed. The experimentally obtained catalytic activities for the catalysts used in the process were included in these calculations.

To calculate the processor efficiency  $(\eta_1)$  it was necessary to consider: (i) the LHV of hydrogen produced and its relation to the LHV of ethanol fed to the processor, (ii) the heat supplied in the vaporization of water and ethanol and (iii) the heat consumed by the steam reforming reaction (1):

$$\eta_1 = \frac{Q_{\rm H_2}}{Q_{\rm ethanol} + Q_{\rm ref} + Q_{\rm vap}} \tag{1}$$

where  $Q_{\rm H_2}$  is the heat generated by hydrogen combustion referred to LHV,  $Q_{\rm ethanol}$  the ethanol combustion heat at standard conditions,  $Q_{\rm vap}$  the heat supplied to vaporize the products feed to the system and  $Q_{\rm ref}$  is the heat consumed by steam reforming reaction.

A processor efficiency improved  $(\eta_2)$  by recovering heat exchanged in the WGS stages is possible by means of (2):

$$\eta_2 = \frac{Q_{\rm H_2}}{Q_{\rm ethanol} + Q_{\rm ref} + Q_{\rm vap} - (Q_{\rm SLT} + Q_{\rm SHT} + Q_{\rm SR})}$$
(2)

where  $Q_{SLT}$  is the heat recovered from WGSR-LT,  $Q_{SHT}$  the heat recovered from WGSR-HT and  $Q_{SR}$  is the heat recovered from reforming reactor outlet stream.

In order to estimate the efficiency of the bioethanol processor-PEMFC system several configurations can be proposed. A plant flowsheet without any energy recovery system is represented in Fig. 1. In this configuration, the heat released by exothermic stages and the enthalpy of the exhaust gases obtained from a PEMFC operation, are not included in the process. Process efficiency ( $\eta_3$ ) was calculated according to the following Eq. (3):

$$\eta_3 = \frac{Q_{\rm FCH_2}}{Q_{\rm ethanol} + Q_{\rm ref} + Q_{\rm vap}} \tag{3}$$

where  $Q_{\text{FCH}_2}$  is the fuel cell electric power.

Including heat exchangers next to reforming, water gas shift and COPROX reaction stages, the unrecovered heat in the scheme proposed in Fig. 1, could be integrated in the process. The heat recovered from these exchangers, would be used to increase the temperature of the stream fed to the reforming reactor.

It is possible to calculate the new process efficiency ( $\eta_4$ ), taking into account the energy recovered from CO purification stages (Fig. 2), from Eq. (4):

$$\eta_4 = \frac{Q_{\rm FCH_2}}{Q_{\rm ethanol} + Q_{\rm ref} + Q_{\rm vap} - (Q_{\rm SLT} + Q_{\rm SHT} + Q_{\rm SR})}$$
(4)

The addition of a further burner which converts the exhaust gases from the fuel cell, can improve the energy efficiency of the system by obtaining part of the heat needed to perform the reforming stage, the most endothermic one of the process (5), (6) (Fig. 3). This exhaust stream is composed of hydrogen, which has not been converted in the fuel cell anode, methane produced as a by-product in the reforming stage and carbon dioxide, final product of water gas shift. For the fuel cell operation, methane



Fig. 1. Bioethanol processor configuration without energy recovery.



Fig. 2. Bioethanol processor configuration with energy recovery.

and carbon dioxide have been considered as inert.

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightleftharpoons 2\mathrm{H}_2\mathrm{O} \qquad \Delta H^\circ = -241.81 \,\mathrm{kJ \, mol^{-1}} \tag{5}$$

$$CH_4 + 2O_2 \rightleftharpoons 2H_2O + CO_2 \qquad \Delta H^\circ = -802.62 \text{ kJ mol}^{-1}$$
 (6)

The process energy efficiency including the energy recovery system and the gas exhaust burner can be estimated by Eq. (7):

$$\eta_5 = \frac{Q_{\rm FCH_2}}{Q_{\rm ethanol} + Q_{\rm ref} + Q_{\rm vap} - (Q_{\rm SLT} + Q_{\rm SHT} + Q_{\rm SR} + Q_{\rm GR})} \quad (7)$$

where  $Q_{GR}$  is the heat from combustion of fuel cell exhaust gas.

The H<sub>2</sub>O/EtOH ratio fed to the processor or steam/carbon ratio (S/C) is an important operation parameter which influences seriously the efficiency results. A high S/C ratio, ensures a good behaviour of reforming catalyst by avoiding carbon deposition on the active phase, and enhances the hydrogen production, as predicted from thermodynamic calculations at these conditions. However, a higher S/C ratio increases the energy necessary to compensate the latent and sensible heat of the additional water feed, to achieve the temperature set points of the reforming reactor inlet, thus diminishing the processor energy efficiency.



Fig. 3. Bioethanol processor configuration with energy recovery and exhaust gas burner.

# 126

# 2.2. Processor design

A 1 kW bioethanol processor was designed and built. In the processor, each reaction stage operates in an isolated mode allowing each catalytic reactor operation be evaluated. High temperature valves were installed, in order to by-pass each reaction stage. Pressure and temperature were recorded continuously. K-type thermocouples placed at the input and output of each catalytic reactor, were used to measure the process temperatures. To measure the pressure drop in different zones of the processor, electronic transducers were used.

For data acquisition and control, SCADA software was designed by the Instrumentation and Process Control Unit of the Institute of Catalysis and Petrochemistry. All reaction parameters such as temperature and pressure, controller output were recorded by means of the *Adkir* user interface software. This software also controlled the set point for mass flow controllers, temperature, liquids flows and pressure. The control architecture of the processor is based on 4–20 mA with a feedback control loop.

Independent diaphragm pumps were used to feed ethanol and water to the system. To achieve the reforming reaction conditions, ethanol and water were first vaporized and subsequently overheated. A Proportional Integral Differential electronic controller TOHO<sup>TM</sup> to control the heat necessary to reach above conditions was used. Plate heat exchangers controlled by PID controllers to adjust the temperature of the streams for WGS and COPROX reactors, were placed before reaction stages. The output control signal was recorded continuously so that the heat supplied to the endothermic process, could be estimated.

To evaluate each reactor conversion as well as the product distribution, several analysis points at different positions were incorporated in the bioethanol processor. The processor performance was monitored with an *Agilent 6890N* chromatograph equipped with TCD and FID detectors. The hydrocarbon products were separated with a porapak Q column. Permanent gases (hydrogen, carbon monoxide, methane and oxygen) were separated by a molecular sieve.

#### 2.3. Catalysts selection and testing

Nowadays, there are no commercial catalysts for ethanol steam reforming, because most catalysts used for these applications suffer from deactivation problems due to carbon deposition on the active phase [7]. Thus, the formulation of a new catalyst able to overcome the operational problems mentioned previously was the first goal. The new bioethanol catalyst developed demonstrated very high activity, with hydrogen production efficiencies close to thermodynamic predictions, 4.5 moles of hydrogen per mole of EtOH feed at the temperature and pressure under consideration (650-700 °C and atmospheric pressure) [8]. An excellent stability for more than 500 h in continuous operation and more than 4000 h for accumulated tests, without deactivation was observed [9]. For water gas shift and COPROX stages, commercial catalysts were used supplied by Süd Chemie and Degussa, respectively. In order to ensure the optimal implementation in a bioethanol fuel cell processor, catalytic activity and endurance tests were performed for the catalyst used in each stage.

To design and size the different reaction stages, numerical simulations of material and energy balances were performed. The conversion and product distribution for each catalyst studied were considered to achieve a final carbon monoxide concentration of 20 ppm.

# 3. Results and discussion

# 3.1. Efficiency estimations of processor and processor-PEMFC system

There are three ways to carry out the bioethanol reforming: steam reforming (8), partial oxidation (9) and auto-thermal reforming (10) [10–14]. Steam reforming is an endothermic reaction, where reaction heat has to be supplied by an external heating device. Conversely, partial oxidation and auto-thermal reforming are exothermic reactions. In these cases, oxygen addition avoids the use of external heating but reduces the efficiency of hydrogen production. The need to feed high purity oxygen is the first drawback of these exothermic processes since the costs of the system for oxygen purification can reach 40% of the final reformer cost [15].

$$CH_{3}CH_{2}OH + 3H_{2}O \rightleftharpoons 6H_{2} + 2CO_{2}$$
$$\Delta H^{\circ} = +173.5 \text{ kJ mol}^{-1}$$
(8)

$$CH_3CH_2OH + \frac{3}{2}O_2 \rightleftharpoons 3H_2 + 2CO_2$$
$$\Delta H^\circ = -620.3 \text{ kJ mol}^{-1}$$
(9)

$$CH_3CH_2OH + 2H_2O + \frac{1}{2}O_2 \rightleftharpoons 5H_2 + 2CO_2$$
$$\Delta H^\circ = -50.3 \text{ kJ mol}^{-1}$$
(10)

In this work, steam reforming was the selected process; because it is possible to produce higher amounts of hydrogen from the ethanol feed, than other reforming processes described previously.

For the processor steady-state operation, the reforming reaction heat is supplied by: (i) exhaust gases not converted in the fuel cell operation, (ii) energy recovered from exothermic stages (water gas shift and preferential oxidation) and (iii) the ethanol combustion, to close the energy balance.

The excess carbon monoxide produced in the reforming stage is converted by the water gas shift reaction (11) which increases the hydrogen production.

$$\operatorname{CO} + \operatorname{H}_2\operatorname{O} \rightleftharpoons \operatorname{H}_2 + \operatorname{CO}_2 \qquad \Delta H^\circ = -41.2 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$$
 (11)

The lower space velocity than that used in reforming is the first drawback of this conversion process. While the reforming reactors usually work around  $100,000 h^{-1}$ , the high temperature water gas shift reactors (WGS-HT) usually work at  $6000 h^{-1}$  and the low temperature ones (WGS-LT) at  $3000 h^{-1}$  [16]. This causes the design volume of the fuel processor to be greatly influenced by the water gas shift reactors size [6], especially in

M. Benito et al. / Journal of Power Sources 169 (2007) 123-130

Table 1			
Process elements used to	evaluate the	process	efficiency

Process component	Model	Reaction parameter	Simulation
Reforming reactor	Yield reactor	$T = 700 ^{\circ}\text{C}, p = 4 \text{bar}$	Product distribution
WGSR-HT reactor	Yield reactor	$T = 400 ^{\circ}\text{C}, p = 2.1 \text{ bar}$	Product distribution
WGSR-LT reactor	Yield reactor	$T = 200 ^{\circ}\text{C}, p = 2 \text{bar}$	Product distribution
COPROX reactor	Stoichiometric reactor	$T = 100 ^{\circ}\text{C}, p = 1.9 \text{bar}$	Product distribution
PEMFC	Stoichiometric reactor	$T = 80 ^{\circ}\text{C}, p = 1.8 \text{ bar}$	Efficiency 80%
B1, B2	Pump	$p = 1$ bar $\rightarrow p = 4$ bar	
B4	Heat exchanger	$T = 25 \circ C \rightarrow 150 \circ C$ , $p = 4$ bar	
B6	Heat exchanger	$T = 700 \circ \text{C} \rightarrow 400 \circ \text{C}, p = 2.1 \text{ bar}$	
B8	Heat exchanger	$T = 400 \circ \text{C} \rightarrow 200 \circ \text{C}, p = 2 \text{ bar}$	
B10	Heat exchanger	$T = 200 ^{\circ}\text{C} \rightarrow 100 ^{\circ}\text{C}, p = 1.9 \text{ bar}$	
B12	Heat exchanger	$T = 100 \circ C \rightarrow 80 \circ C$ , $p = 1.8$ bar	
B14	Heat exchanger	$T = 80 \circ \text{C} \rightarrow 25 \circ \text{C}, p = 1.7 \text{ bar}$	

Reactor models used to simulate the process: yield reactor (product distribution and conversion are established) and stoichiometric reactor (conversion is controlled by reagent ratios).

on-board applications. To increase the gas hourly space velocity to  $30,000 \text{ h}^{-1}$  and decrease catalyst costs to \$ 1 kW<sup>-1</sup> [17] are DOE goals for this purification stage, in order to apply this technology in on-board processors, where the processor size is a critical issue.

The process parameters used to calculate the mass and energy balances for different process configurations are shown in Table 1. The reforming reaction was estimated to minimize the pressure effect on water gas shift reaction, at 700 °C and 4 bar. Although improvement of the reforming process at low pressures is well known, since the number of moles of products is higher than the number of moles fed to the system. The reactors for bioethanol reforming and water gas shift were simulated as reactors where the yield and product distribution are fixed (R. Yield), with basis in the catalytic activity and product distribution evaluated experimentally. Additionally, the water gas shift stage was split into two reaction steps at different temperatures (400 and 200 °C, respectively).

The COPROX and PEMFC were simulated as stoichiometric reactors where conversion is controlled by  $CO/O_2$  and  $H_2/O_2$  ratios, respectively (R. Stoic.).

To evaluate the enthalpy of the exhaust anode gas stream, a hydrogen conversion of 80% was considered, with basis in the state of the art for PEMFC simulation.

For efficiency calculations, the S/C ratio has a great influence. These estimations for some processor configurations, recovering the heat of different process streams, are compiled in Fig. 4. The energy balances in each reaction stage from fuel processor are summarized in Table 2. For processor operation without recovery of energy, the efficiency values oscillate between 55% for the higher S/C ratio (6.5) and 65.5% for an S/C ratio of 3.2. Using the heat exchanged from steam reforming reactor, WGS-HT and WGS-LT to adjust the temperature of the streams which each reactor needs to operate, improved the processor efficiency. With this process configuration efficiencies between 67.2% for S/C ratio of 6.5 and 73.7% for S/C ratio of 3.2 were achieved.

For processor-PEMFC system operation it is possible to use the energy content of exhaust gases unconverted in the fuel cell operation. In this case, the influence of the S/C ratio on system efficiency is also remarkable.



Fig. 4. Processor efficiencies calculated for different configurations vs. S/C ratio.

Table 2	
Enthalpies estimation vs. S/C ratio for each stage of the bioethanol	processo

Enthalpy (kW)	S/C ratio		
	6.5	4.8	3.2
$\overline{Q_{\text{EtOH}}}$	2.70390	2.76923	2.83456
WBEtOH	0.00004	0.00004	0.00004
W <sub>BH<sub>2</sub>O</sub>	0.00016	0.00012	0.00008
$Q_{\rm vap}$	1.33921	1.05420	0.75444
$Q_{\rm ref}$	1.09152	0.98621	0.86991
$Q_{\rm SR}$	0.39404	0.32540	0.25230
QWGSRHT	0.02901	0.03629	0.04579
$Q_{\rm SHT}$	0.24767	0.20578	0.16109
QWGSRLT	0.00650	0.00934	0.01550
$Q_{SLT}$	0.28506	0.09919	0.07790
$Q_{\rm PROX}$	0.00153	0.00381	0.00709
$Q_{\mathrm{H}_2}$	2.82723	2.90102	2.92400

Table 3 Enthalpies estimation vs. S/C ratio for each stage of the bioethanol processor-PEMFC system

Enthalpy (kW)	S/C ratio			
	6.5	4.8	3.2	
$\overline{Q_{\text{EtOH}}}$	2.70390	2.76923	2.83456	
WBEtOH	0.00004	0.00004	0.00004	
W <sub>BH2O</sub>	0.00016	0.00012	0.00008	
Qvap	1.33921	1.05420	0.75444	
$Q_{\rm ref}$	1.09152	0.98621	0.86991	
$Q_{\rm SR}$	0.39404	0.32540	0.25230	
Q <sub>WGSRHT</sub>	0.02901	0.03629	0.04579	
$Q_{\text{SHT}}$	0.24767	0.20578	0.16109	
QWGSRLT	0.00650	0.00934	0.01550	
$Q_{SLT}$	0.28506	0.09919	0.07790	
$Q_{\rm PROX}$	0.00153	0.00381	0.00709	
$Q_{\rm EPC}$	0.49117	0.39540	0.12910	
$Q_{\rm SPC}$	0.21653	0.21960	0.22074	
$Q_{\rm H_2}$	1.00000	1.00000	1.00000	
Q <sub>GR</sub>	0.56545	0.58020	0.59848	

To reduce the S/C ratio and maintain the hydrogen production from the bioethanol processor it is necessary to increase the EtOH flow. When the H<sub>2</sub>O fed to the system is depleted a sharp drop in the vaporization enthalpies ( $Q_{vap}$ ) (Table 3) is produced and the efficiency of the processor-PEMFC system is enhanced (Fig. 5). Similar results were obtained by Lin et al. [18].

Reducing S/C ratio fed to the processor from 6.5 to 3.2 the system efficiency was enhanced from 19.5 to 22.4%. Recovering additional heat, according to the process flowsheet modifications described above, the system efficiency was improved from 23.7% for S/C ratio of 6.5 to 25.2% for S/C ratio of 3.2. Moreover, using the heat produced by the combustion of the exhaust gases unconverted in the fuel cell operation the efficiency was increased to 27.4–29.7% for S/C ratios between 6.5 and 3.2, respectively.



Fig. 5. Process efficiencies calculated for different configurations vs. S/C ratio.

For the processor-fuel cell system operation with a S/C ratio of 3.2 an energy efficiency of 30% was achieved. This is a high value compared to the efficiency of internal combustion engines. However, operating with a S/C of 4.8 the risk of carbon deposition and therefore deactivation of the reforming catalyst is greatly reduced without showing a sharp drop in the energy efficiency (27%). Heinzel et al. [19] improved the fuel cell processor efficiency up to 30%, by recovering the anode off-gas in a multifuel (natural gas, LPG) ATR processor, including water gas shift and CO preferential oxidation as purification stages. Hence, the feasibility of bioethanol processor-fuel cell system operation, is confirmed by the results shown in this work. The final efficiency of the system will depend on the future fuel cell development.

In this work, the technical possibility to produce a rich hydrogen stream with carbon monoxide content lower than 50 ppm will be demonstrated using the current catalysis knowledge. Nowadays, there are commercial catalysts for the water gas shift and COPROX reactions. For WGS reaction, the aim is to develop a new catalyst formulation, which allows operation of this process at high gas hourly space velocities  $(30,000 \text{ h}^{-1})$ without a pyroforic behaviour and at low cost. So, for COPROX process the targets for catalyst development are to increase the carbon monoxide conversion without hydrogen consumption, to improve the performance operation with  $O_2/CO$  ratios close to the stoichiometric one and to reach an oxygen conversion of 100%. It is important to remember that a small amount of oxygen, not converted at the COPROX stage will be able to produce microcombustion inside fuel cell anode and damage the polymeric membrane.

The applications of membrane reactors to produce CO-free hydrogen streams are limited because palladium, the active phase, is so expensive [20,21] and also the costs associated with pressure control system required for their operation [22].

Taking into account previous considerations, a 1 kW processor was designed and built. It is remarkable that, the operation of three catalytic reactors coupled in series is so difficult, in order to control and stabilize all the operational parameters. To operate the processor, the procedure followed, was in essence, to stabilize each reaction stage connected sequentially.

#### 3.2. Processor performance

The processor of 1 kW was operated in open mode without any energy recovery system with a S/C ratio of 4.8. For reformer operation, a hydrogen rich stream with a carbon monoxide concentration of 5% was yielded. Previously to attach the water gas shift reactor the catalyst must be reduced *in situ* with hydrogen. This reduction process is a critical step because it is a very exothermic reaction and the temperature must be carefully controlled. For the addition of WGS stage to the reforming reactor the CO concentration was reduced to 1%, with a CO conversion close to 95%. The WGS stage strongly influences the CO reduction but not the hydrogen production, only around 0.75 moles of hydrogen were produced per mole of ethanol fed.

The hydrogen yield, defined as moles of hydrogen yielded per mole of ethanol fed to the processor, is shown in Fig. 6. During



Fig. 6. Evolution of EtOH, CO, O2 conversion and H2/EtOH vs. time.

the whole run an ethanol conversion of 100% was achieved. Furthermore, it is remarkable that the hydrogen yield was 4 moles of hydrogen per mole of ethanol fed since taking into account the thermodynamic predictions for this value 5.5 (at 700 °C and S/C ratio of 4.8), although lower than stoichiometric, this process had a hydrogen production efficiency of 72%.

The CO concentration versus time in operation is shown in Fig. 7. For the operation of water gas shift reactors coupled to the reforming one, a CO concentration of 0.1% was measured. When the COPROX reactor was connected to the process line the CO concentration obtained was lower than 3 ppmV and this value was maintained throughout the time in operation. It is remarkable that the carbon monoxide concentration obtained is really low and similar to CO concentration obtained by membrane reactors or PSA systems [23].

The reforming of heavy alcohols is a complex process where many reaction paths are possible and many by-products can be obtained [24]. The aim of the bioethanol processor designed was to reduce the CO production, as well as to avoid the intermediates production such as acetaldehyde or by-products such as ethylene. From this point of view, it is important to note that



Fig. 7. CO concentration vs. time obtained for the different reaction stages.



Fig. 8. Product distribution vs. time obtained for the different reaction stages connected in the processor.

the only intermediate product obtained was methane (Fig. 8) which reached 10%. Methane production has a great influence on hydrogen efficiency because between 3 and 4 moles of hydrogen per mole of methane yielded are consumed; which reduces the hydrogen production. Nevertheless, for bioethanol processor efficiency, the methane does not represent a serious problem, since it is reused by burning to supply the heat necessary for the ethanol reforming stage. Moreover, it can be considered as inert for PEMFC performance.

# 4. Conclusions

A bioethanol processor was designed and studied thermodynamically in order to demonstrate that hydrogen production from this fuel is an efficient process reaching values close to 74%. Coupling bioethanol processor and PEMFC (with current fuel cell development) a theoretical efficiency close to 30% was obtained (higher than that for an internal combustion engine) without net CO<sub>2</sub> emissions. Once the processor was built and operated in open mode without any energy recovery system, a CO-free hydrogen rich stream (<3 ppmV CO) with an enough quality to be fed to PEMFC, was produced. Hydrogen production efficiency reached close to 72%, or 4 moles of hydrogen per mole of ethanol fed to the processor. These results are one of the first steps to achieve a sustainable development.

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#### Glossary

- COPROX: CO preferential oxidation
- LHT: lower heating value
- MCFC: molten carbonate fuel cell
- *PAFC*: phosphoric acid fuel cell
- PEMFC: polymeric electrode membrane fuel cell
  - $Q_{EPC}$ : heat exchanged before PEMFC
  - $Q_{ethanol}$ : ethanol combustion heat at standard conditions
  - $Q_{GR}$ : heat obtained by combustion of fuel cell exhaust gases
  - $Q_{H_2}$ : fuel cell electric power

 $Q_{PROX}$ : heat yield in COPROX

- Q<sub>ref</sub>: reforming heat
- $Q_{SHT}$ : heat recovered from WGSR-HT
- $Q_{SLT}$ : heat recovered from WGSR-LT
- QSPC: heat exchanged after PEMFC
- $Q_{SR}$ : heat recovered from reforming reactor outlet
- $Q_{vap}$ : heat supplied to vaporize the product feed to the system
- $Q_{WGSRHT}$ : heat yield in high temperature WGS
- $Q_{WGSRLT}$ : heat yield in low temperature WGS
- *R. Stoic.:* stoichiometric reactor, where conversion is fixed according to stoichiometry
- R. Yield: yield reactor, where product distribution is fixed
- SOFC: solid oxide fuel cell
- $W_{BEtOH}$ : ethanol pump power
- $W_{BH_2O}$ : water pump power
- WGS: water gas shift