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BIOGAS AS A FUEL SOURCE FOR PROTON-EXCHANGE MEMBRANE FUEL CELL

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ABSTRACT

This paper discusses the use of biogas in Proton exchange Membrane fuel cells. Biogas is a mixture of gases, mainly methane and carbon dioxide. This mixture must be purified and then reformed, producing syngas and separating hydrogen from its composition. The CO present in the reformed gas in contact with the surface of the catalyst particles (a platinum-based) of the anode of PEM fuel cell is adsorbed impairing the oxidation of hydrogen, which leads to a decrease in cell efficiency. The reformed gas may not contain in its composition carbon monoxide concentrations greater than 50 ppm. The operating conditions of the system and the cost of the process are the main challenges of using biogas in PEM fuel cells

INTRODUCTION

The use of biogas for power generation is an alternative regarding environmental impacts and fossil fuels dependency. Its proper treatment and subsequent application in Fuel Cells has great advantages in the production of electricity. When comparing Fuel cells to the conventional generation systems, lower noise, lower maintenance costs and higher levels of reliability are obtained due to the fact that they have no moving parts. These systems can be implemented near the site of consumption to reduce transmission costs and transmission loss. Fuel cells are usually classified by their operating temperature and the type of electrolyte they use. Some types of fuel cells work well for use in stationary power generation plants. Others may be useful for small portable applications or for car powering [1]. This paper discusses biogas reforming for use in a polymer exchange membrane fuel cell (PEMFC), one of the most promising fuel cell technologies.

BIOGAS CHARACTERISTICS

Biogas is a mixture of methane, carbon dioxide and trace gases such as nitrogen, ammonia sulfur dioxide and hydrogen sulfide [2]. The relative percentage of these gases in biogas depends on the feed material and management of the process. Methane is the main component of biogas. It is present in biogas in a proportion ranging from 50% to 80%. Living conditions of the bacterias in the biodigestor must be controlled because it directly affects the production. These conditions are shown in table 1.

Factor	Condition
Temperature	308K to 318K, It is important not to have abrupt variation
pH	6,5 to 8
Water content	60 to 90% of the total content weight
Nutrients	The main nutrients are Carbon, Nitrogen and Organic Salts. In a proportion of Carbon to Nitrogen between 20:1 to 30:1
Time for Biogas production	10 to 30 days

Table 1 Living conditions of the bacterias [3]

Air impermeability must be respected otherwise there will be only Carbon Dioxide production. [3]

The biogas has a lower heating value and it ranges from 19 to 26 MJ/m^3 [4].

PURIFICATION FOR FUEL CELL APLICATION

An important step for a better biogas energy utilization is the elimination of impurities such as siloxanes, complex hydrocarbons, halogenated compounds, ammonia compounds, fine particles and mainly H_2S, which erodes the Fuel Cell.

According to Silva (2009), several methods of purifying biogas can be used. The most commonly used method consists in passing biogas through a filter composed of iron oxide (Fe_2O_3). Figure 1 illustrate this method. In this case, it consists of two filter elements developed by Godoy Jr. et al, (2011).

The filters are arranged in parallel and only one is open to retain the passage of H_2S while the other waits until the first saturate [5].

An estimation of the cost for building the filter was made by Johann C. D. (2012) and is presented in table 2.

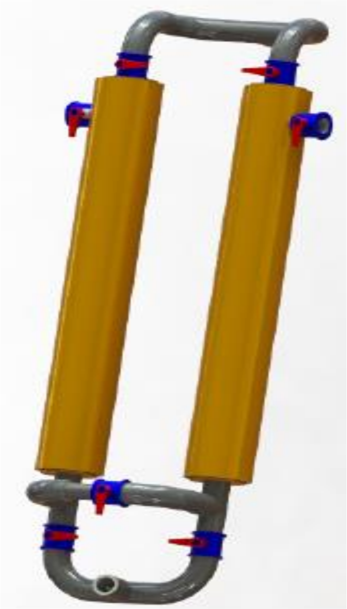

Figure 1 Filter system [6]

Quantity	Description	Unit Price	Total Price
7	Ball valve 50mm	\$ 11.50	\$ 80.50
8	Pipe elbow 90º 50mm	\$ 0.90	\$ 7.20
2	Pipe in T. 50mm	\$ 0.80	\$ 1.60
1	Pipe 50 mm (6m)	\$ 13.80	\$ 13.80
1	Pipe 110 mm (6m)	\$ 18.90	\$ 18.90
4	Reduction 110 x 50	\$ 2.50	\$ 10.00
1	Others	\$ 16.70	\$16.70
Total	\$ 148.70		

Table 2 List of materials and prices for filter manufacture [5]

Other well known methods are the Pressure Swing Adsorption (PSA), Walter Scrubbing (SW) and the method for membrane that is the passage of the gas through a membrane of cellulose acetate.

When working with a reformer coupled to fuel cells like polymer membrane (PEMFC) in addition to attention to the presence of hydrogen sulfide it is important to consider their sensitivity to the presence of carbon monoxide. Supported catalysts based on platinum and platinum alloys are used on the anode and cathode sides of PEM fuel cells. It is known that low temperatures (less than 422K) adsorption of CO onto a platinum catalysts blocks the reaction. In other words, traditional platinum catalysts are very sensitive to poisoning by carbon monoxide. This applies in particular to a PEM fuel cell, which is especially sensitive to CO poisoning as a result of its low operating temperatures of 343 to 373K.

Theoretically, the syngas consists of 75 vol. % hydrogen and 25 vol. % carbon dioxide. In practice, however, this gas also contains nitrogen, oxygen and, depending on the degree of purity and varying amounts of carbon monoxide (up to 1 vol. %).

The Autothermal reforming of methane, which produces syngas, and its further purification in order to obtain hydrogen, will be discussed below.

METHANE REFORMING

The most economical and common way (considering large-scale production) to produce hydrogen is by Steam Methane reforming (SMR). About 50% of all hydrogen produced worldwide is produced from methane, and 40% of that comes from the SMR method [7].

The steam methane reforming, according to the suitable conditions, leads to the formation of synthesis gas (H_2, CO_2, CO, N_2 and $H_2O(v)$). It converts a hydrocarbon in a mixture of hydrogen, carbon monoxide and carbon dioxide, in two stages, as shown in equations (1) and (2):

$$\mathbf{CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^o = 206\ kJ/mol \quad (1)}$$

$$\mathbf{CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^o = -41\ kJ/mol \quad (2)}$$

Reaction (1) is called steam reforming reaction. In this reaction, methane is mixed with steam and reacted with nickel catalyst. It occurs at high temperature, around 1100K [8], involving the breakdown of methane directly to synthesis gas, which consists of a mixture of hydrogen and carbon monoxide in a molar ratio of 3:1, without the formation of intermediate products.

Reaction (2) is a step in the production of hydrogen. It is the reaction of water displacement, WGS ("Water Gas Shift Reaction"), to produce additional hydrogen. It is favored at low temperatures and is little affected by changes in pressure.

The main advantage of this reforming reaction is that it produces a higher molar fraction of hydrogen for each mole of methane; however, the steam reforming process is costly, because it is endothermic and thus it requires high temperatures. Besides that, it requires large heat exchange reactors, which demands a large initial investment [9]. These reaction conditions lead to catalyst deactivation by carbon deposition on its surfasse (coke formation).

An alternative syngas generation is the reforming process by partial oxidation (PROX). In this process, generally represented by equation (3), fuel (methane) reacts with a limited amount of oxigen producing hydrogen, which is then purified.

$$\mathbf{CH_4 + \frac{1}{2} O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H^o = -36\ kJ/mol} \quad \mathbf{(3)}$$

The partial oxidation reaction is exothermic, which means energy saving, while the presence of O_2 reduces carbon deposits at high temperatures and increases the lifetime of the catalyst. To avoid energy loss associated with compression of hot, high hydrogen content gases, the CPOX reactor shoud be operated at pressures in the range of 0.5 to 4 MPa, varing as shown in figure 2 [9]. For H_2 production it may varie between 1 to 2 MPa.

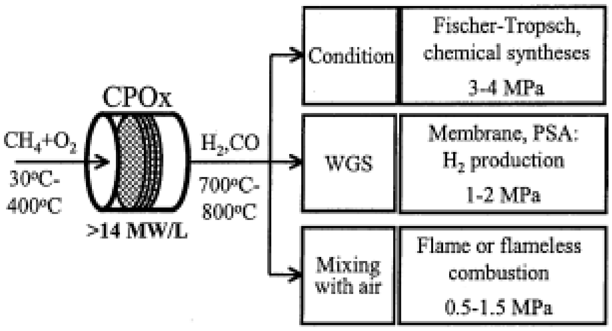

Figure 2 Routes for natural gas utilization opened or facilitated by conversion of natural gas into syngas in a high power density CPOX recto. [9]

However it has disadvantages because it requires the use of pure O_2. This increases the cost of the plant, because it requires a cryogenic separation unit air. The direct use of air would require equipment of great volume due to the presence of N_2 [10]. In addition, the low ratio of H_2/CO requires little or no steam used in the process. Due to the absence of catalyst, the reformer operates at an outlet temperature of approximately 1670K. This high temperature, together with the absence of catalyst, has some disadvantages when compared to autothermal reforming as the formation of soot and very high levels of ammonia and HCN, which results in the need for a cleaning gas and a high consumption of fuel (methane).

Partial oxidation reactors are more compact than the steam reformers, but have lower efficiency due to high temperatures and the associated heat wasted.

A third method for methane reforming is the autothermal reformer. It is an association between the steam reforming and the methane reforming by partial oxidation. Its main advantage is due to the fact that an exothermic and an endothermic reaction occurs in the same reactor chamber.

Thus, the steam reforming uses part of the heat generated in the partial oxidation, resulting in a slightly exothermic process, which occurs in the presence of a catalyst. This association presents itself as an attractive alternative from the technical and economic point of view: the reduction of the amount of energy required by the process, due to the contribution of the exothermic partial oxidation of methane, lower consumption of reagents and the production of syngas with greater flexibility in the ratio H_2/CO [11].

By using the autothermal process it is possible to obtain greater flexibility in the H2/CO relation, through manipulation of the relative amounts of O_2 and H_2O in the feed [12]. In addition, the combination of the reforming and partial oxidations reactions allows a better control of reactor temperature and prevents the formation of hot spots in the catalyst. It reduces catalyst deactivation [13]. The autothermal process has been considered as the most suitable to generate H_2 for automotive fuel cells, due to greater compactness and energy efficiency [14].

COUPLING A REFORMER WITH A PEMFC

After reformed, the syngas contains amounts of CO that still restricts its application in a PEM fuel cell. Figure 3 shows a schematic diagram of a steam reformer coupled with a PEMFC. The main involved reactions in the process are between CO and H_2O in a water gas shift reactors in high (HT) and low (LT) temperatures, and in a PrOx used as CO purification in low temperatures. This process decreases CO concentration enabling the gas application in the fuel cell. In the study of J. Mathiak (2004) no significant performance loss was reported for carbon monoxide concentration less than 50 ppm.

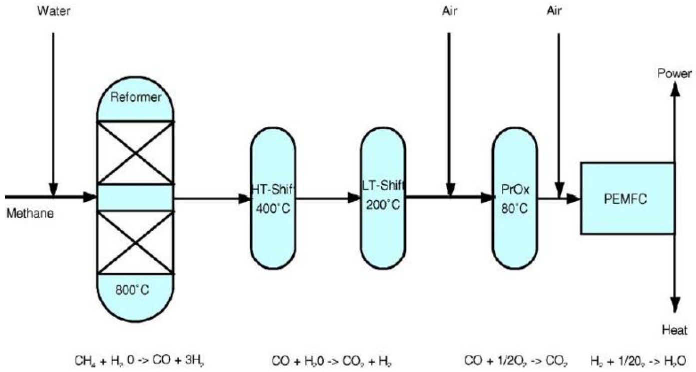

Figure 3 Principle scheme of main reactions of a steam reforming process [15]

CONCLUSION

As discussed in this paper, different methods can be applied to electrical power generation from fuel cells running on biogas. To avoid corrosion the gas must be purified, in order to eliminate H_2S from its composition. The ideal fuel for PEM fuel cells is pure hydrogen, with less than 50 ppm carbon monoxide, as dictated by the poisoning limit of Pt fuel cell catalyst [16]. According to FuelCell Energy, Inc. website, more than 300 megawatts of power generation capacity have been installed or are in backlog at more than 50 locations worldwide [17]. In 2012 the world's largest biogas fuel cell stationary power plant, with a capacity of 2.8 megawatt, was installed at a water treatment facility in California by the company [18]. This numbers is an example that the use of biogas for fuel cells application is a promising alternative source of energy and its knowledge is under development.

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