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Molten carbonate fuel cell system fed with biofuels for electricity production

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ABSTRACT

This study investigates on the efficiency of integrated reformer-MCFC system. Performances of a Ni catalyst working under steam reforming conditions of three different biofuels (biogas, ethanol and glycerol) are experimentally evaluated. Reformers outlet stream were applied as fuel for a MCFC stack in order to estimate the total integrated system efficiencies.

It is found that the large amount of heat (20%–54% of the inlet fuel – LHV basis) is employed for the reforming of the biofuel during the heating phase of inlet stream to the reforming operative temperature. Moreover, among the examined biofuels the highest amount of externally supplied energy (~79% of the inlet fuel – LHV basis) is wasted in the fuel processor unit for the steam reforming of ethanol, mostly due to the high amount of the water required (S/C = 4.2 mol/mol). Finally, it is also found that the combined biogas reformer-MCFC system is exhibited the highest electrical efficiency (76%).

Introduction

The growing need to reduce the environmental impact of the modern lifestyle imposes a continuous development and novel technologies (based on conventional and renewable sources e.g. wind turbines [1]) aimed at a severe reduction on pollutant emissions, mainly from mobile sources, to ensure a tolerable quality of life in metropolitan areas. Fuel cell has been identified as one of the most promising technologies for the future clean energy industry [2]. It converts the energy chemically stored in a fuel, such as hydrogen, into an electrical energy output by electrochemical reactions. Due to their high efficiency, low emissions and the possibility to use alternative fuels, molten carbonate (MCFC) and solid oxide (SOFC) fuel cells are considered as the most promising technologies for the energy generation in stationary applications such as distributed generation [3,4] more than internal combustion engine [5]. Hydrogen and methane (in the form of natural gas) are currently considered to be the main fuels for fuel cells. In particular, the hydrogen is a very versatile fuel and it can be produced from various materials and by several methods. In this way, steam reforming is a known technology that is used industrially to produce hydrogen from different "alternative fuels". Thus, a lot of research have reported in the literature about direct production of hydrogen rich syngas by utilization of bio-fuels (such as ethanol, biogas and glycerol) due to its innate advantages over conventional fossil fuels. Biogas is produced by anaerobic biological waste treatment

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and it mainly contains methane and CO_2 (50–75% CH_4, 50–25% CO_2) [6,7]. The biogas can be converted into syn-gas either by dry reforming or by a combination of dry and steam reforming using appropriate catalysts [8,9]. Since the CH_4 to CO_2 ratio in biogas is 1.5 mol/mol, dry reforming alone can lead to significant carbon deposition within the reactor [10]. Therefore, it is desirable to mix biogas with steam for reforming and generally the H_2O to CH_4 ratio (S/C) is maintained at 3 to avoid any coke formation [11].

Bio-ethanol have been the most commonly used biomass-derived fuels for fuel cell systems due to the advantages in terms of power density, non-toxicity, storage, transportation, and safety [12]. However, because of incomplete oxidization, the ethanol processing by steam reforming process consists of more complicated multistep reaction mechanism and involves a number byproducts [13]. Studies, however, highlighted that a steam to ethanol ratio above 6 and temperatures greater than 900 K produce a high hydrogen yield with low carbon monoxide (CO) and carbon formation in the steam reforming environment [14].

Bio-glycerol is a byproduct of biodiesel production and it is an alcohol which has a high energy density [15]. On the other side, the glycerol is non-toxic, non-volatile and it provides the possibility to use as a source of producing hydrogen for fuel cells in large-scale application. Thermodynamic studies of glycerol steam reforming concluded that optimal conditions for hydrogen production from glycerol were a temperature of 925–975 K and a water/glycerol ratio of 9–12 at atmospheric pressure [16–18]. Under these conditions, methane production is minimized and the carbon formation is thermodynamically inhibited. Catalytic investigations also [19,20] indicated that under the same catalyst (such as Ni/Al_2O_3), the hydrogen selectivity for glycerol was much less than that for ethanol (<60%) due to the formation of light alkanes under the same operating condition.

Comparatively, bio-fuels, appear to be more suitable for fuel cells in both stationary and portable applications because most of the biomass-derived fuels in either liquid or gas form are easy to transport and the infrastructures needed are readily available. Although many studies on SOFC systems fed by biofuels are available in literature [21–24] few paper report direct comparison of biofuel combined to MCFC system. Hence, the aim of this study was to analyze a MCFC system integrated with a steam reforming process and compare the overall system efficiency as a fraction of different important renewable resources for hydrogen production: biogas, ethanol and glycerol. The effect of operating conditions on the reformer performance were experimentally investigated in terms of outlet stream composition and carbon formation. Successively, the energy requirements of reformer system fed by different bio-fuels were also examined. In addition, the efficiencies of the reformer-stack MCFC integrated system for power generation were evaluated.

To perform reliable comparison of the reformer supplied by biogas, ethanol and glycerol streams the electric power released by MCFC was fixed at 125 kWe and the inlet anode flow has been considered as conventional $H_{2equivalent}$ for each biofuel. More detailed definition of such a boundary definitions is given in following paragraph.

Fuel processor – MCFC system

Fig. 1 shows the flow diagram of fuel processor-MCFC system. The combined plant highlights two sections: i) fuel processor and ii) MCFC.

The fuel processor is composed by different heater elements devoted to vaporize, to mix and to convert the bio-fuels into hydrogen rich syn-gas ($\dot{m}_{syngas}$). Water ($\dot{m}_{water}$) and fuel ($\dot{m}_{raw-fuel}$) are mixed, then heated at operating temperatures ($\dot{Q}_{vap}$ and $\dot{Q}_{Treac}$) and fed to catalytic reactor where the bio-fuels steam reforming reactions take place. From the reformer section the syn-gas moves to a molten carbonate fuel cell going by cooling system where gaseous stream has cooled to 923 K (MCFC operative temperature) and a heat recovery ($\dot{Q}_{cool}$) has been considered exclusively working with biogas reformed stream. The MCFC system produces electrical energy (P_{El}), heat loss by radiation phenomenon ($\dot{Q}_{rad}$) and exhaust gases. In general, MCFCs cannot be operated at complete fuel utilization, thus, the residual fuel can be combusted to generate heat ($\dot{Q}_{MCFC}$) for other heat-requiring units of the system.

Fuel processor

Different biomass fuels could be considered as the raw fuel for hydrogen production in fuel processor–fuel cell systems. Most of them are hydrocarbons or oxidative hydrocarbons that can be catalytically converted via steam reforming. In this study, biogas (composed of 60 vol.% CH_4 and 40 vol.% CO_2), ethanol and glycerol were considered as potential bio-fuels to produce hydrogen rich syngas for MCFC systems. The overall steam reforming reactions of biogas, ethanol and glycerol can be given as following:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \quad (1)$$

$$C_2H_5OH + 3H_2O = 2CO_2 + 6H_2 \quad (2)$$

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2 \quad (3)$$

However, the reactions that are most likely to lead to carbon formation in the hydrocarbons reforming process are as follows:

$$2CO = CO_2 + C \quad (4)$$

$$CH_4 = 2H_2 + C \quad (5)$$

$$CO + H_2 = H_2O + C \quad (6)$$

$$CO_2 + 2H_2 = 2H_2O + C \quad (7)$$

From a thermodynamic viewpoint, the Boudouard reaction (Eq. (4))operative is considered the major carbon generation

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