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DESIGN AND VALIDATION OF AN ETHANOL AUTOTHERMAL REFORMER

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Abstract. *The use of hydrogen H_2 as a fuel has been extensively studied due to its high calorific power and for being a green energy source. H_2 can be obtained by various processes, which include hydrocarbon reforming reactions and water electrolysis. H_2 produced from ethanol reforming seems to be a good trade-off between avoiding pollutant emissions and process efficiency for on-board applications since ethanol is a renewable and ecological fuel. This calls for the development of highly compact and efficient ethanol reformers. This work describes the design and validation of an ethanol autothermal reformer for H_2 production for fuel cells applications. A screening of operational conditions was performed to avoid the flammability of the air/ethanol/water mixture, aiming at the complete evaporation of fluids was performed. Water/Ethanol and oxygen/ethanol molar rations were kept at 3:1 and 0.5:1, respectively, while the reaction temperatures varied between 500°C to 700°C. The catalyst is composed of a Ni/Al_2O_3 monolith made by commercial foams of Al_2O_3, with 40 pores per inch (PPI), a thickness of 20mm and a diameter of 80mm. The monolith was washcoated with a porous layer of α-Ni/Al_2O_3 particles, in order to increase surface area. Ni catalyst was impregnated using the wetness technique. The catalyst were characterized by scanning electron microscopy (SEM). Investigations were focused on the ethanol/water mixture vaporization, reform temperature, catalysts quantities and preheat of ethanol/water mixture.*

Keywords: *Ethanol Reformer, Hydrogen, Fuel Cell, Autothermal Reaction, Ni-Based Catalyts.*

1. INTRODUCTION

The demand for energy in the world is growing every year, due to the great impact that fossil fuels have caused to the planet, by their high emissions of carbon monoxide CO, carbon dioxide CO_2, and emissions of nitric oxides NOx. Different alternatives have been studied to reduce emissions from fossil fuels, one of the promising alternatives is the use of hydrogen as a fuel Najjar (2013). Due to its good properties, hydrogen has been extensively studied by researchers for use in spark ignition engines Sun *et al.* (2012b). For example, the adiabatic flame speed of the hydrogen is approximately three times faster than ethanol and gasoline, witch improves thermal efficiency and combustion stability of the engine, due to its high calorific value. The lower calorific value of hydrogen is approximately four times greater than ethanol and three times greater than gasoline; in addition, the hydrogen diffusion coefficient is much higher than gasoline and ethanol, thus improving the homogeneity of the air-fuel mixture Verhelst and Wallner (2009); Ghazal (2013); Bauer and Forest (2001); Sun *et al.* (2012a); Tippawan and Arpornwichanop (2014).

Several studies have reported that the addition of H_2 to gasoline in a spark ignition engine increases the temperature inside the cylinder, this fact is due to the fast laminar flame speed of H_2. In this way, with high temperatures in-cylinder chamber, occur sharp increases in NOx emissions. On the other hand, emissions of NOx can be greatly reduced using the technique of Exhaust Gas Recirculation (EGR), where part of the exhaust gases return to the combustion chamber, changing the concentration of oxygen within the combustion chamber, thus obtaining a greater concentration of fresh air inside the cylinder chamber and reducing the emission levels of NOx (Yu *et al.*, 2017; Greenwood *et al.*, 2014). Thus, for internal combustion engines, where H_2 is used mixed with another hydrocarbon, such as gasoline and ethanol, for a reduction in temperature inside the combustion chamber, and without the system losing thermal efficiency, the EGR technique it is widely applied, significantly reducing emissions of NOx, since this emission is one of the most undesirable characteristics of a fuel mixture containing H_2 (Alrazen *et al.*, 2016).

The H_2, in addition, to being widely used as a blending fuel in hydrocarbons, such as gasoline and ethanol, to increase thermal efficiency in the engine, is also considered a promising fuel for feeding in SOFC's. Where, from in general, hydrogen and oxygen react chemically, thus generating electricity, in a clean and renewable way, generating as reaction products only water and heat, being able to use this energy in several applications, such as in homes, as well as in on-board automotive systems (Ni *et al.*, 2007).

Hydrogen is obtained by various processes, fuel reform is a technique widely applied within industries, where, in general a hydrocarbon reacts in a catalyst at a certain temperature, generating several reaction products, among them the H_2. The most popular fuel reform processes are: Steam Reform (SR), Autothermal Reform (ATR) and Partial Oxidation (POX). Among the various existing fuels for reform, ethanol is the most promising of all, as it is a renewable and ecological fuel. Steam Reform is a process that requires high energy rates for the reaction to occur efficiently, that is, it is an endothermic reaction, on the other hand, it is the process in which high rates of H_2 production are obtained. Partial Oxidation has an exothermic character, however, its production rates of H_2 are not very attractive. To reduce the rate of energy used in the reform, and obtain satisfactory H_2 yield an Autothermal Reform is used, where, in this process the energy required is nearly to zero, thus the reaction becomes thermoneutral, because this reform is a combination of SR and POX (Rabenstein and Hacker, 2008; Vasudeva *et al.*, 1996; Sun *et al.*, 2012a; Chiu *et al.*, 2013).

The configuration and experimental studies of reactors for ethanol autothermal reform is little discussed in the literature, and one of the major problems to be solved is the behavior of the fluid operating in a reactor in a steady state, the complete vaporization of water/ethanol mixture, as the reactor must operate in an isothermal manner to ensure that the reform temperature is maintained. Pasel *et al.* (2007) developed an auto-thermal reformer project to reform JET A-1 fuel (aviation kerosene). In the configuration water + air are injected into an annular region external to the reforming region where the mixture is superheated up to 200°C, using part of the heat of the reaction, after which an additional heating raises the temperature of the mixture to approximately 480°C and then enter the reactor, against the current of the fuel fluid + air mixture, at room temperature, represented by the green line, and injected into the reactor by an injection nozzle, so the fluids enter the evaporation and mixing region, which precede the catalyst. The ATR 5 configuration showed evaporation instabilities, leading to auto-ignitions of the mixture, and a deactivation of the catalyst after approximately 90 hours of work. In this work, the problem was solved with a dilution of the reagent mixture with N_2.

The main objective of this work is the design, development and validation of a compact ethanol reformer for H_2 generation. To do so, the following steps are addressed: (i) construction of an experimental bench for ethanol autothermal reforming and H_2 production; (ii) Investigate the vaporization of the water/ethanol based on reactants pre-heating; (iii) Synthesis of the catalytic monolith.

2. LITERATURE REVIEW

H_2 is considered one of the most promising fuels for the future, due to its excellent physico-chemical properties, so it can be used in several applications, such as addition in ignition engines together with another hydrocarbon, such as gasoline or ethanol, for example, as well as in the supply of fuel cells to obtain electricity.

Table 1 shows the physical and chemical properties of H_2 comparing them with other hydrocarbons. As can be seen, H_2 has a higher flame speed and diffusivity when compared to ethanol (C_2H_5OH), gasoline (C_8H_{18}), methane (CH_4), diesel ($C_{12}H_{26}$) and methanol (CH_3OH). When H_2 is mixed with hydrocarbons in spark ignition engines, its properties help to increase engine efficiency and reduce emissions (except for NOx emissions); the addition of hydrogen helps in the combustion stability due to the high laminar flame speed and the high diffusivity, besides having higher Lower Heating Value (LHV), because the value is three times higher than gasoline and four times higher than ethanol (Karagöz *et al.*, 2019).

The disadvantage of hydrogen is its low density, making transport and storage difficult, requiring high pressures to transport it compactly. Another disadvantage of adding hydrogen to internal combustion engines is the high temperature of the adiabatic flame, which causes high temperature levels inside the cylinder, thus helping in the emission of nitric oxides (NOx) (Alrazen *et al.*, 2016).

The auto thermal reform reaction (ATR) is a process that combines Steam Reforming (SR) and Partial Oxidation (POX), this fuel reform method is a thermo-neutral process, that is, its process does not require nor does it yield energy for it to occur. For this thermo-neutral process to take place 1.78 mol of water vapor and 0.61 mol of oxygen per mol of ethanol, thus obtaining a production of H_2 of 4.78 mol of H_2 per mol of ethanol, represented by Equation 1 (Graschinsky *et al.*, 2012).

$$\mathrm{C_2H_5OH} + 0{,}61\,\mathrm{O_2} + 1{,}78\,\mathrm{H_2O} \longleftrightarrow 2\,\mathrm{CO_2} + 4{,}78\,\mathrm{H_2}, \Delta_r \approx 0kJ/mol \tag{1}$$

2.1 Thermodynamics of ethanol reformers

The ethanol reform has been studied by many researchers, due to the great availability of ethanol, mainly in Brazil, thus becoming a clean and sustainable alternative for the generation of hydrogen and subsequent generation of electric energy resulting from a fuel cell powered by H_2. For Tippawan and Arpornwichanop (2014) several factors influence the

Table 1. Fuel properties.

Properties Formula	**Hydrogen** H_2	**Ethanol** C_2H_5OH	**Gasoline** C_8H_{18}	**Methane** CH_4	**Diesel** $C_{12}H_{26}$	**Methanol** CH_3OH
Molecular weight [g/mol]	2.016	46.07	114.22	16.04	178.6	32.04
Density [kg/m^3]	0.08	785	740	0.65	815	792
Peak flame temperature [°C]	2210	1920	2030	2226	1720	1949
Lower calorific value [MJ/kg]	119.9	26.9	44.5	52.42	42.5	20.09
Energy density (LHV) [MJ/m^3]	11	15.84	34.32	34.07	35.8	17.3
Flame speed [m/s]	1.7	0.61	0.57	0.45	0.3	0.48
Auto-ignition temperature [°C]	572	558	440	450	355	465
Minimum ignition energy [mJ]	0.02	0.7	2.4	0.28	-	0.14
Quenching distance [mm]	0.64	0.9	2.84	2.5	2.1	1.8
Diffusion coefficient in air [cm^2/s]	0.096	0.021	0.012	0.16	0.004	0.15

Adapted from (Glassman *et al.*, 2014; Turns *et al.*, 1996; Boles and Cengel, 1989; Heywood, 1988; Agarwal, 2007; Petkov *et al.*, 1989; Ragland and Bryden, 2011)

efficiency in ethanol reform, directly influencing the efficiency of the Solid Oxide Fuel Cell (SOFC). According to the thermodynamic study in an autothermal reform, the reform temperature is a fundamental factor for the efficiency of the system, as well as the steam/ethanol ratio (S/E) in the reactor supply, because in low temperatures and S/E rates below 2, in an oxygen/ethanol ratio (O/E) of 0.61, there is a large formation of solid carbon, an element that is harmful to SOFC. The optimal point of operation, in the autothermal reforming studied, considers high hydrogen production and the non-formation of solid carbon, citing an optimum operating temperature above 900 K and S/E ratios above 6, in a O/E ratio of 0.61.

Sun *et al.* (2012a), in a similar thermodynamic study, evaluated the autothermal reforming of ethanol for hydrogen production, via minimization of Gibbs free energy, simulating equilibrium conditions in a temperature range of 700 to 1200 K, oxygen/ethanol (O/E) ratios equal to 0.25; 0.50 and 0.75; and steam/ethanol ratios of 1; 4; 7 and 10. Under these conditions the maximum hydrogen production obtained was at temperatures above 900 K, that is, at 1000 K, O/E = 0.25 and S/E = 7 a hydrogen production was 4.71 moles of H_2 per mole of ethanol, obtaining a thermal efficiency of 85 % in the autothermal reform of ethanol.

In a similar study, Rabenstein and Hacker (2008) evaluated the autothermal reforming of ethanol, using the Gibbs free energy minimization method, thus evaluating the composition of the products in equilibrium. In a temperature range of T = 200 - 1000 ºC, O/E ratios = 0.00 - 0.75 and S/E ratios = 0.00 to 10.00; and concluded that the best operation occurs at temperatures above 600 ºC, thus, at a temperature of 727 ºC, a O/E ratio = 0.25 and a S/E ratio = 7, hydrogen production was 4.8 moles of H_2 per mole of ethanol.

For Baruah *et al.* (2015), the choice of the catalyst in an autothermal ethanol reforming is essential, as it plays an important role with regard to ethanol conversion, hydrogen selectivity and solid carbon formation. Each catalyst has a different catalytic activity, promotes different reaction paths and has different costs for its characterization, and can be coated with noble metals or non-noble metals.

In an experimental study, Hung *et al.* (2012) investigated the autothermal reform of ethanol under various catalyst metals (Cobalt (Co), Nickel (Ni), Copper (Cu), Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Silver (Ag), Iridium (Ir), Platinum (Pt) and Gold (Au)), on alumina oxide (Al_2O_3), reforming temperature ranges between 400 ºC and 600 ºC, S/E = 3 and O/E = 0.3. The results obtained were based on the catalytic performance, and evaluated the maximum conversion of ethanol and hydrogen production, thus, the study shows that at a reform temperature of 600 ºC, the rhodium catalyst (Rh), presented better performance, obtaining an efficiency of ethanol conversion in the range of 97% and production of H_2 in 94 %. For these results, the characterization of the catalyst in Rh, has the following characteristics: surface area of 79.9 m^2/g; metal loading (wt%) of 1.6; and particle size at 15.00 nm.

In another similar experiment, carried out by Chiu *et al.* (2013), seven catalysts (Ferro (Fe), Cobalt (Co), Nickel (Ni), Platinum (Pt), Palladium (Pd), Rhodium (Rh) and Ruthenium (Ru)), on alumina oxide (Al_2O_3) in autothermal reform of ethanol, with specifications of metal loading (wt%) of 6; density of 50 g/ft^3; and dimensions of diameter = 60 mm for a length of 50 mm. The best performances among the evaluated catalysts, in decreasing order of H_2 production, were Rh>Ru>Pd>Pt>Ni>Co>Fe, thus confirming the great efficiency of the Rhodium (Rh). In the same study, the heat recirculation configuration with heated air was used, and together with the Rhodium catalyst, it was the largest production of H_2, when compared to the system without heat recirculation.

3. MATERIALS AND METHODS

In this section a schematic representation of the experimental apparatus is presented, describing the operation of the bench as well as the materials used for this purpose. A detailed description of the reactor design is also presented in this chapter.

3.1 Catalyst synthesis

The production of alumina paste was adapted from the methodology proposed by Agrafiotis and Tsetsekou (2000); Palm (2018). To produce the washcoat, a slurry was prepared by mixing alumina powder with 0.5 to 2 m particle diameter (CT 3000 LS SG supplied by Almatis) with distilled water for 1 h using a magnetic stirrer. Then, sodium silicate (1 wt%) and nitric acid (1 wt%) were added, and the solution was stirred for an additional 2 h. The solution's ph was controlled between 4 and 4.5. A slurry with 40% alumina mass concentration was prepared. Before coating, the foams were dried at 110 °C for 1 h and weighed in an analytical balance. The foams were then immersed in the slurry for 1 min. After immersion, the excess slurry was removed by contacting the foams with an absorbent paper. The foams were dried at 110 °C for 90 min, with a heating rate of 6°C·min1 to eliminate solvents and residues, and then calcined at 600 °C for 2 h at the rate of 6°C·min1. The impregnation of the active phase was based on the methodology used by Pinna (1998); Palm (2018). A Ni precursor was prepared using an aqueous solution of hexahydrate nickel nitrate (Ni(NO3)2·6H2O, 97% purity, supplied by VETEC) with a concentration of 2.5 M. The foams were then immersed in the solution for 16 h, dried at 150 °C for 24 h with a heating rate of 6°C·min1, and calcined at 700 °C for 2 h, with a heating rate of 6°C·min1. The Figure 1 shows the synthesis process of nickel and alumina catalyst (Ni/Al2O3) monoliths.

3.2 Catalyst characterization

Scanning Electron Microscopy was used to observe the morphology and topography of the monolith and also if the layer of washcoat and impregnation were homogeneous.

Insulating samples tend to accumulate the electrical charge of the primary beam and generate artifacts in the image. Thus, it becomes necessary to cover the samples with a conductive layer, usually gold or carbon, evaporated in a vacuum. Gold is usually deposited by the sputtering process. In the sputtering system atoms reach the surface from all directions. In summary, the metal is stripped from a gold-coated electrode by the energetic bombardment of positive ions; the gold electrode is connected to the negative potential of a voltage source on the order of 1 to 2 kV. Positive ions are produced by the ionization of argon, injected into the discharge chamber. The thickness of the gold layer must be thin enough to not affect the resolution of the image, but thick enough to guarantee a good production of secondary electrons, which will be used to form the image Stokes (2008).

Depending on the specimen's dimensions, various types of adhesives can be used. These samples were secured using carbon conductive glue and adhesive tapes and then subjected to the sputtering process with gold to avoid charge accumulations Echlin (2009).

The images were obtained using a Scanning Electron Microscope Field Emission at the Electronic Microscopy Laboratory of the Center for Technological Sciences (CCT) at the State University of Santa Catarina (UDESC).

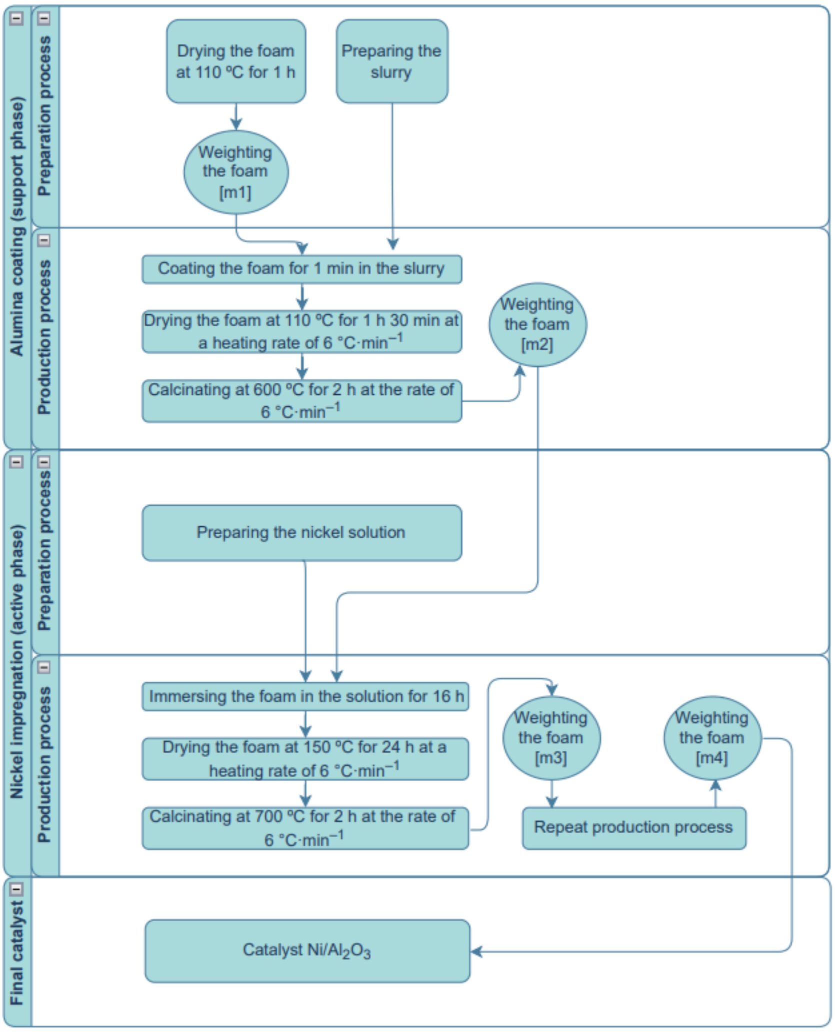

Figure 1. Flowchart of the methodology process used in the preparation of nickel and alumina (Ni/Al2O3) catalytic monoliths.

3.3 Experimental Apparatus

The Figure 2 provides a schematic representation of the experiment. The experiment is divided into two flow lines, one for ethanol and water and the other for air (Oxygen/Nitrogen), where they are located in the reactor. In the first line we have Nitrogen (1), which is used to pressurize the tank containing water and ethanol (3), later passing through a ball valve (2), then the fluid is heated by the electrical resistance (5), which is monitored by a temperature sensor (7) and controlled by a temperature controller (6), arriving at the injector nozzle (10), which is controlled by pulses generated by a Pulse Width Modulation (PWM) interface (9), so the fluid is injected inside the reactor (11). In the second line we have compressed air (1), where its flow is controlled by a flow meter (4), later heated by the electrical resistance (5), which is monitored by a temperature sensor (7) and controlled by a temperature controller (6), reaching the air inlet (8) in the reactor (11). The reactor (11) is made of STAINLESS STEEL 310 and contains the catalyst for the reform, right after the reactor the reformed gases reach the heat exchanger (12), due to the limitation of the chromatograph (13) for high temperatures. The chromatograph (13) measures the composition of the reformed gases.

The reactor illustrated in Figure 3 is built in order to preheat the air to a temperature of 300°C, where it is injected against the current with the water/ethanol mixture, facilitating the vaporization of the reactants in this region. After vaporization, the gases pass through the homogenization region and proceed to the reforming region, where they pass through the catalysts and reform occurs. The reforming region is heated by means of an electrical resistance.

The Figure 4 shows the assembled system, with its sub-parts identified, as well as the entire electrical flow and temperature control system.

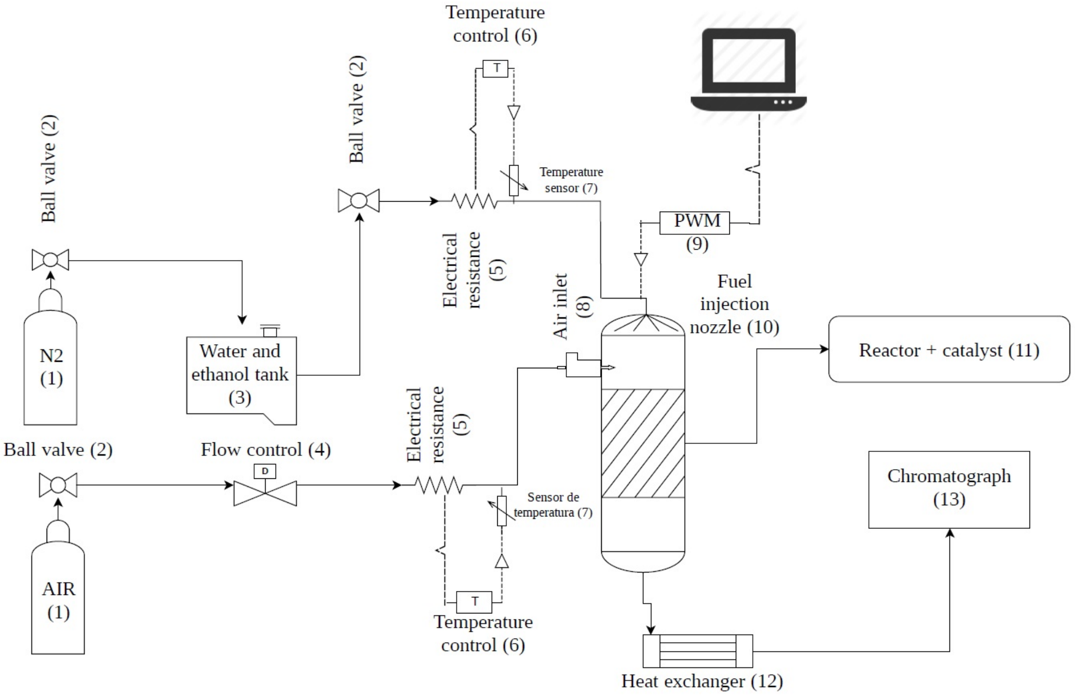

Figure 2. Schematic representation of the experimental bench.

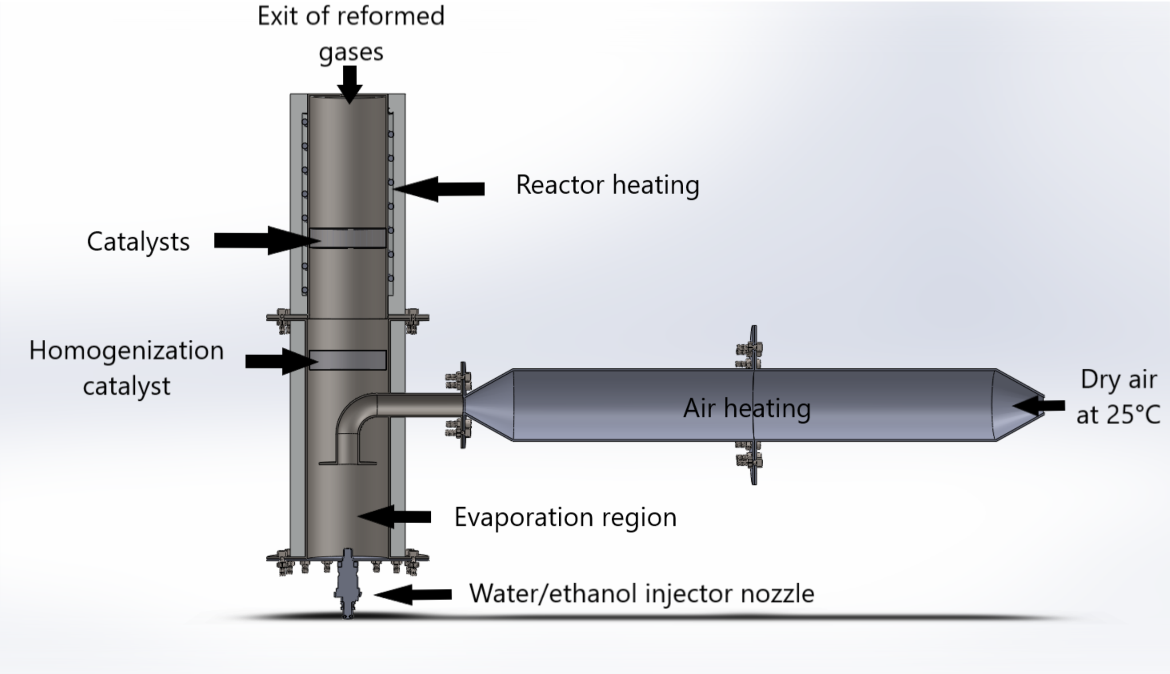

Figure 3. Section view of the reactor.

4. RESULTS

4.1 Vaporization test

Vaporization tests were performed, with air inlet temperature settings of 300°C, and four temperatures in the reactor: 400°C, 500°C, 600°C and 700°C. The equivalence ratio of the air/ethanol mixture was set at 6, that is, oxygen/ethanol molar ratio of O/E = 0.5:1, obtaining a mixture rich in fuel, and moving away from the flammability region of this mixture, which finds in terms of the equivalence ratio in the range of 0.41 (Lean Limit) and 2.8 (Rich Limit) according to Sharpe (2007). The feed rate of the water/ethanol mixture was set at 2 g/min, in a molar ratio of water/ethanol of S/E = 3:1. The air flow rate was set at 1.33 lpm (liters per minute) and to facilitate vaporization, Nitrogen was used as a diluent at a flow rate of 15.66 lpm.

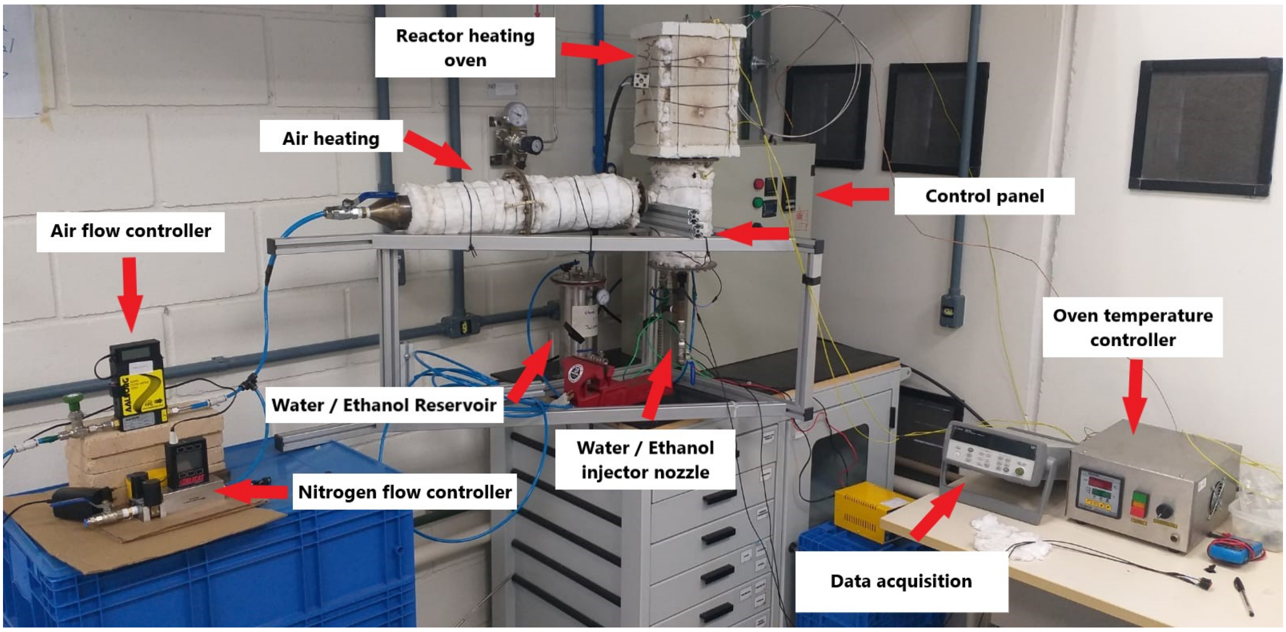

Figure 4. View of the assembled reformer.

4.2 Scanning Electron Microscope

Despite all previously described treatments and two coatings of sputtering with gold, the sample did not conduct properly, which caused artifacts to be generated in the image. It is believed that the poor conduction is due to the high porosity of the sample, as at the time of cutting, small particles were expelled due to the friction of the blade with the catalyst, increasing its porosity even further.

The Figure 5 shows no apparent clogging of the pores.

In the Figure 6 it is possible to observe the alumina grains of the washcoat layer with approximately 1 µm and the nickel grains of the impregnation layer with approximately 0.2 µm. It is possible to observe that the nickel particles were well dispersed in the alumina grains. However, the distribution of the grains was not homogeneous, with spaces without the washcoat and impregnation layer.

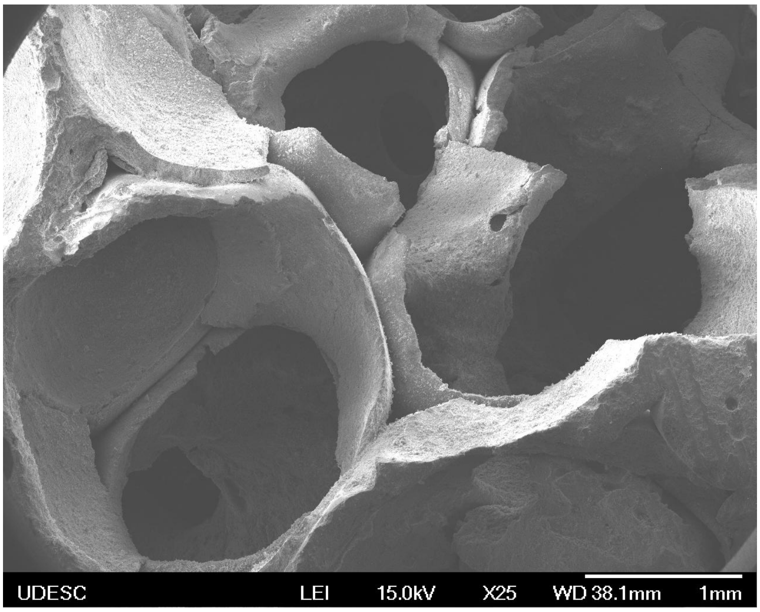

Figure 5. SEM images of washcoated and Ni-impregnated foam amplified by 25x.

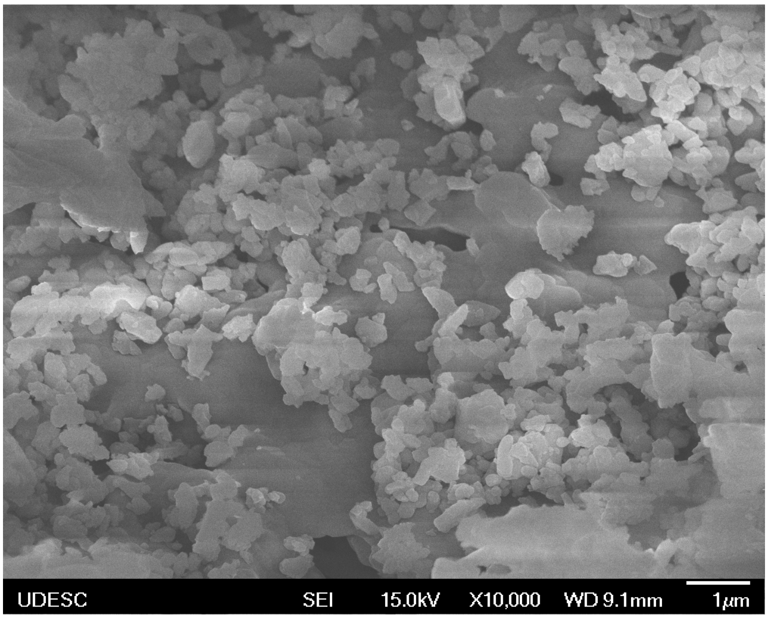

Figure 6. SEM images of washcoated and Ni-impregnated foam amplified by 10000x.

5. CONCLUSIONS

The distribution of the washcoat and impregnation layers were investigated by the SEM. The next steps for the characterization includes X-ray diffraction analysis (XRD).

The vaporization of the water/ethanol mixture was possible only for low rates, i.e., less than 2 g/min of ethanol/water mixture. This is due to the lower heat capacity of the heated air, when the oxygen/ethanol molar ratio is 0.5:1. New steps includes the vapor generation in an external unit and to carry out tests with catalyst at different proposed temperatures and different GHSV (Gas Hourly Space Velocity) as well as evaluate the composition of reformed gases.

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7. RESPONSIBILITY NOTICE

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