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Biogas steam reformer for hydrogen production: Evaluation of the reformer prototype and catalysts

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ABSTRACT

This work aims to investigate a biogas steam reforming prototype performance for hydrogen production by mass spectrometry and gas chromatography analyses of catalysts and products of the reform. It was found that 7.4% Ni/NiAl₂O₄/γ-Al₂O₃ with aluminate layer and 3.1% Ru/γ-Al₂O₃ were effective as catalysts, given that they showed high CH₄ conversion, CO and H₂ selectivity, resistance to carbon deposition, and low activity loss. The effect of CH₄:CO₂ ratio revealed that both catalysts have the same behavior. An increase in CO₂ concentration resulted in a decrease in H₂/CO ratio from 2.9 to 2.4 for the Ni catalyst at 850 °C, and from 3 to 2.4 for the Ru catalyst at 700 °C. In conclusion, optimal performance has been achieved in a CH₄:CO₂ ratio of 1.5:1. H₂ yield was 60% for both catalysts at their respective operating temperature. Prototype dimensions and catalysts preparation and characterization are also presented.

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Introduction

Global warming is caused mainly by an excessive fossil fuel use, which has encouraged researchers to develop studies on efficient technologies and renewable sources for generating clean energy in order to replace traditional sources being used nowadays. Hydrogen is a relevant alternative for reducing environmental impacts which are usually caused by greenhouse gas emissions from fossil fuel use, since it is produced sustainably from renewable energy sources [1]. The most representative example of fuel to produce hydrogen is biogas that is typically generated by anaerobic digestion or biomass fermentation [2]. The main components of biogas are methane (CH₄) 50–70 vol % and carbon dioxide (CO₂) 25–50 vol

%, which also contains <1 vol% H₂ and <3 vol% H₂S, as well as traces of NH₃ [3]. Catalytic steam reforming is the most common process to obtain hydrogen, which is usually chosen due to its high efficiency. Moreover, its simplicity and low implementation costs should be compared to other technologies, such as partial oxidation reforming, auto-thermal reforming, dry reforming, and dry oxidation reforming [4]. This technology has been widely applied in chemical industries for large scale H₂ production, which is accountable for 50% of hydrogen generated worldwide by using natural gas as main hydrocarbon source [5]. It is a well-known process which has been described by several authors, e.g. Steinberg [6] and Poirier [7] who reported hydrocarbon reactions, like those of methane, naphtha and ethanol with water (pre-vaporized by a steam

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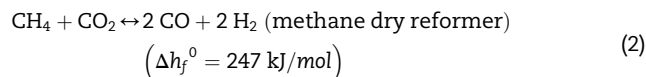
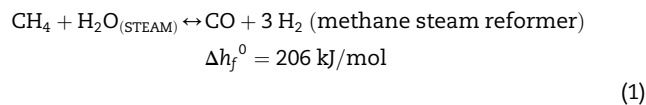
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Nomenclature

Δh_f^0	Enthalpy of formation [kJ/kmol]
HTS	High Temperature Shift
LTS	Low Temperature Shift
MCFC	Molten Carbonate Fuel Cell
RWGS	Reverse Water Gas Shift
SOFC	Solid Oxide Fuel Cell
SRB	Steam reform of Biogas
TCD	Thermal conductivity detector
TPO	Temperature programmed oxidation
TPR	Temperature programmed reduction
WGS	Water Gas Shift

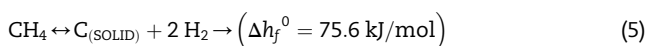
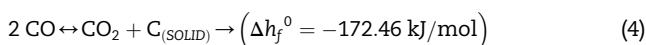
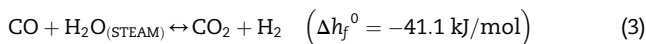
generator). The reactions that occur in this process primarily produce H_2 , CO_2 , CO and CH_4 , but there is no set quantity for these compounds whose concentration depend on several factors, such as reagents concentration, temperature and pressure of the reformer, as well as the physical and chemical characteristics of the chosen catalyst.

Steam reform of biogas (SRB), according to Bollini et al. [1], consists essentially in methane steam reforming and methane dry reforming as the following reactions:



Reaction (1) is the overall reaction that occurs in the steam reforming process and occurs at temperatures between 650 and 850 °C, thus obtaining H_2 yields of 60–70%, and the H_2/CO ratio is generally three, i.e. the most appropriate ratio for H_2 production [4]. Reaction (2) depicts methane dry reforming, which generally occurs at temperatures ranging between 700 and 900 °C by using a CH_4/CO_2 molar ratio of 1–1.5, with H_2 yields of around 50%. This reaction is more suitable for Fischer-Tropsch synthesis of biogas to produce liquid hydrocarbons and oxygenated derivatives, thus yielding H_2/CO ratio close to 1. Both reactions are highly endothermic and are favored by low pressures and high temperatures.

In addition to these main reforming reactions, other reactions can occur simultaneously that modify the equilibrium conversion of CO_2 and CH_4 , which are going to be presented as follows [4]:



Reaction (3) corresponds to the Water-Gas Shift Reaction (WGS), whose catalysts and reaction temperatures can be found in Table 1. The process can operate at high (HTS) or low (LTS) temperatures for eliminating CO produced in the

Table 1 – Catalysts and temperatures in the shift reactor [8].

Catalyst based on Cu/Fe/Cr →	Reactions HTS (250–450 °C)
Catalyst based on Cu/Zn →	Reactions LTS (150–250 °C)

reforming reactor, which enables the production of an additional amount of H_2 [4]. Unlike other reactions, it is exothermic and may occur at lower temperatures.

Bouduard's reaction (Eq. (4)) describes carbon formation by carbon monoxide decomposition. This reaction is very important for the process, since it is responsible for solid carbon deposition in catalysts. Methane dehydrogenation, shown in reaction (Eq. (5)), is one of the reactions that produce hydrogen while the reforming process is taking place, which also occurs in the reformer.

In biogas steam reforming processes, numerous supported catalysts have been tested. Catalysts are substances that are used in chemical reactions with the aim of accelerating them without being depleted. The materials which are mostly used as catalysts are palladium, ruthenium, iridium, tungsten, manganese, iron, silver, tantalum, titanium, vanadium, nickel, copper, and platinum [9]. In Table 2, examples of commonly used catalysts and their operating temperatures are listed, as well as the preparation technique being used. In the reforming process, most catalytic components are Ni-based, as Ni/Al_2O_3 [10]. This fact is due to the low cost of the component and its satisfactory efficiency.

Many supported catalysts in steam reforming have been tested, specially Ni-based catalysts, by some researchers, such as Kolbitsch et al. [12], Goula et al. [17], Urasaki et al. [18], Fonseca et al. [19] and Sabirova et al. [20]. However, one of the main problems of Ni-based catalysts is that they are subject to several types of deactivations, e.g. sintering, oxidation, carbon deposition and sulfur poisoning [15]. Among them, the most serious one is the formation of carbon deposits on catalysts which, consequently, lead to a blockage of catalyst pores by the deposited carbon, a separation of the catalyst by its support and lock on gas flow, due to an increase in pressure caused by pore blockage [21]. It occurs when the decomposition reaction of carbon monoxide, together with the decomposition reaction of methane (Reaction 5) are faster than the carbon removal rate is [4].

One common way to avoid these problems is to add suitable promoters that increase the stability of Ni-based catalysts, or to introduce a second metal component to form a

Table 2 – Catalysts for the biogas steam reforming system.

Catalyst	Preparation technique	Temp. (°C)
15% Ni/10% ZrO ₂ /Al ₂ O ₃ [3]	Co-impregnation	500–700
5% Ni/5% La ₂ O ₃ /Al ₂ O ₃ [11]	Impregnation/Calcination	550–800
11,5% Ni/Al ₂ O ₃ [8]	Reduction	650–850
CaO/Al ₂ O ₃ [12]	Impregnation	650–860
5% Pt/γ-Al ₂ O ₃ [13]	Impregnation	500–900
Ni/Mg/Al ₂ O ₄ [14]	Impregnation	650–800
Ni ₃ Al [15]	Impregnation	600–800
Ni–Ti xerogel [16]	Sol-gel/Calcination	200–700

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