ENVIRONMENTALLY CONSCIOUS DESIGN OF ETHANOL FED FUEL CELL SYSTEM

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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 BioH2 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/cm³ 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](image)

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) (Athanasiou, et. al., 2002) (Athanasiou, 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 registered 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 (Athanasiou, et. al., 2004), Rhodium on TiO2 (Rask6, 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

\[ C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad \Delta H_{rx} = 1.704 \times 10^5 \text{kJ / kg mole} \quad (1) \]

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).

\[-r_{C_2H_5OH} = 280075 P_2^{2.52} P_3^{7} \]

Where \(-r_{C_2H_5OH}\) is the rate of consumption of bioethanol \([\text{mol/g-cat h}]\) and \(P\) is the pressure \([\text{atm.}]\). 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.
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 by using 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.

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