A Model Development and Sensitivity Analysis of a Multitubular Thermochemical Recovery for Internal Combustion Engine Exhaust Heat

Victor E. Morales-Olmedo, Ricardo Morales-Rodriguez, Jesus I. Minchaca-Mojica, Ignacio R. Galindo-Esquivel\*

Departamento de Ingeniería Química, Universidad de Guanajuato, Noria Alta S/N, Noria Alta, Guanajuato, Guanajuato, 36050, México.

igalindo@ugto.mx

Abstract

A mathematical model is proposed for the recovery of the internal combustion engines exhaust heat to produce hydrogen using methanol reforming, which was constructed coupling mass and energy conservation principles, chemical reaction, and the heat transfer phenomena to represent an integrated tube and shell reactive heat exchanger. The results showed that it is feasible to design a multitubular reactor for hydrogen production with a good level of conversion; however, both performance criteria depend on several design variables, and it is difficult to identify which are the most relevant. Thereby, a sensitivity analysis (SA) was performed to find the most critical variables, where the diameter of the tubes, feed temperature of methanol, catalyst thickness and number of tubes result as the key design variables for the selected performance criteria. SA was done using the standardized regression coefficient using the results previously obtained using a Monte Carlo simulation, the last allowed to find designs that could provide a 99 % of methanol conversion with feasible dimension to be implemented in a vehicle.

**Keywords**: Methanol steam reforming, hydrogen production, Monte Carlo Method.

* 1. Introduction

A large portion of the energy demanded in modern society is used by the transport sector, where private vehicles play a predominant role. Internal Combustion Engines (ICE) have been the main devices used as vehicle’s propulsion systems. However, the thermodynamic efficiency of the ICE is generally from 20 % to 40 %, this low efficiency may be identified in the exhaust gases produced from combustion that leave the engine at high temperatures (over 673 K), and the thermal energy that remains in them that is dissipated to the atmosphere without further use. In recent years, thermochemical recovery (TCR) of this residual thermal energy has attracted renewed interest, as a possibility to use the residual heat of the exhaust gases to sustain an energy demanding endothermic reaction, such as alcohols or light hydrocarbons reforming.

Fomin and Makunin (2009) performed a thermodynamic assessment of the effectiveness of a thermal power-producing cycle of an ICE with and without TCR implementation, demonstrating the potential of this technology. Afterwards, Chakravarthy et al. (2010) made a thermodynamic study about the theoretical potential of using TCR applying different fuels: methanol, ethanol, and iso-octane, determining an increase of thermodynamic efficiency of 5 %, 9 %, and 11 %, respectively.

Kirillov et al. (2013) evaluated the production of syngas from methanol and ethanol dry reforming over different catalysts, using a configuration that resembles monolithic reactors. The results showed that the implementation of TCR and the addition of the syngas produced to the feed of the ICE decreased fuel consumption by 11 to 22 %, and furthermore, induced a reduction in the concentration of hazardous emissions (8-12 times for CO, 2-3.5 times for CH4, and 18-25 times for NOx). With a different reactor design, Chen et al. (2017) evaluated an onboard methanol steam reformer for hydrogen production on an ICE vehicle, observing a decrease in fuel consumption between 15 % and 25 %, a reduction of pollutant concentration in exhaust gases between 40 % and 50 %, and a 70 % reduction of exhaust smoke.

The previous results have shown that coupling an ICE with TCR represents a real available low-cost option, with the possibility to increase the thermodynamic efficiency of an ICE, simultaneously decreasing fuel consumption and pollutant emissions. On the other hand, all reactor designs have been developed empirically, and a chemical equilibrium is frequently considered in the reactor. Thereby, this research proposes a theoretical model for a multitubular TCR reaction system that considers the catalytic kinetics and heat transport phenomena fundamentals. To the best of our knowledge, this is the first fundamentally based design of this kind of configuration. The proposed system is based on a shell and tube heat exchanger, where the reaction proceeds in the shell side, and the catalyst is deposited in the external wall of the tubes. After model development, a sensitivity analysis is performed to identify the most determinant variables for the system design and construction.

* 1. Methodology

A mathematical model was developed coupling the fundamental principles of mass and energy conservation, as well as the heat transport phenomena and reaction kinetics, to reach the necessary temperature conditions.

The system is based on the configuration of a shell and tube heat exchanger, considering one pass on the tube side and a thin layer of catalyst applied to the external surface of the tubes. Therefore, the reaction takes place in the shell side of the system, while the exhaust gases flow through the interior of the tubes. The system considers a cocurrent flow system. The endothermic reaction chosen for the TCR system is steam reforming of methanol [Eq. (1)].

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| $$CH\_{3}OH+H\_{2}O\rightarrow CO\_{2}+3H\_{2}$$ |  (1) |

The reaction kinetics for methanol steam reforming catalyzed by Cu-ZnO/Al2O3, was previously reported by Santacesaria and Carrá (1983) [Eq. (2)].

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| --- | --- |
| $$R\_{CH\_{3}OH}=ρ\_{b}\left(\frac{K\_{c}b\_{M}P\_{M}}{1+b\_{M}P\_{M}+b\_{W}P\_{W}}\right)$$ | (2) |

Methanol is considered as the limiting reactant and its mass balance is developed for the shell side assuming plug flow in a steady state [Eq. (3)]. The equation is expressed in terms of the conversion reached at each point along the length of the system. The effect of catalyst layer thickness is analyzed, keeping values equal or lower than 0.0005 m to avoid significance of the internal mass transfer phenomena.

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| $$\frac{dX\_{CH\_{3}OH}}{dz}=\frac{R\_{CH\_{3}OH}π(r\_{4}^{2}-N\_{t}r\_{2}^{2})}{F\_{CH\_{3}OH\_{o} }}$$ | (3) |

The overall heat transfer coefficient is calculated considering the tubes and the catalyst conductivity, and convection in the exhaust gases, while the convection in the reactor stream does not affect the surface temperature. Also, a homogeneous distribution of the tubes is considered so that all tubes have the same contribution to the total heat transfer. As a result, the energy balance for each tube will result in [Eq. (4)].

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| --- | --- |
| $$\frac{dT\_{a}}{dz}=-\frac{2πr\_{3}U\_{z}(T\_{a}-T)}{\sum\_{}^{}\left(\frac{F\_{it}}{N\_{t}}\right)Cp\_{i}}$$ | (4) |

In the shell side, the temperature of the reactants and products stream is the same as the surface catalyst temperature along the system. The resultant energy balance is expressed by [Eq. (5)].

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| --- | --- |
| $$\frac{dT}{dz}=\frac{2πr\_{3}N\_{t}U\_{z}\left(T\_{a}-T\right)-π\left(r\_{4}^{2}-N\_{t}r\_{2}^{2}\right)H\_{rxn}R\_{CH\_{3}OH}}{\sum\_{}^{}F\_{i}Cp\_{i}}$$ | (5) |

This model considers that the heat transferred from the exhaust gases causes a decrease in their temperature (*Ta*), and allows the determination of the temperature profiles along the reactor. Since all fluids in the system are in a gaseous state, their thermophysical properties will experiment significant changes due to temperature variation along the reactor. Hence, the thermophysical properties of exhaust gases are recalculated in every step of the numerical method to determine the heat transfer coefficient. The model is solved with an in-house built code developed in Matlab® applying a first order Runge-Kutta method. Independence test was carried out monitoring the error variation at a fixed point and it was found that the appropriate step size is of 1x10-3 m with an error of 7.68E-5 for the temperature.

The proposed mathematical model includes diverse design variables that might generate some complexity to find an optimal design. In a previous work, the implementation of a sensitivity analysis before performing the optimization tasks, allowed the identification of the most critical variables (Villarreal-de-Aquino et al., 2023). To this end, in this work 6,000 samples were generated using the Latin hypercube method (LHM) followed by a Monte Carlo simulation to generate enough data and perform a global sensitivity analysis using the standardized regression coefficient method (SRC), which permits to identify the importance of the input variables on the selected performance criteria output variables.

* 1. Base case

The base case considers the inlet temperature of exhaust gases as 673 K, an estimate of this stream temperature after it passes through the catalytic converter. The reactant feed stream is considered as an equimolar vapor mixture of water and methanol, both in a gaseous state at about 453 K. The shell inside diameter is initially set as 5 cm and a reactor length of 1 m. The methanol molar flow rate (FM), tube external diameter (DT), pipe schedule (PS), tube array configuration (TP), number of tubes (NT) and thickness of catalyst layer (ThCat) considered initially are illustrated in Table 1. The tube arrays considered a fixed pitch of 1.25 of the external tube diameters. No heat loss to the environment was considered (insulated shell).

Table 1. Nominal values for design variables and the variation used in the LHM.

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| --- | --- | --- | --- | --- | --- | --- | --- |
|  | **DT** | **PS** | **TR** | **ThCat** | **FM** | **TP** | **NT** |
| Nominal value | 1/8”, ¼” and 3/8” | 10, 40 and 80 | 453 K | 0.0002 m | 75 mol/h | Square/ triangular | 1, 2, 3 and 4 |
| Percentage of variation | 50 % for each diameter | 50 % for each schedule | 25 % | 50 % | 35 % |  | 50 % for each NT |

DT: Tube diameter for exhaust gases; PS: Pipe schedule; TR: Feed temperature of methanol and water; ThCat: thickness of catalyst; FM: Methanol feed flowrate; TP: Tube pattern; NT: Number of tubes.

* 1. Results

The modelling of the limit base case scenarios corresponding to the shortest and largest dimensions for the diameter of the tube and the schedule: (i) 1/8” of diameter using a schedule of 10 and, (ii) 3/8” of diameter using a schedule of 80 was performed initially. For scenario (i) a conversion of 52.88 % for methanol was obtained producing 118.98 mol/h of hydrogen; in case of scenario (ii) the hydrogen production was 73.09 mol/h with a methanol conversion of 32.49 %. These results evidenced the opportunity for further analysis to find the best design of the reactive system. Hence, a global sensitivity analysis was performed to examine the effect of the design variables (input variables) in the selected performance variables, such as, methanol conversion, rate of hydrogen production, number of tubes, temperature of the reactants, temperature for the exhaust gas and shell diameter. The first evaluated scenario considers a fixed shell inside diameter of 5 cm, while in the second scenario the shell diameter is calculated for a fixed number of tubes. The design variables variations of the nominal values for both assessed scenarios are shown in Table 1.

Figure 1 illustrates the ranking of the significant output variables for a) methanol conversion; b) temperature for the exhaust gas; c) temperature of the reactants and products; d) hydrogen production. The diameter of the tubes and the feed temperature for the reactants are identified as significant variables in all the analyzed output variables. The third design variable with more significance in the output variables was the catalyst thickness. The methanol feed flowrate has the highest impact in the methanol conversion; however, it is important to highlight that the feed temperature of the reactants has the highest impact in hydrogen production, which means that higher temperatures induce more total hydrogen production even if methanol is not completely consumed.

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Figure 1. Variable significance ranking for output variables criteria: a) methanol conversion; b) temperature for the exhaust gas; c) temperature of the reactants and products; d) hydrogen production. DT: Tube diameter for exhaust gases; PS: Pipe schedule; TR: Feed temperature of methanol and water; ThCat: catalyst thickness; FM: Methanol feed flowrate; TP: Tube pattern.

Although an optimization task is not the main objective of the present research, the results showed that it is possible to find a better design variables combination when compared with the base case scenario (see Table 2). The results show that a higher temperature of the reactants and products improves the hydrogen production and conversion when compared to the base case. Sensitivity analysis also illustrates that reducing the diameter of the tube promotes conversion and hydrogen production, while the reduction of methanol feed flowrate only improves methanol conversion. In both cases the number of tubes for the exhaust gas flow was 6. It is suspected that the reduction in tube diameter increases the heat transfer efficiency of the system, which improves hydrogen production.

Table 2. Improved design variables for the reactive system maintaining the internal shell diameter of 5 cm and the reactor length of 1 m.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **DT** | **PS** | **TR, K** | **ThCat, m** | **FM, mol/ h** | **TP** | **Methanol conversion, %** | **Hydrogen production, mol/h** |
| 1/8” | 80 | 531 | 2.94E-4  | 89.54  | Square | 66.06 | 177.46 |
| 1/8” | 40 | 541 | 2.99E-4  | 50.49 | Square | 98.09 | 148.56 |

DT: Tube diameter for exhaust gases; PS: Pipe schedule; TR: Feed temperature of methanol and water; ThCat: catalyst thickness; FM: Methanol feed flowrate; TP: Tube pattern.

Based on the results from the first scenario, the sampling for the tubes number was varied from 1 to 4 considering the frequency of number of tubes in the first designs. Figure 2 depicts the ranking of the significant input variables on the temperature of the exhaust gas and feed temperature of the reactants and products (Figure 2.a), which are highly influenced by the methanol flowrate and its intake temperature. Regarding the Reynolds number, the number of tubes (where the flowrate is divided) and tube diameter are naturally significant variables that affect it; moreover, it is important to highlight that monitoring the Reynolds number is critical in this model since correlations and properties were determined by correlations applicable for Re > 3000. Finally, the internal shell diameter is highly dependent on the number and diameter of the tubes, since spatial (geometrical) limitations require more space for more tubes or larger diameters.

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Figure 2. Variable significance ranking for output variables criteria: a) temperature of the exhaust gas and feed temperature of the reactants and products; b) Reynolds number; and c) Internal shell diameter. DT: Tube diameter for exhaust gases; PS: Pipe schedule; TR: Feed temperature of methanol and water; FM: Methanol feed flowrate; TP: Tube pattern

The results of the Monte Carlo simulation provided better design configurations.

Table 3 shows two design configurations with better conversion and hydrogen production when compared with the base case scenarios. The results illustrate that it was possible to obtain the 99 % of methanol conversion with suitable dimensions, just above 1 m and a diameter with one extra cm. The results showed that it is possible to have feasible TCR device designs to render higher conversions of methanol. The necessary number of tubes for both improved designs was 4.

Table 3. Improved design variables for the reactive system calculating the internal shell diameter and reactor length to achieve 99 % methanol conversion.

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| --- | --- | --- | --- | --- | --- | --- | --- |
| **DT** | **PS** | **TR, K** | **ThCat, m** | **FM, mol/ h** | **Hydrogen production, mol/h** | **Length of the reactor, m** | **Internal shell diameter, m** |
| 1/4” | 80 | 553 | 2.65E-4  | 49.34 | 146.53 | 1.13 | 0.061 |
| 1/4” | 10 | 563 | 2.78E-4  | 51.67 | 153.46 | 1.45 | 0.061 |

DT: Tube diameter for exhaust gases; PS: Pipe schedule; TR: Feed temperature of methanol and water; ThCat: catalyst thickness; FM: Methanol feed flowrate.

* 1. Conclusions

A mathematical model for the design of a shell and tube TCR reactor was developed based on fundamental heat transport and reaction engineering principles. The model enables the possibility to design systems for different reactions, catalysts, reactant feeds and determines the amount of energy that may be transferred from a hot exhaust gas to revalorize thermal energy to produce hydrogen using methanol reforming. The sensitivity analysis demonstrated that it is possible to improve the TCR system design. To this end, the tube diameter and reactor inlet temperature were determined to be of particular importance. The results showed that is possible to make further analyses to obtain an optimal design from the techno-economic perspective, moreover, the mathematical model has the flexibility to evaluate and combine diverse materials for the unit, tailor-made catalysts, internal configuration, etc.

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