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Modeling and simulation of an isothermal reactor for methanol steam reforming

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ABSTRACT. Due to growing electricity demand, cheap renewable energy sources are needed. Fuel cells are an interesting alternative for generating electricity since they use hydrogen as their main fuel and release only water and heat to the environment. Although fuel cells show great flexibility in size and operating temperature (some models even operate at low temperatures), the technology has the drawback for hydrogen transportation and storage. However, hydrogen may be produced from methanol steam reforming obtained from renewable sources such as biomass. The use of methanol as raw material in hydrogen production process by steam reforming is highly interesting owing to the fact that alcohol has the best hydrogen carbon^{-1} ratio (4:1) and may be processed at low temperatures and atmospheric pressures. They are features which are desirable for its use in autonomous fuel cells. Current research develops a mathematical model of an isothermal methanol steam reforming reactor and validates it against experimental data from the literature. The mathematical model was solved numerically by MATLAB® and the comparison of its predictions for different experimental conditions indicated that the developed model and the methodology for its numerical solution were adequate. Further, a preliminary analysis was undertaken on methanol steam reforming reactor project for autonomous fuel cell.

Keywords: mathematical modelling, methanol, steam reforming, hydrogen.

Modelagem e simulação de um reator isotérmico de reforma a vapor de metanol

RESUMO. A demanda por energia elétrica é crescente e fontes baratas e renováveis de energia são necessárias, com este propósito as células a combustível são uma alternativa interessante para a geração de energia elétrica, pois utilizam hidrogênio como principal combustível e apenas liberam água e calor ao meio ambiente. As células a combustível apresentam grande flexibilidade quanto ao seu tamanho e também quanto a sua temperatura de operação sendo que alguns modelos operam a baixas temperaturas, porém essa tecnologia esbarra na necessidade de transporte e armazenamento do seu principal combustível: o hidrogênio. No entanto, o hidrogênio pode ser produzido a partir da reação de reforma a vapor de metanol, o qual pode ser obtido a partir de fontes renováveis como a biomassa. A utilização do metanol como matéria-prima no processo de reforma a vapor para produção de hidrogênio é muito interessante, pois este álcool é o que apresenta a melhor proporção entre hidrogênio e carbono (4:1), além de poder ser processado a baixas temperaturas e pressão atmosférica o que é desejável na utilização em célula autônoma a combustível. Neste contexto, o objetivo desse trabalho foi desenvolver um modelo matemático de um reator isotérmico de reforma a vapor de metanol e convalidá-lo frente a dados experimentais de literatura. O modelo matemático proposto foi resolvido numericamente no MATLAB® e as comparações das suas previsões em diversas condições experimentais indicam que tanto o modelo desenvolvido como a metodologia empregada para a sua solução numérica foram adequados. Adicionalmente é feita uma análise preliminar sobre o projeto de reatores de reforma a vapor de metanol para células autônomas a combustível.

Palavras-chave: modelagem matemática, metanol, reforma a vapor, hidrogênio.

Introduction

Hydrogen is not only widely used in chemical industry but has been underscored as a promising energy source owing to the increasing search for renewable energy sources necessary for the development of human society. Hydrogen may be used as fuel in fuel cells which produce electricity from the hydrogen-oxygen reaction. However, the production, transportation and storage of hydrogen increase the cost of this technology and hinder its availability (KIM; KWON, 1998; OUZOUNIDOU et al., 2009; PETERS et al., 2000).

An alternative to difficulties presented by the direct use of hydrogen is the use of a less reactive precursor source of hydrogen that may be easily stored. Methanol has been widely studied as a source of hydrogen and it has been shown to be an attractive alternative, as hydrogen is made available via steam reforming reaction. Methyl alcohol with its high concentration of hydrogen (4 hydrogen atoms for each carbon atom) may be obtained from biomass. It may therefore be characterizes as a biofuel. Methanol steam reforming reaction is very convenient for hydrogen production since it occurs at relatively low temperatures (200-350°C) when compared with other reform reactions. Further, it exhibits good conversion at atmospheric pressure warranting its use as a source of hydrogen for autonomous fuel cells, especially on a small scale. Methanol steam reforming is the chemical reaction of water and methanol in the presence of a catalyst, usually CuO, ZnO and Al_2O_3 (JONES et al., 2008). The reaction produces hydrogen, carbon dioxide, water and carbon monoxide. However, the presence of carbon monoxide in the reactor production stream is an obstacle to the direct use of the hydrogen from the reactor by the fuel cell, as carbon monoxide is a contaminant to the fuel cell anode (NARUSAWA et al., 2003; TRIMM, 2005). The poisoning of the platinum anode of the fuel cell impairs and in some cases impedes its operation (FISHTIK et al., 2000; PEÑA et al., 1996; TAKEZAWA; IWAZA, 1997).

Modelling and simulation are powerful tools in the analysis and synthesis of autonomous systems of electricity production using fuel cells coupled to reforming reactors. The development of a mathematical model that represents the process of methanol steam reforming in a fixed bed reactor is a key step in the design of an autonomous fuel cell. This is due to the possibility of achieving rapid results that provide time and resource savings and studying different operating conditions that minimize CO production (AVCI et al., 2001; LENZI et al., 2010; SHAHROKHI; BAGHMISHEH, 2005).

An important development of a mathematical model is its validation by experimentally obtained data. It is thus possible to design a system capable of feeding an autonomous fuel cell from a methanol steam reforming reactor and to evaluate optimum operating conditions (IPSAKIS et al., 2012; SECANELL et al., 2011; WANG; WANG, 2008; ZERVAS et al., 2008).

Current research develops a simple and realistic mathematical model of an isothermal methanol reforming reactor using an industrial catalyst and the kinetic equations and data presented by Purnama et al. (2004) and validates the model by experimental data from the literature.

Material and methods

Research by Purnama et al. (2004), which demonstrated methanol steam reforming at atmospheric pressure in a tubular stainless steel reactor (10 mm i.d.), was the main source for the development of current study. The commercial catalyst used by Purnama et al. (2004) in all experiments consisted of $CuO/ZnO/Al_2O_3$ with a copper mass fraction of approximately 50%. The reactor was placed in an aluminium heating block with six 125W cartridge heaters for better heat transfer. The reactor temperature was adjusted by a PID controller connected to the cartridge heaters. Two type J thermocouples (Fe versus (Cu+43%Ni)) were used, or rather, one was placed in the aluminium block and the other in the catalyst bed. Purnama et al. (2004) used a stainless steel grid to support the catalyst. For gas flow conditioning, inert Pyrex® beads with the same size as the catalyst were placed on top of and below the catalyst bed.

In their studies Purnama et al. (2004) used the mechanism of methanol steam reforming taking into consideration two reactions, namely, the steam reforming reaction (SR), Equation 1, and the reverse water-gas shift reaction (WGS), Equation 2. According to the above kinetic model, CO production occurred as a side product due to the water-gas shift reaction (AGRELL et al., 2002; BREEN; ROSS, 1999; JIANG et al., 1993; LEDJEFF-HEY et al., 1998; PEPPLEY et al., 1999; PETERS et al., 2000; WIESE et al., 1999).

$$CH_3OH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3H_2 + CO_2 \tag{1}$$

$$\mathrm{CO_2 + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO + H_2O} \tag{2}$$

From the treatment of experimental data, Purnama et al. (2004) assumed that the kinetic equation of methanol steam reforming could be approximated by a power law equation and that the water-gas shift reaction was elementary, thus obtaining kinetic equations 3 and 4, where: r_{SR} is the SR reaction rate; r_{rWGS} is the reverse WGS reaction rate; k_1 is the SR reaction rate constant; k_2 is the direct WGS reaction rate constant; k_{-2} is the reverse WGS reaction rate constant, and P_{CH3OH}, P_{CO}, P_{CO2}, P_{H2O}, and P_{H2} are the partial pressures of methanol, carbon monoxide, carbon dioxide, water and hydrogen, respectively.

$$r_{SR} = k_1 P_{CH_3OH}{}^{0.6} P_{H_2O}{}^{0.4} \tag{3}$$

$$r_{rWGS} = k_2 P_{CO_2} P_{H_2} - k_{-2} P_{H_2O} P_{CO} \tag{4}$$

The reaction enthalpies ΔH^{o}_{298} for the SR reaction and for the reverse WGS reaction are +49 and +41 kJ mol^{-1}; the reaction entropies are +177 and +42 kJ mol^{-1}; and the Gibbs free energies ΔG^{o}_{298} are -3.8 and +28.6 kJ mol^{-1}, respectively (ATKINS, 1987).

The kinetic parameters of the methanol steam reforming reaction obtained by Purnama et al. (2004) were 76 kJ mol^{-1} and 8.8 x 10^{8} s^{-1}g$_{cat}{}^{-1}$ for apparent activation energy and pre-exponential factor, respectively. The kinetic parameters of the reverse water-gas shift reaction were 108 kJ mol^{-1} and 6.5 x 10^{9} bar^{-1} s^{-1} g$_{cat}{}^{-1}$ for apparent activation energy and pre-exponential factor, respectively.

The same kinetic mechanism for Equations 3 and 4 was adopted in current assay for the development of the mathematical model of the methanol steam reforming reactor in a fixed bed. The mathematical model used a pseudo-homogeneous, one-dimensional approach, without axial dispersion. It consisted of five differential equations (Equations 5 to 9) obtained from component mass balances (for CH_3OH, H_2O, H_2, CO_2 and CO) in a differential volume element of the reactor.

$$\frac{dF_{CH_3OH}}{dZ} = -r_{SR} \cdot Ac \cdot \rho_b \tag{5}$$

$$\frac{dF_{H_2O}}{dZ} = \left(r_{rWGS} - r_{SR}\right) \cdot Ac \cdot \rho_b \tag{6}$$

$$\frac{dF_{H_2}}{dZ} = \left(3 \cdot r_{SR} - r_{rWGS}\right) \cdot Ac \cdot \rho_b \tag{7}$$

$$\frac{dF_{CO_2}}{dZ} = \left(r_{SR} - r_{rWGS}\right) \cdot Ac \cdot \rho_b \tag{8}$$

$$\frac{dF_{CO}}{dZ} = r_{rWGS} \cdot Ac \cdot \rho_b \tag{9}$$

In these equations, F_{CH_3OH}, F_{H_2O}, F_{H_2}, F_{CO_2}, and F_{CO} were the molar fractions of methanol, water, hydrogen, carbon dioxide and carbon monoxide; Z was the reactor length; Ac was the cross-sectional area; ρ_b was the catalytic bed density.

The partial pressure of CH_3OH, H_20, H_2, CO_2 and CO was obtained by Equation (10)

$$p_i = x_i \cdot P \tag{10}$$

where p_i, was the partial pressure to component i; x_i was mole fraction of component i in the mixture of gas; P was total pressure.

The bulk density ρ_b comprised the porosity of the material and represented the catalyst mass that filled a unit volume of the reactor. In this case, the bulk density was calculated from the rates of particle density (ρ_p) of the industrial CuO/ZnO/Al_2O_3 catalyst and bed porosity (ε), using Equation 11 to obtain a rate of 1426.55 kg m^{-3} used in the simulations.

$$\rho_b = \rho_p (1 - \varepsilon) \tag{11}$$

The mathematical model represented by Equations 1 - 8 was numerically solved with solver ODE23TB from software MATLAB®. Figure 1 shows the flowchart of the simulation routine.

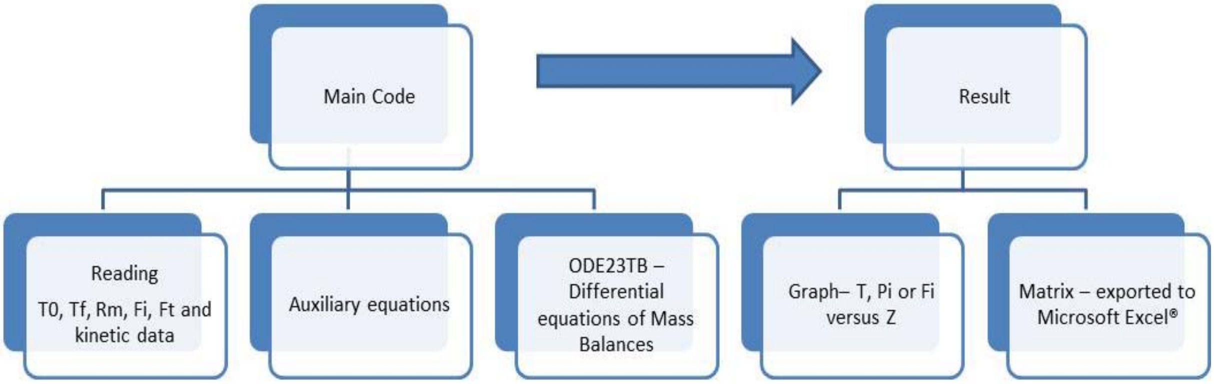

Figure 1. Flowchart for the solution of the developed mathematical model using MATLAB.

Results and discussion

Figures 2 to 5 illustrate the simulation results of the mathematical model compared with the experimental data obtained by Purnama et al. (2004). It might be observed that the reactor behaviour in the four operational conditions showed experimentally by Purnama et al. (2004) was well represented by the model proposed in which one of the main objectives of a methanol steam reforming was to produce hydrogen for use in a fuel cell. However some aspects must be taken into consideration, such as the 10 part per million (ppm) of carbon monoxide in the feed of fuel cells, because it contaminated the anode of proton exchange membrane fuel cell (PEM) (KIM; CHA, 2003; KIM; LIM, 2002; LEE et al., 2004).

Figure 2 shows that contact time, obtained from the ratio of the mass of catalyst by the input flow of the reactants in the reactor, affected the trend in hydrogen production profile. Experimental data were virtually linear, 0.5s to 0.6 seconds, after which there was a significant increase in hydrogen production. The proposed mathematical model used an equation of the type of law powers for the rate law of the steam reforming reaction. The mathematical model employs a power law equation to represent the reform of steam reaction rate. Due to this choice, the model's intermediate points show a significant deviation with regard to the experimental data by Purnama et al. (2004). The model adjusts itself to the total production of hydrogen and other compounds and to temperature conversion at 230°C. When experimental data by Purnama et al. (2004) and the model given in Figures 3 to 5 were compared, the fact revealed that the latter was duly adjusted and represented the process´s main trends. It may be observed that only the partial pressures of H_2 at 230°C (Figure 2) could not be well represented by the model for low contact times ($<$ 0.70). This fact suggested the possibility that measurement errors had occurred to H_2 concentration in this range contact time.

The adjustment quality quantification might be carried out by inspecting Table 1 as a function of the relative deviation means for component i (RDMC) and the global mean deviation (GMD) respectively defined by Equations 12 and 13. As Table 1 shows, the relative deviation mean for component, ranging from 2 to 29%, failed to demonstrate a clear trend due to temperature. However, the global mean deviation indicated that as the temperature rose, there was an improvement in the fitness quality of the model, or rather, from 19.8% DMG at 230°C to 9.6% DMG at 300°C.

$$RDMC\ i = \frac{\sum_{j=1}^{n} \frac{\left|P_{\exp}^{j} - P_{calc}^{j}\right|}{P_{\exp}^{j}} x100}{n} \tag{12}$$

$$GMD = \frac{\sum_{i=1}^{c} DRMC\ i}{c} \tag{13}$$

where:

c is all components; n is all points; $P_{\exp}^{j}$ is experimental partial pressure of component i and P_{calc}^{j} is the calculated partial pressure of component i.

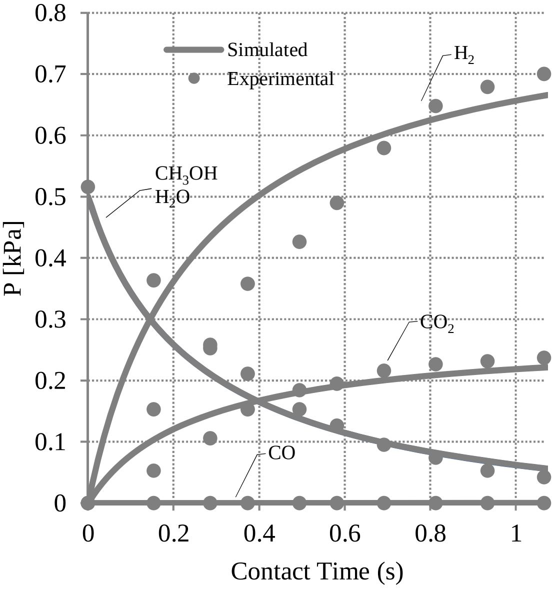

Figure 2. Model predictions and experimental data at 230ºC.

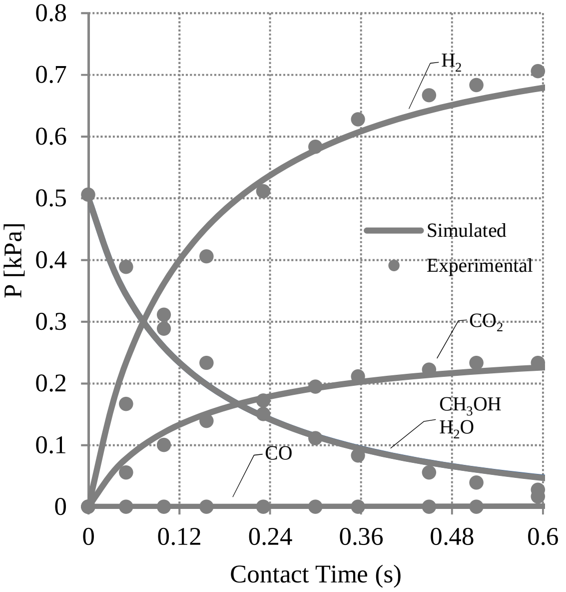

Figure 3. Model predictions and experimental data at 250ºC.

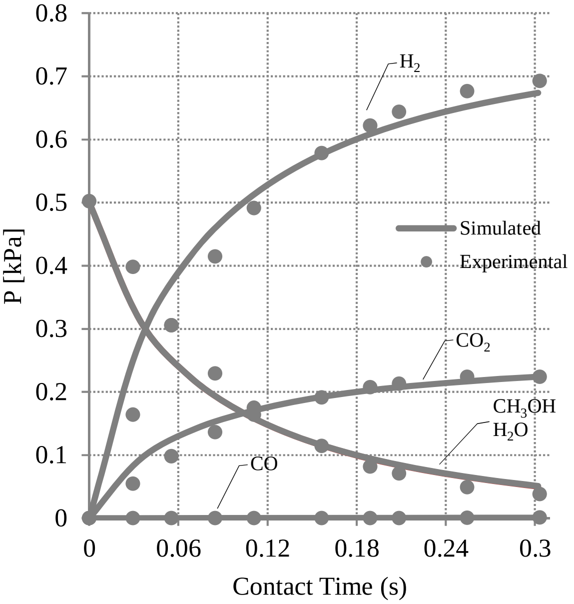

Figure 4. Model predictions and experimental data at 270ºC.

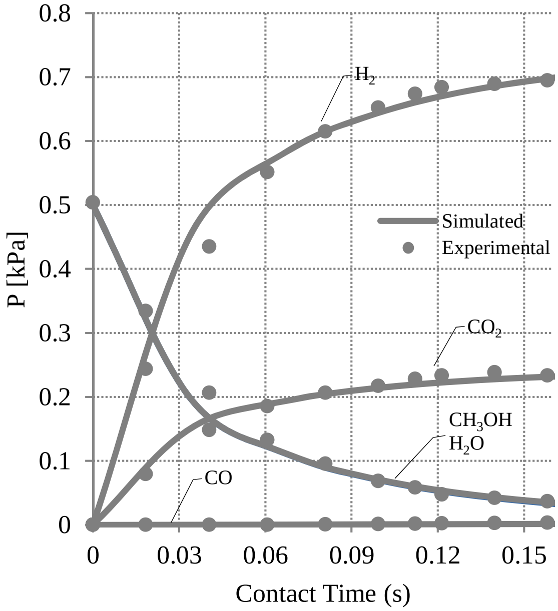

Figure 5. Model predictions and experimental data at 300ºC.

Table 1. Mathematical simulation of global error compared to experimental data.

Temperature (ºC)	DMG (%)	DRMC (%)				
		CH_3OH	H_2O	H_2	CO_2	CO
230	19.8	16	16	29	18	-
250	15.8	22	22	13	12	10
270	13.2	16	16	14	15	5
300	9.6	8	8	2	2	28

CO was not detected at 230oC, which made impossible the calculation of DRMC.

Methanol steam reforming occurred at lower temperatures for copper-based catalysts (230 to 300ºC), generating mostly hydrogen and carbon dioxide and a small amount of CO, usually less than 1% (LEDJEFF-HEY et al. 1998; PETERS et al. 2000; WIESE et al. 1999). The mathematical model used in this study may be used to determine the condition of operating a reactor of autonomous fuel cell that produces low level carbon monoxide (contaminant). The process of producing hydrogen from methanol is simple and it is possible to build compact reformers for adequate hydrogen production on-board. Figure 6 shows the dependence of methanol conversion by temperature and length of catalyst bed (contact time). Temperatures above 270ºC favor a high conversion, which tends towards equilibrium with low contact time, corresponding to the use of a small amount of catalyst. The above is desirable because of deployment costs and volume of the autonomous fuel cell.

Therefore, the project of a methanol steam reforming reactor attached to a fuel cell and separation or purification units, which comprises the platform for an autonomous fuel cell, implies a reflection on two distinct possibilities.

First, the design of a reactor operating at high temperature: it implies the use of small amounts of catalyst (low contact time) and consequently a reduced size reactor to achieve high conversions of methanol (approximately 100%, Figure 6); however, there is a need for subsequent purification steps in the hydrogen stream to compensate for a large amount of CO in the effluent stream (Figure 7).

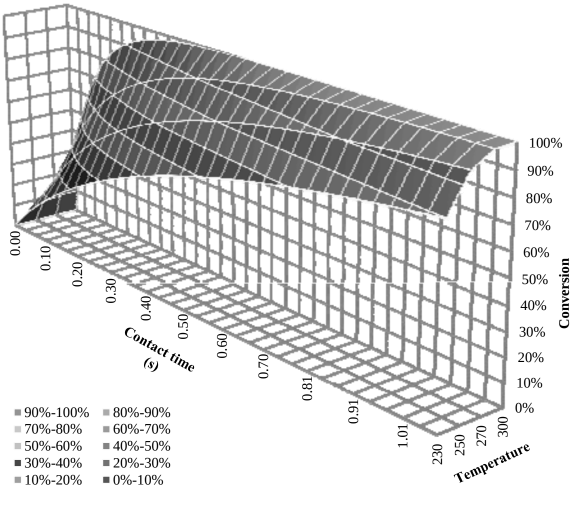

Figure 6. The simulation of conversion methanol at a temperature range between 230 and 270°C, with a contact time of 7.1 seconds.

Second, the design of a reactor operating at low temperatures: in this case, the effluent stream from the reactor would present a low concentration of CO, less than 10 ppm (Figure 7). The inconvenience of low conversions of methanol (approximately 70%, Figure 6) is that they require subsequent operations for the separation of the residual methanol, possibly by condensation, followed by re-feeding of the reactor.

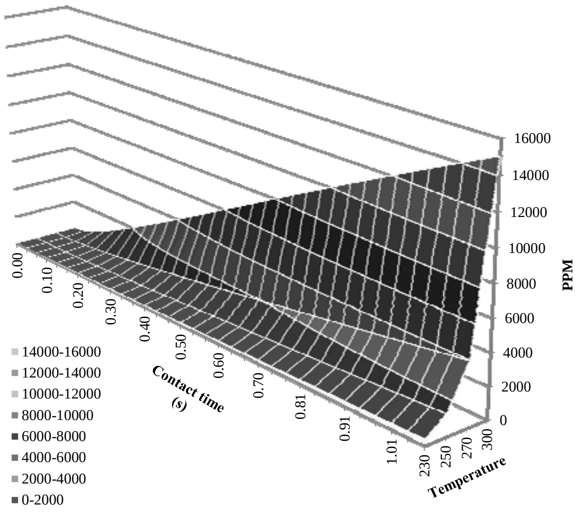

Figure 7. Simulation of the concentration of carbon monoxide (PPM) to a temperature range between 230 and 270°C, with a contact time of 7.1 seconds.

The choice of one from the project's two concepts will depend on a detailed study of deployment costs.

Conclusion

The developed model was adequate to model and simulate a methanol steam reforming reactor operating isothermally. The use of MatLab and its solver ODE23TB was found to be an appropriate strategy for solving the model.

The predictions of the mathematical model with global deviations of 19.8, 15.8, 13.2, and 9.6% from the experimental measurements at 230, 250, 270 and 300°C respectively, was observed only for the temperature 230°C. A representation suitable for hydrogen production failed to occur; however, when analyzed globally, there was a significant 16% deviation. The model showed a consistent decrease in the deviations with increasing temperature. Although the model showed deviations from the experimental data, it proved its robustness as a model without adjustments. The model developed from analytical literature data was able to satisfactorily represent the methanol steam reforming process in an isothermal integral fixed bed reactor which enabled the model to search for information for the design of reform reactors that operate in autonomous fuel cells.

Results point to the possibility of designing two types of autonomous fuel cell which depend on the operating temperature. High temperature will be employed in small reactors with high methanol conversion and high CO concentration in the effluent stream. The above requires the implementation of further steps to remove CO to acceptable levels (< 10 ppm) to the perfect operation of the PEM fuel cell. Moreover, low temperature reactor will be larger and it will present low conversion and a significant amount of residual methanol. The above requires subsequent stages for the separation and recycling of the reagent at levels below 10 ppm of CO, which makes the removal of this contaminant unnecessary.

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