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CFD STUDY OF CATALYTIC ETHANOL STEAM REFORMING ASSOCIATED WITH EXHAUST GAS RECIRCULATION

Ana Luiza Gonçalves Eurides
Igor Marques Alves
Lucas dos Santos Fernandes
Laura Hamdan de Andrade
Department of Chemical Engineering - Pontifical Catholic University of Minas Gerais. ZIP 30.535-901, Belo Horizonte, MG, Brazil.
lauraandrade@pucminas.br; analuiza.eurides@hotmail.com; igor.marques.alves@hotmail.com; lucas.sfernandes07@gmail.com
Cristiano Henrique Gonçalves de Brito
Cristiana Brasil Maia
Department of Mechanical Engineering - Pontifical Catholic University of Minas Gerais. ZIP 30.535-901, Belo Horizonte, MG, Brazil.
cristianohbrito@gmail.com; cristiana@pucminas.br

Abstract. *The excessive use of fossil fuels has led to several environmental problems, which directly affect the ecosystem, implying the adoption of stricter legislation. Studies for replacing these fuels with clean and renewable energy sources, without affecting the efficiency and applicability of the processes are needed. Thus, hydrogen has become an interesting alternative since it can be obtained from renewable and non-polluting sources. The association of hydrogen to diesel, used in combustion engines, can reduce pollutant emissions, mainly NO_x. One way of achieving such an association between fuels is the incorporation of a steam reforming step of an organic fuel, such as ethanol, mixed with recirculated exhaust gases. Thus, in this work the hydrogen generation was investigated through computational simulations of the steam reforming of ethanol over nickel, together with exhaust gases from diesel engines. The results showed a high formation of acetaldehyde overlapping the products of the other reactions, leaving them in insignificant values. It is not possible, therefore, to conclude, with exactness, the influence of the parameters studied, temperature, steam/ethanol molar ratio and the introduction of exhaust gases.*

Keywords: *diesel engines, exhaust gas recirculation, ethanol steam reforming, nickel*

1. INTRODUCTION

The uncontrolled increase in pollutant sources has contributed to the reduction of air quality and vehicular sources have a significant part in this effect, especially in large urban centers. The vehicular emissions carry in its composition several substances that can cause negative effects to human, animal and plant health, deterioration of the patrimony and natural resources. Diesel powered engines are responsible for most of the emission of nitrogen oxides (NO_x) and sulfur oxides (SO_x) (Teixeira *et al.*, 2008).

In this context, much research is being done on the development and implementation of new technologies to reduce pollutant emissions, to comply with increasingly stringent legislation, and to keep the engine efficiency standard in a reasonable level (Chaichan, 2018).

Researches have shown hydrogen (H_2) as an interesting alternative fuel because it has excellent combustion properties, does not emit pollutant gases, and mainly because it is of clean and renewable origin and can be generated in many different ways (Chen *et al.*, 2004; Jafarmadar and Nemati, 2017; Liew *et al.*, 2012). According to the Office of Energy Efficiency & Renewable Energy of the United States (EERE), the hydrogen can be produced by biological, direct solar water splitting, electrolytic and thermochemical processes, being able to mention, in the last one, the steam reforming. The fuel that has been highlighting in this scenario is ethanol, mainly because it can e obtained from renewable sources and through processes that are less aggressive to the environment (Maia *et al.*, 2007).

Several technologies have been developed in order to generate in situ the hydrogen to feed in the combustion reaction, in particular the reformed exhaust gas recirculation (REGR), which incorporates a catalytic reformer in the recirculated stream, yielding hydrogen through chemical reactions (Dimitriou and Tsujimura, 2017; Wang *et al.*, 2016). This method reduces fuel consumption and has a favorable energy recovery, maintaining the combustion stability (Bogarra *et al.*, 2016).

Steam reforming is a highly endothermic process, involving a reaction between hydrocarbon fuel and water, with the aid of catalysts to increase reaction rates, resulting in a gaseous mixture containing carbon dioxide, carbon monoxide, methane, hydrogen and water (Teixeira *et al.*, 2016). The main reaction that describe the ethanol steam reforming is shown by the Equation 1.

$$\mathbf{C_2H_5OH(v) + 3H_2O(v) \rightarrow 6H_2(g) + 2CO_2(g)} \quad (1)$$

The noble metal catalysts, such as Pt and Rh, are interesting due to good activity and stability, but the high cost makes to study other cheaper alternatives (Ma *et al.*, 2016; Vicente *et al.*, 2014). Nickel is a good choice for use in steam reform due to high activity and relatively low cost (Palma *et al.*, 2013).

In order to identify the conditions that maximize the hydrogen production, studies that analyze the reform's parameters have received great attention among the researchers of the area (Vicente *et al.*, 2014). According to Sun *et al.* (2012), the increase in temperature promotes an increase in the conversion of ethanol and in the production of hydrogen. Vicente *et al.* (2014) found ethanol complete conversion at 700 °C using nickel as the catalyst. Still according to them, the increase of the steam/ethanol molar ratio, increases almost linearly the ethanol conversion and H2 production. For a steam/ethanol ratio of 10, 98% conversion and 49% yield were obtained, the yield being given by the actual H_2 production related to the production if 100% ethanol was converted to H_2. Bshish *et al.* (2011) emphasize that the injection of water in the feed decreases the methane generation by parallel reactions and limits the carbon deposit in the catalyst.

In order to optimize the engines performance, regarding gas flow and heat transfer, studies of the exhaust gases dynamics behavior through catalytic reformers have started. With the great technical-scientific advance over the past years, such studies were explored through computational simulations, which enable to approach more detailed phenomena, mainly the events that occur in the catalyst (Martins, 2006).

The purpose of this work is to simulate the steam reforming of ethanol over nickel fed by diesel engine recirculation gases using the Ansys Fluent® 19.0 simulation software, incorporating all the working conditions and chemical reactions involved in the process. The influence of the dilution ratio of ethanol on exhaust gases on hydrogen formation will be evaluated.

2. MATERIALS AND METHODS

All the simulations will be conducted with commercial software Ansys Fluent® 19.0, which solves conservation equations by the finite volume method. The computer used has the Windows 7 64-bit operating system, 32GB of RAM and Intel® Xeon™ processor E5-1660 @ 3.30 GHz 6-core processor.

2.1 GEOMETRY AND MESH SETUP

The proposed reforming will be carried out within a catalytic converter of a diesel engine, with the inner walls lined with nickel catalyst, supported in Al_2O_3, with a specific metal area of 350 cm^{-1}. Since the channels are similar to each other and symmetrical, for the purpose of calculation, the domain to be simulated corresponds to 1/8 of a microchannel, being a triangular base prism with dimensions 0.90 x 0.90 x 1.273 mm and a length of 60 mm. The elaboration of the simplified geometry consists in the construction of a computational model that demands little time and processing resources. Figure 1 shows the microchannel geometry and the computational domain generated for the simulations. The mesh generated was composed of 210000 cells, 662201 faces and 243243 nodes.

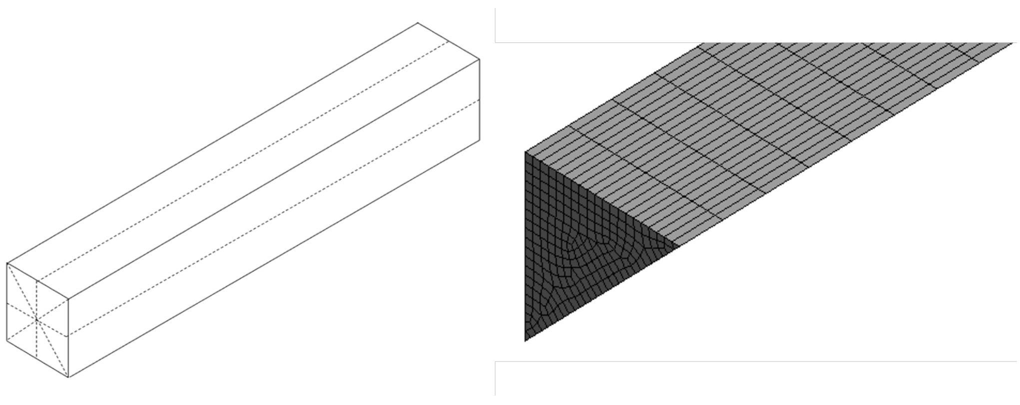

Figure 1. Geometry of the catalytic converter microchannel and the mesh used in simulations.

All reactions involved in the reform process will be introduced into Ansys Fluent® through CHEMKIN software from a kinetic and thermodynamic database.

2.2 INITIAL AND BOUNDARY CONDITIONS

For the problem approached it was considered: steady state, incompressible and laminar flow; ideal gas behavior; absence of heat exchange by radiation. Besides, the PRESTO! interpolation scheme was applied and the pressure-velocity coupling was treated with simultaneous resolution method combined with the fluidodynamic variables interpolation scheme Second-Order Upwind. The convergence criterion used was 10^{-3}.

The experimental data of the exhaust gases proposed by Brito *et al.* (2016) used in the simulation are described in Table 1.

Load (kW)	Exhaust gas flow (kg/h)	Temperature (°C)		Mass fraction (%)					
		Ambient	Exhaust gas	CO_2	CO	O_2	N_2	H_2O	H_2
37.5	150.8	30	579.2	16.231	0.0852	5.37	72.10	6.122	0.0896

Table 1. Experimental data of the exhaustion gases. Source: (Brito *et al.*, 2016)

The boundary conditions used were an input current of 0.01 m/s, steam/ethanol molar ratio of 12:1, temperature of 579.2 °C and atmospheric pressure at outlet. The system was simulated in two different setups: one without recirculated exhaust gases and another with 3% of the diesel engine exhaust stream.

Gas phase reactions were considered based on literature research. A total of 7 main reactions were adopted, and are listed below.

$$\text{Ethanol dehydrogenation:} \quad C_2H_5OH \rightleftharpoons C_2H_4O + H_2 \tag{2}$$
$$\text{Ethanol dehydratation:} \quad C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{3}$$
$$\text{Ethanol decomposition:} \quad C_2H_5OH \rightarrow H_2 + CO + CH_4 \tag{4}$$
$$\text{Decomposition of Acetaldehyde:} \quad C_2H_4O \rightarrow CH_4 + CO \tag{5}$$
$$\text{Steam Reforming of Acetaldehyde:} \quad C_2H_4O + H_2O \rightarrow 2CO + 3H_2 \tag{6}$$
$$\text{Steam Reforming of Methane:} \quad CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{7}$$

Heterogeneous chemical reactions were represented by a microkinetic model based on the density functional theory (DFT), proposed by (Catapan, 2012). An amount of 33 surface reactions and 27 species were considered in the mechanism. The main pathways for the ethanol steam reforming at over Nickel catalyst are shown in Figure 2.

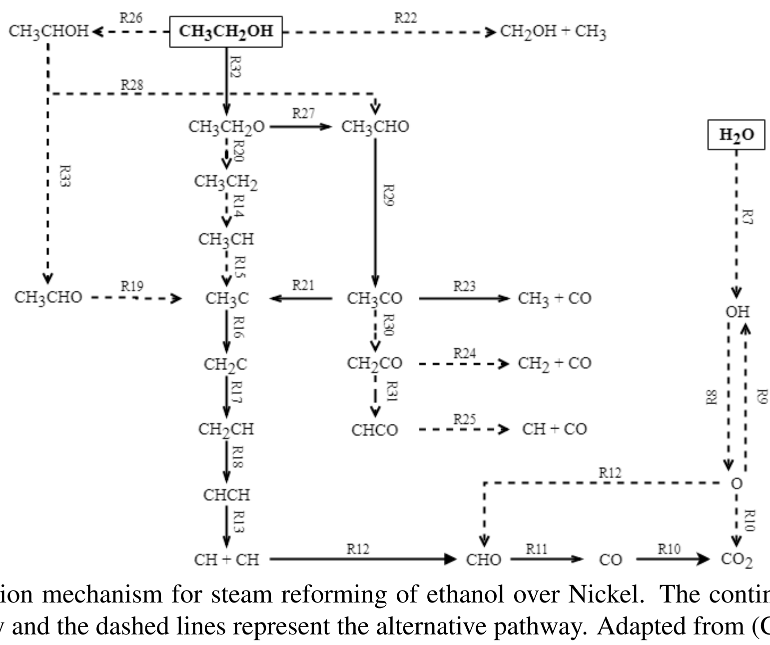

Figure 2. Surface reaction mechanism for steam reforming of ethanol over Nickel. The continuous lines represent the main pathway and the dashed lines represent the alternative pathway. Adapted from (Catapan, 2012)

All reactions involved in the reform process will be introduced into Ansys Fluent® through CHEMKIN software from a kinetic and thermodynamic database.

3. RESULTS AND DISCUSSION

After the simulation run and analysis of results, the species mass fraction was obtained. Figure 3 shows the gas mixture composition along the microchannel in the simulation without exhaust gas recirculation.

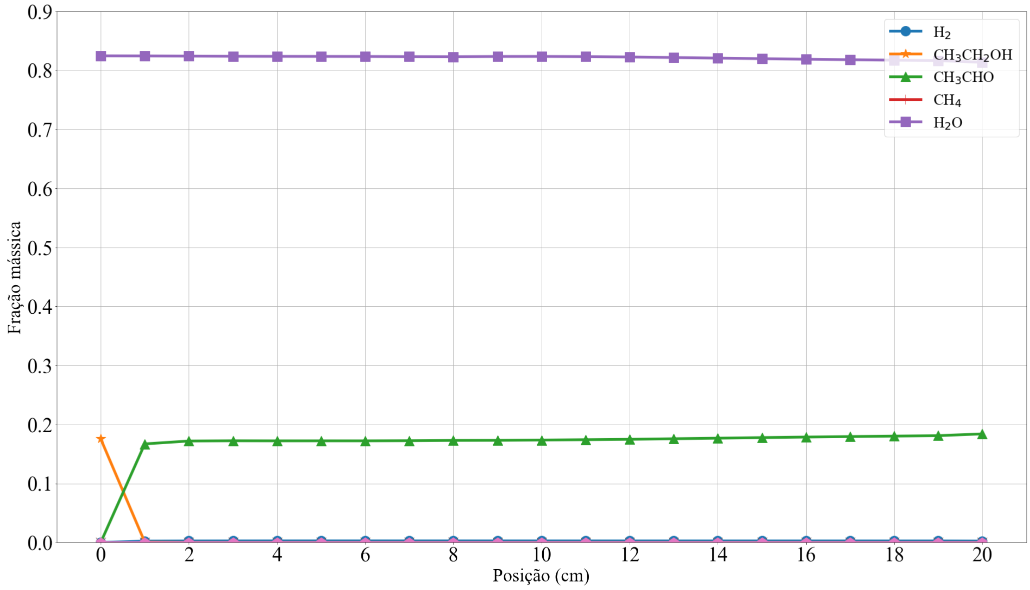

Figure 3. Species mass fractions along the microchannel. System simulated without exhaust gas recirculation

Looking to the graph we can observe that the majority variation of the composition of the system occurs in a small entrance region, of about 2 centimeters of the microchannel. We also note the almost complete consumption of ethanol and the formation of acetaldehyde in the same proportion. The mass fraction of the water remained constant throughout the simulation, indicating that there was no consumption or formation of water by the chemical reactions.

Similar results were found for the reform with exhaust gas recirculation, as shown in Figure 4. Despite the insertion of the exhaust gases, it was not possible to obtain comparable values and understand the effect of exhaust gases insertion on hydrogen formation.

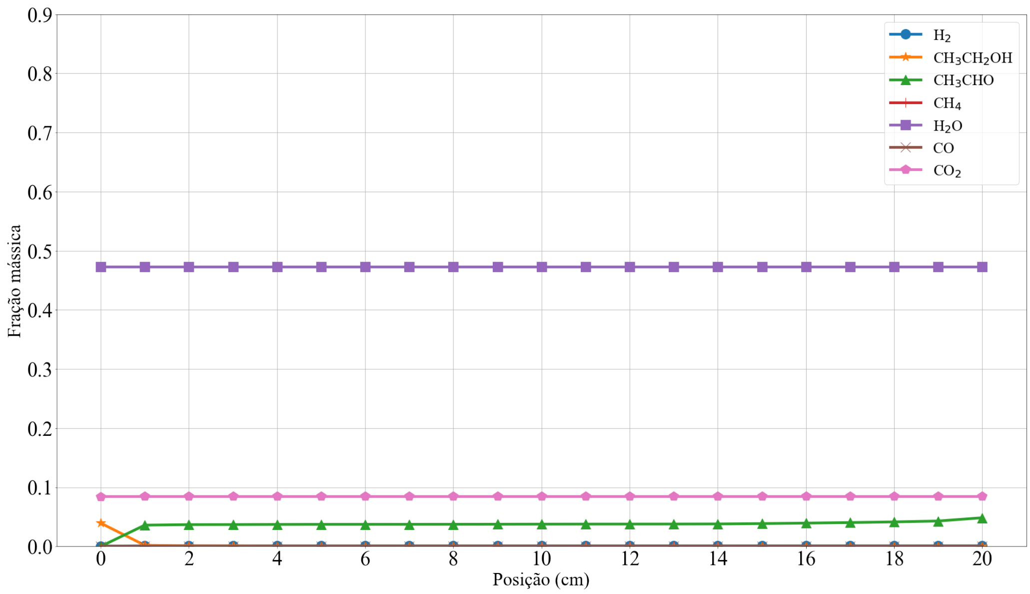

Figure 4. Species mass fractions along the microchannel. System simulated with exhaust gas recirculation of 3%

Figure 5 shows the temperature profile in the simulation without exhaust gases. There is a temperature decay in the initial part of the domain of approximately 60K due to occurrences of endothermic reactions. This temperature drop is attributed to the acetaldehyde formation reaction, that is observed in the mass fraction variation graph.

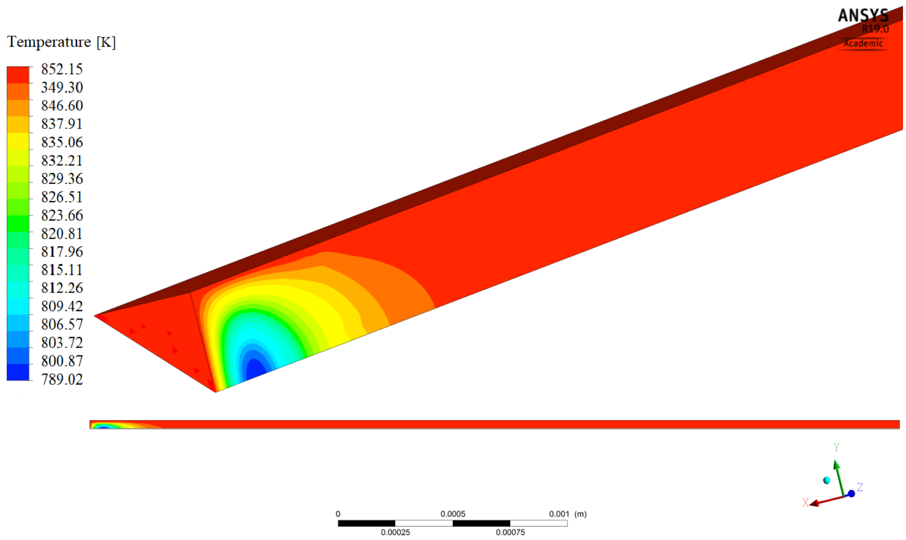

Figure 5. Temperature profile at the symmetry, wall and inlet faces. System simulated without exhaust gas recirculation

The thermal profile obtained for the reforming with exhaust gas recirculation, Figure 6, is similar to the previous one, with temperature decay in the initial part of the geometry, justified by the formation of acetaldehyde by the ethanol consumption.

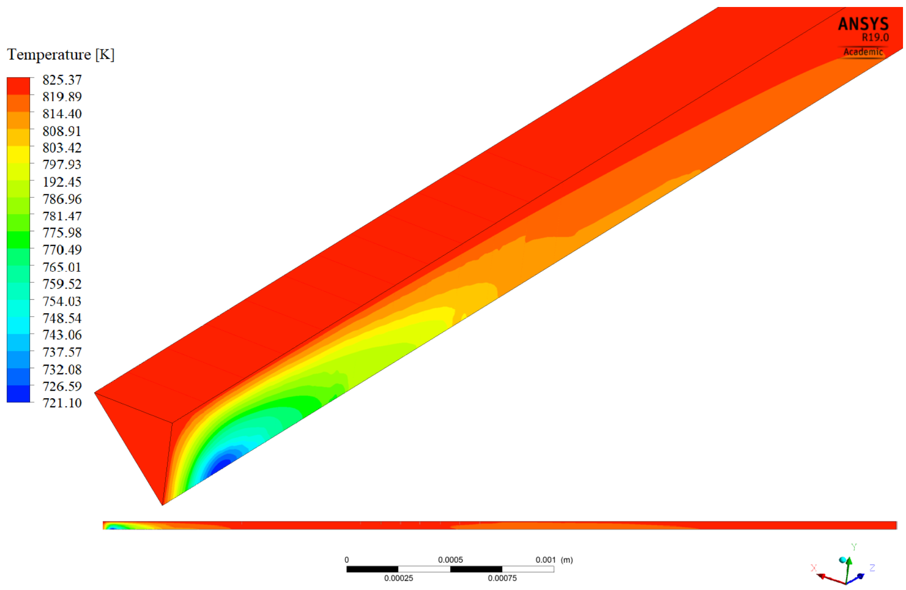

Figure 6. Temperature profile at the symmetry, wall and inlet faces. System simulated with exhaust gas recirculation of 3%.

In order to evaluate the occurrence of the reactions modeled in the system, the average kinetic rate of each one in the first 20 centimeters of the microchannel was calculated. Results are shown in Table 2.

Reaction	Rate ($mol.m^3.s^{-1}$)
R1	1,32E-12
R2	1,20E+02
R3	6,37E-07
R4	-
R5	6,13E-21
R6	3,44E-06
R7	5,47E-10

Table 2. Average kinetic rate of each gas phase reaction

It was noted that the only reaction that occurred at a considerable rate was the ethanol dehydrogenation, which is consistent with the large amount of acetaldehyde formed. Thus, it is noticeable that the hydrogen present in the system comes only from this reaction.

Reaction 5, which promotes methane formation, and reaction 16, which promotes hydrogen formation, showed negligible average rates. This fact is consistent with the fraction of species involved remaining practically constant throughout the reactor.

The slower rate of these reactions can be attributed to the kinetic parameters used in the system chemical reactions modeling phase. Thus, it was realized that the estimated values that were incorporated into the model were not well established. This was due to the consolidation of several kinetic data involving the ethanol vapor reform reported in the literature, which presented incompatibility with the model that was worked. There are two possible sources for this problem, the dispersivity of the reported data, relative to the adopted kinetic models, and the systems variability studied in the literature regarding the different catalyst types and operating conditions. In order to visualize the effects of the gas mixture flow inside the simulated channel, a local velocity vector graph was projected on the symmetry surface. The result is shown by Figure 7.

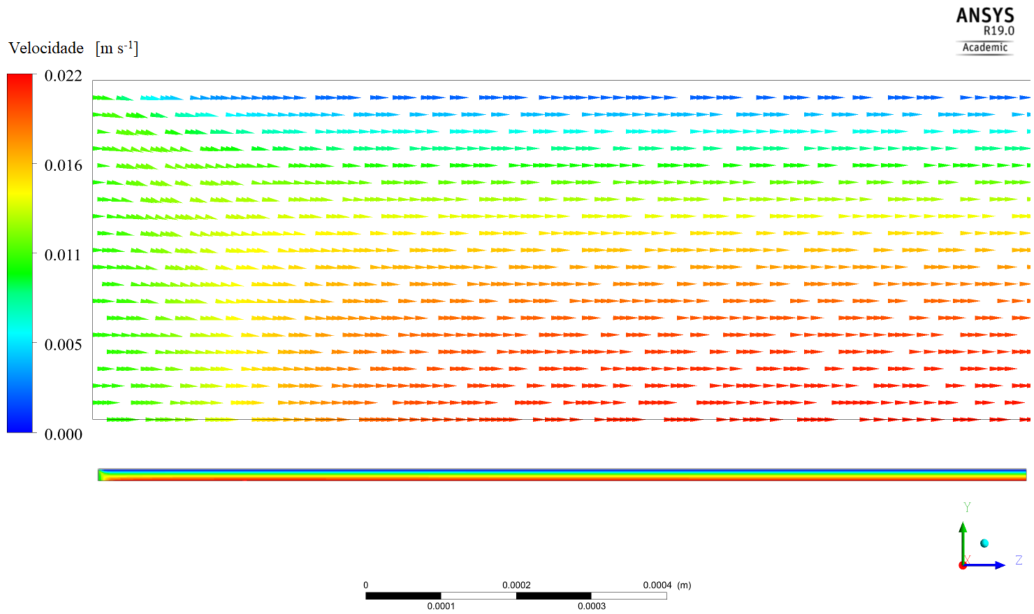

Figure 7. Vector plot of velocity magnitude at inlet region of the channel. System simulated without exhaust gas recirculation

It can be noticed that the flow velocity profile changes from the inlet region, thus the mixture is decelerated in the region closest to the wall and accelerated in the region closest to the central axis. The stagnant gas presence near the wall can be explained by the non-slip condition considered as boundary condition, and gas acceleration in the central region is an effect of mass conservation due to the reduction in cross-sectional area that occurs in passage of the mixture. Such explanation can be applicable to all simulations studied.

4. CONCLUSION

In the present work, Ansys Fluent® software was used to simulate a catalytic reaction of ethanol steam reforming on nickel, in configurations involving or not the exhaust gas recirculation of a diesel engine. The effects of variables temperature and steam/ethanol molar ratio were evaluated, as well as characteristics about the thermofluidodynamic flow profile.

From the obtained results it was observed that the monolith presented a critical region for the occurrence of the phenomena associated with the chemical reactions that was related to the channel entrance region, in which the velocity profile was variable. It was also noted that the ethanol dehydrogenation reaction, in which acetaldehyde is produced, occurred to a greater extent compared to the other reactions of the reform, being these, fundamental for the formation of the desired product, hydrogen. Therefore, it was noticeable that the hydrogen production in all simulations did not reach significant values. This can be verified from the analysis of the average speed of occurrence of reactions in the critical flow region.

The incongruity of the results obtained in the present work with those of the literature can be justified by the dispersiveness of the data related to the kinetic reaction models and by the variation of the systems studied in the literature, in which the fuel and the catalyst used change mainly. Therefore, it was not possible to accurately evaluate the relationship between the studied parameters, temperature, molar ratio and the introduction of recirculating gases, aiming at the maximum hydrogen production, as well as if the catalyst used was satisfactory for steam reforming.

5. ACKNOWLEDGEMENTS

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