16th European Symposium on Computer Aided Process Engineering
and 9th International Symposium on Process Systems Engineering
W. Marquardt, C. Pantelides (Editors)

ENVIRONMENTALLY CONSCIOUS DESIGN OF ETHANOL FED FUEL CELL SYSTEM

Liliana Hernández, Viatcheslav Kafarov

Center for Simulation and Control of Process, Industrial University of Santander. A.A. 678, Bucaramanga, Colombia

Abstract

In this work, a clean technology for electricity production from renewable sources is proposed. For this aim, an integration of bioethanol steam reforming and a fuel cell system (SOFC) was developed by computer aided design using HYSYS®. For process integration, was taking into account that steam reforming of bioethanol is an endothermic process and this reaction improves its conversion with fed steam excess. Moreover, typical SOFC operational conditions were used. An integrated flowsheet was developed using heat and mass integration of several process streams achieving high energy efficiency. Additionally, a discussion about other integration schemes is presented.

Keywords: computer aided design, SOFC, bioethanol steam reforming, heat integration, mass integration.

1. Introduction

Currently the hydrogen is considered as the new "energetic vector" because of its advantages related to possibility its production from renewable sources with an important positive environmental impact and its high mass energetic density (Zabalza, et. al. 2005). Hydrogen can be obtained from biomass or its products as bioethanol which is produced by fermentation.

Hydrogen from bioethanol can be produced by partial oxidation, autothermal reforming or steam reforming. The last, has the disadvantage that involve an endothermic reaction but with this process best conversions to hydrogen can be obtained. Electricity production from bioethanol and its steam reforming to hydrogen for fuel cells is a clean technology which offers high energy efficiency and zero emissions pollutants. Solid oxide fuel cells (SOFCs) are one of the most attracting kinds of fuel cells, for its advantages as high efficiency (near to 60%), high rate in reaction kinetics and high quality heat, which can be used as source for heat integration with endothermic bioethanol steam reforming.

The SOFC – based power plants fuelled by bioethanol have been studied for recent 3 years. The most of these researches are focused on SOFC direct ethanol fed because the high operational temperatures of these fuel cells which can let the reforming of this fuel inside the device (Gupta, et. al., 2005, Douvatzides, et. al., 2004, Assabumrungrat, et. al., 2004), but the slow diffusion of ethanol on electrodes and the coke deposition at those temperatures (1000°C) are some challenges that must be solved.

Other kind of these power plants is which the bioethanol reforming take place on external reformer at SOFC. In this case, the reformer operation can be improved to get more hydrogen quantities and the reforming can be operated at moderated temperatures to avoid the coke deposition on the catalyst. The state of the art about this process is on developing and we can make mention of one work only of Douvartzides, et. al. (2003), although at the present on Europe are going ahead several research projects as $BioH_2$ and many others. In Douvartzides work, energy – exergy analysis and optimization of operational conditions was made, using an afterburner to develop the heat integration of this process.

In this work, other alternative for this process integration is discussed. Typical operational conditions for SOFCs are used and, the favorable conditions for bioethanol steam reforming as moderate temperatures and steam excess on the fed stream was taking into account. The research is a part of joint international project "Bioethanol fed fuel cells" CYTED IV.21 with the participation of eight European and Latinamerican countries in a frame of program "Biomass as source of energy and chemical products".

2. Bioethanol as Hydrogen Storage

Bioethanol as hydrogen has several advantages such as hydrogen carrier for fuel cells, because of it is easy to store, handle and transport in a safe way due to its lower toxicity and volatility. Moreover, bioethanol is a chemical substance which can storage hydrogen at greater than its liquid density at atmospheric pressure, it has a hydrogen volume density more than other organic compounds as ethane, propane and methanol. Additionally, bioethanol as storage medium has a total density near to 1 g/cm^3 because of this it is among the most promising hydrogen storage fuel cell substances (see Figure 1).

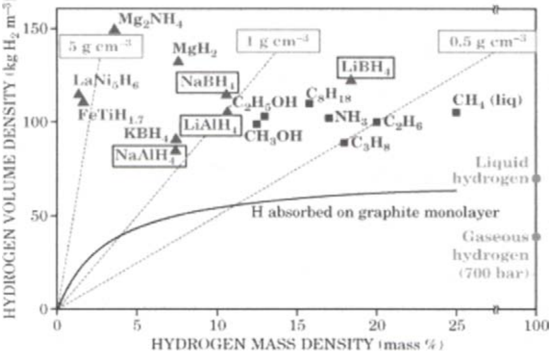


Figure 1. The storage density of hydrogen plotted as a function of the hydrogen mass fraction. Crabtree, 2005

3. Modelling of Bioethanol Steam Reforming

The most of research made about bioethanol steam reforming is addressed to develop catalyst for this process and to study its behaviour, but only few works have been reported about the development of reaction mechanisms and kinetics models. For catalyst development, different metals with several supports of metallic oxides have been probed among them: Rhodium: (Diagne, et. al., 2004) (Diagne, et. al., 2002); Platinum: (Freni, et. al., 2003); Nickel: (Laborde, et. al., 2004 a) (Sun, et. al., 2005) (Sun, et. al., 2004) (Athanasios, et. al., 2002) (Athanasios, et. al., 2003) (Freni, et. al., 2003); Cobalt: (Batista, et. al., 2004) (Llorca, et. al., 2003 b); Gold: (Freni, et. al., 2003); Palladium: (Goula, 2004) (Freni, et. al., 2003) and Ruthenium: (Dimitris, 2003). Also, have been studied metallic oxides on metallic oxides as Copper oxide (Nishiguchi, et. al., 2005) and bimetallic catalyst as Cu-Ni/Al2O3 (Laborde, et. al., 2004 b) and Cu-Ni/SiO2 (Fierro, et. al., 2002).

For feed ratio of ethanol/water have been probed experimentally ratios from 1:6 (Laborde, et. al., 2004 a) to 1:13 (Llorca, et. al., 2003 a), but for ratios superior at 1:8 was not registred an improving of conversion and selectivity for bioethanol steam reforming (Diagne, et. al., 2004). In relation to the discernment of reaction mechanisms for steam reforming of bioethanol, have been found only few such as for Nickel catalyst supported on La2O3 (Athanasios, et. al., 2004), Rhodiun on TiO2 (Raskó, 2004), Nickel on Al2O3 (Laborde, et. al., 2004 b) and Cobalt on ZrO2 (Benito, et. al., 2005). About kinetic models only have been found one complete work for Ni/Al2O3 catalyst (Therdthianwong, 2001) and this model was correlated for only one temperature of 400°C. In this work, was considered that bioethanol is vaporized and reformed by mixing to steam in a packed bed reactor which contains a Ni-based catalyst where its overall reaction can be represented by the irreversible process between one ethanol molecule and three water molecules according to the reaction

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad \Delta H^o_{Rx} = 1.704x10^5 kJ/kgmole \qquad (1)$$

Bioethanol steam reforming take place for temperatures more than 250°C. In this work the reformer is operated to 400°C with a non elemental kinetic, Therdthianwong, 2001 (see Equation 2).

$$-r_{C_2H_5OH} = 280075 P_{EtOH}^{2.52} P_{H_2O}^{7}$$

Where $-r_{C_2H_5OH}$ is the rate of consumption of bioethanol [mol/g-cat h] and P is the pressure [atm.]. Reformer was simulated by a one dimensional pseudohomogeneous model for packed bed reactors considering a plug flow for gas phase and calculating the pressure variation throughout reactor using traditional Ergun equation.

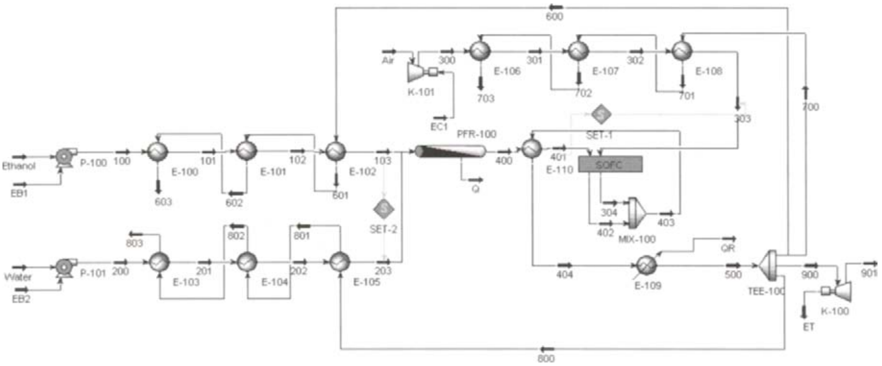
4. Modelling of Solid Oxide Fuel Cells (SOFC) and Co-generation

Solid oxide fuel cells with operating temperature of >800°C promotes rapid kinetics by no precious materials, and produces high quality by-product heat for cogeneration. For SOFC modelling on recent years, it has been developed complex models 3D using finite elements (Khaleel, et. al., 2004), CFD using commercial software (Autissier, et. al., 2004) (Lockett, et. al., 2004), finite volume analysis (Campanari and Iora, 2004) and thermo-electrochemical models (Petruzzi, et. al., 2003) to calculate profile temperatures, currents, electrical and thermal power density and gases concentrations. However the knowledge about steam reforming is limited and to avoid the introduction of information noise for joint process was selected uncomplicated SOFC model based on HYSYS®. For process integration was using SOFC with typical operational conditions: T=1000°C, fuel utilization: 85% and oxidant utilization: 25%.

5. Simulation Results: Process Description, Design and Integration

5.1. Process Description

The system to produce electricity from bioethanol by steam reforming and fuel cells (SOFC), can be described as follow. The bioethanol is vaporized and fed at a packed bed reactor which contains a Ni-based catalyst. Additionally, water is vaporized and fed at reactor too, and the molar ratio between bioethanol and steam fed was 1:6 to improve the reaction conversion to 99%. The reaction products are fed to SOFC at 485°C after a heating with a hot flow from SOFC. This stream has a volume composition on hydrogen of 53% and taking into account that a typical fuel stream for SOFC has a 67% of hydrogen (Allied-Signal, 1992), is assumed that the SOFC performance no is affected considerably. An air stream is fed to SOFC is also preheated to 485°C to improve the fuel cell performance. Finally, the SOFC stream products are used to heat the steam reformer and after that, they are split on four streams to vaporize the bioethanol, the water, to preheat the air and to feed a turbine to produce more energy



Name	**Ethanol**	**Water**	**Air**	**100**	**103**	**200**	**203**	**300**	**303**
Temperature(°C)	25	25	25	25	400	25	400	45,939	485
Pressure (kPa)	101,325	101,32	101,3	131	120,7	131	120,7	121,36	117,2
Molar flow (kgmole/h)	58,068	348,34	3198	58,068	58,07	348,3	348,3	3198,2	3198
Mass flow (kg/h)	2675,187	6275,3	92268	2675,2	2675	6275	6275	92268	92268
Name	**304**	**400**	**401**	**404**	**500**	**603**	**703**	**803**	**901**
Temperature(°C)	1000,012	400	485	985,58	903,3	82,75	64,73	108,14	895
Pressure (kPa)	110,3312	118,6	117,2	108,95	105,5	101,4	101,4	101,37	101,3
Molar flow (kgmole/h)	3055,737	629,83	629,8	3685,6	3686	165,9	1548	751,85	1220
Mass flow (kg/h)	87710,21	8950,5	8951	101218	1E+05	4555	42512	20649	33503

Figure 2. Electricity from bioethanol by steam reforming and fuel cell (SOFC) flowsheet

5.2. Process Design

For process design following criteria was used. Environmental criteria: the process has zero emissions of SO_x (raw materials does not contain sulphur components), NO_x (electrochemical process without combustion) and CO_2 produced on bioethanol reforming it is consumed for the biomass growth. Heat integration criteria: the high heat content of SOFC product stream which has a temperature of 1000°C, provides the necessary duty for the endothermic reaction of bioethanol reformer and the preheating requirements of streams fed to process such as bioethanol, water and air.

The process was designed to produce 1MW by SOFC on steady state conditions join with an additional cogeneration by gas turbine. As row materials were used liquid bioethanol, and water to feed the reformer and to produce hydrogen as fuel, and air to feed the SOFC as oxidant. This design was computer aided for HYSYS® software. The process flowsheet is showed on Figure 2. For SOFC simulation in HYSYS, was used a subflowsheet, where the fuel cell was simulated as a chemical reactor by using the typical reactions that take place on SOFC (Fuel Cells Handbook, 2000).

5.3. Process Integration

For process integration, a Pinch analysis to hot and cool process streams was made, and the splitting of streams was used to satisfy the process requirements. A heat exchanger network for each stream to preheat was designed. Minimum heat exchangers topology were calculated taking into account the phase changes involved on this stage for bioethanol and water streams. To find out this topology, an equilibrium point between the heat transfer efficiency and the heat exchangers number was found. The best process flowsheet found is showed on figure 2 and described as follows. The SOFC product streams were mixed and used to heat the steam reformer up to reaction temperature 400°C. The hot stream leaves the reformer at 903°C then; it is split on four streams to vaporize and preheat bioethanol, water, to preheat air and to feed a gas turbine. For each of three heating flows, a network of three heat exchangers was designed to heat cold streams, with the purpose to improve the heat transfer between the streams and avoid the energy losses for thermal shock due to big streams temperature differences. For the design of each heat exchangers network was taking into account, that the process cold streams had a temperature of 25°C and the hot streams was exhausted thermally and its out temperatures was between 87°C and 116°C. The process designed is a net energy exporter because, it produces 1MW from SOFC and 100 kW from turbine K-100, and process energy requirements are only for two pumps to move the bioethanol and water which consume 63.35 W and 116.2 W respectively and one compressor to fed air for SOFC which consume 543.5 kW. Finally this process can produce net 556.32 kW.

6. Conclusions

The environmentally conscious design proposed is a base to develop clean technologies to produce electricity by using renewable sources such as bioethanol. A new proposal of a clean technology to produce electricity from bioethanol by steam reforming and SOFC using are designed. This alternative can produce net 556.32 kW and a burner to heat the steam reformer no is required. The heat process integration was made using the hot streams that leaves the SOFC and optimizing the heat transfer process using an appropriate heat exchangers network design.

Acknowledgements

We thank the international project CYTED IV.21: "Bioethanol fed fuel cells" and at the Colombian Institute for Science and Technology Development "Francisco José de Caldas" – COLCIENCIAS and Iberoamerican Cooperation on Science and Technology for the Development for the financial support of this research.

References

Allied-Signal Aerospace Company (1992). In: Fuel Cells Handbook. EG&G Services Parsons, Inc. Science Applications International Corporation. U.S. Department of Energy. Office of Fossil Energy. National Energy Technology Laboratory. 5th edition. Morgantown. 2000.

Assabumrungrat, S. et. al. (2004). Thermodynamic analysis for a solid oxide fuel cell with direct internal reforming fueled by ethanol. Chemical Engineering Science. 59 (24) 6015-6020.

Athanasios, N. et. al. (2002). Production of hydrogen for fuel cells by reformation of biomass-derived ethanol. Catalysis Today. 75.145–155.

Athanasios, N. et. al. (2003). Steam reforming of biomass-derived ethanol for the production of hydrogen for fuel cell applications. chemcomm communication.

Athanasios, N. et. al. (2004). Reaction network of steam reforming of ethanol over Ni-based catalysts. Journal of Catalysis. 225. 439–452.

Autissier, N. et. al., (2004). CFD simulation tool for solid oxide fuel cells. Journal of Power Sources. 131. 313–319.

Batista, M. et. al. (2004). High efficiency steam reforming of ethanol by cobalt-based catalysts. Journal of Power Sources. 134. 27–32.

Crabtree, G. (2005). The hydrogen economy. www.physicstoday.org/vol-57/iss-12/p39.html

Benito, M. et al. Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production. Journal of Power Sources. Article in press.

Campanari, S. and Iora, P. (2004). Definition and sensitivity analysis of a finite volume SOFC model for a tubular cell geometry. Journal of Power Sources. 132. 113–126.

Diagne, C., et. al. (2002). Hydrogen production by ethanol reforming over Rh/CeO2–ZrO2 catalysts. Catalysis Communications. 3. 565–571.

Diagne, C. et. al. (2004). Efficient hydrogen production by ethanol reforming over Rh catalysts. Effect of addition of Zr on CeO2 for the oxidation of CO to CO2. C. R. Chimie. 7. 61–622

Dimitris, K. (2003). Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. Applied Catalysis B: Environmental. 43. 345–354.

Douvartzides, S. et. al. (2004). Electricity from ethanol fed SOFCs: the expectations for sustainable development and technological benefits. International Journal of Hydrogen Energy. 29 (4) 375-379.

Douvartzides, S., Coutelieris, F. and Tsiakaras P. (2003). On the systhematic optimization of ethanol fed SOFC-based electricity generating systems in terms of energy and exergy. Journal of Power Sources. 114. 203-212.

Fierro, V. et. al. (2002). Oxidative reforming of biomass derived ethanol for hydrogen production in fuel cell applications. Catalysis Today. 75. 141–144.

Freni, S. et. al. (2003). Production of hydrogen for MC fuel cell by steam reforming of ethanol over MgO supported Ni and Co catalysts. Catalysis Communications. 4. 259–268.

Fuel Cells Handbook. EG&G Services Parsons, Inc. Science Applications International Corporation. U.S. Department of Energy. Office of Fossil Energy. National Energy Technology Laboratory. Fifth edition. Morgantown. 2000.

Gaurav, G. Comparison of conversion and deposit formation of ethanol and butane under SOFC conditions. Journal of Power Sources, Article In Press.

Goula, M. (2004). Hydrogen production by ethanol steam reforming over a commercial Pd/ -Al2O3 catalyst. Applied Catalysis B: Environmental. 49.135–144.

Khaleel, M., et. al. (2004). A finite element analysis modeling tool for solid oxide fuel cell development: coupled electrochemistry, thermal and flow analysis in MARC®. Journal of Power Sources. 130. 136–148.

Laborde, M. et. al. (2004 a). Bio-ethanol steam reforming on Ni/Al2O3 catalyst. Chemical Engineering Journal. 98. 61–68.

Laborde, M. et. al. (2004 b). Hydrogen production via catalytic gasifcation of ethanol. A mechanism proposal over copper–nickel catalysts. International Journal of Hydrogen Energy. 29. 67 – 71.

Llorca, J., et. al. (2003 a). CO-free hydrogen from steam-reforming of bioethanol over ZnO-supported cobalt catalysts Effect of the metallic precursor. Applied Catalysis B: Environmental. 43. 355–369.

Llorca, J., et. al. (2003 b). In situ magnetic characterisation of supported cobalt catalysts under steam-reforming of ethanol. Applied Catalysis A: General. 243. 261–269.

Lockett, M., Simmons, M. and Kendall, K. (2004). CFD to predict temperature profile for scale up of micro-tubular SOFC stacks. Journal of Power Sources. 131. 243–246.

Nishiguchi, T., et. al. (2005). Catalytic steam reforming of ethanol to produce hydrogen and acetone. Applied Catalysis A: General. 279. 273–27.

Petruzzi, L., Cocchi, S. and Fineschi, F. (2003). A global thermo-electrochemical model for SOFC systems design and engineering. Journal of Power Sources. 118. 96–107.

Raskó, J. (2004). Surface species and gas phase products in steam reforming of ethanol on TiO2 and Rh/TiO2. Applied Catalysis A: General. 269. 13–25.

Sun, J. et. al. (2004). Hydrogen from steam reforming of ethanol in low and middle temperature range for fuel cell application. International Journal of Hydrogen Energy. 29. 1075 – 1081.

Sun, J. et. al. (2005). H2 from steam reforming of ethanol at low temperature over Ni/Y2O3,Ni/La2O3 and Ni/Al2O3 catalysts for fuel-cell application. International Journal of Hydrogen Energy. 30. 437 – 445.

Therdthianwong, A., Sakulkoakiet, T. and Therdthianwong, S. (2001). Hydrogen production by catalytic ethanol steam reforming. Science Asia. 27. 193-198.

Zabalza, I, Valero, A. and Scarpellini, S. Hidrógeno y pilas de combustible: Estado de la técnica y posibilidades en Aragón. Fundación para el desarrollo de las nuevas tecnologías del hidrógeno en Aragón. Zaragoza. 2005.