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Dynamic Modeling, Simulation and Control of a Methanol Steam Reformer for Hydrogen Production

Dimitris Ipsakis[a,b*], Symeon Savvopoulos[c], Panagiotis Karageorgos[b], Dimitris Trigkas[b,d], Panos Seferlis[e], Simira Papadopoulou[b,d] and Spyros Voutetakis[b]

[a] *School of Production Engineering & Management, Technical University of Crete, Chania, Greece*
[b] *Chemical Process & Energy Resources Institute, Centre for Research & Technology Hellas, Thermi-Thessaloniki, Greece*
[c] *Center for Membrane and Advanced Water Technology, Department of Mechanical Engineering, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates*
[d] *Department of Industrial Engineering & Management, International Hellenic University, Sindos-Thessaloniki, Greece*
[e] *Department of Mechanical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Greece*

Abstract

In this study a control-oriented mathematical model for a catalytic reactor suited for the steam reforming of methanol towards rich hydrogen production is presented. The model consists of partial differential equations that capture the concentration (or equivalently mass) and temperature time variation, by including a validated reaction kinetics scheme from a previous work. Based on this model, sensitivity analysis is performed with an aim to elucidate the effect of key process variables on the reformer's temperature and hydrogen production. As will be shown, the feed ratios of steam/methanol and oxygen/methanol affect significantly the reformer's temperature and hydrogen production and are selected as manipulated variables in our control analysis. The latter, is developed on the basis of comparing two PID controllers versus a model predictive controller (MPC) that is used to regulate simultaneously the operating temperature and hydrogen production (set-point tracking and disturbance rejection). Overall, this study can be used in control-oriented advanced schemes that can lead to the efficient production of energy carriers via cost friendly feedstock.

Keywords: *dynamic modeling, model predictive control (MPC), PID control, hydrogen, autothermal steam reforming*

1. Introduction

The past few years we are witnessing an alarming concern regarding the gradual deterioration of the environment in all sectors (air, water, land). Of course, this can be directly related to the excessive anthropogenic use of fossil fuels for the production of energy, fuels, and added-value chemicals. These "heavy" industrial sectors are responsible for the increasing greenhouse gas emissions (CO_2, CH_4, N_2O, Fluorinated gases) and consequently to Global Warming consequences.

In order to alleviate these problems, novel and with a high TRL (Technology Readiness Level) energy technologies should be integrated into the industrial sector. These technologies shall be based on renewable and alternative energy sources and can gradually replace conventional technologies, mitigating in this way carbon emissions. A widely adopted option of a global energy carrier is hydrogen [1], [2], as it brings together a series of advantages such as light weight, high energy content (~12 MJ/kg), clean combustion in fuel cells and an abundance of raw materials that can be used for its production. At the same time, disadvantages such as the high cost of transportation and storage, as well as the development of more efficient fuel cells for on-board consumption and/or production are under discussion. Apart from the "green-H_2" systems that use water electrolysis assisted by RES (renewable energy sources), the option of steam reforming is gaining attention [3], [4]. Among the C_1-C_4 hydrocarbons that can be used as "hydrogen carriers", methanol (CH_3OH) is an excellent choice due to its availability and flexibility in transportation and also due to its lower contribution to gaseous pollutants during conversion to hydrogen under mild reforming conditions [5].

The most prominent method to extract hydrogen via methanol is autothermal reforming, which is a combination of steam reforming and partial oxidation with air. The heat generated during the fast partial oxidation is used to initiate the slow endothermic reactions of steam reforming. Specifically, the steam/methanol and air/methanol feed ratios are those that determine the autothermal nature of the process and are usually chosen with an aim to reach high methanol conversions [5]. Modeling, simulation, and control play a crucial role in optimizing batch and continuous chemical and energy systems, enabling efficient operation and improved performance [6], [7], [8], as is the need for the presented system. In the case of methanol reformers, recent studies have adopted simplified, yet

* Corresponding author. Tel.: +30 28210 37362
E-mail: dipsakis@tuc.gr

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effective mathematical models and control schemes in order to enhance efficiency and reliability. A dynamic mechanistic model for a reformer-SOFC (solid oxide fuel cell) system was developed by Q. Li et al. in order to control (via PID) the SOFC operation and in the same time, maintain a high system efficiency [9]. T. Hos et al. [10], designed a process model for an integrated system consisting of a reformer, a hydrogen purification unit and the exhaust gas treatment system. There, it was stated that controlling the reformer's temperature is among the main requirements during operation. In an applied study by T. Zheng et al. [11], it was shown that the design optimization of a self-thermal methanol steam reformer should be accompanied by hydrogen and temperature control. Earlier studies on the field also proved the need to provide combined modeling and control studies. A.T. Stamps and E.P. Gatzke [12] developed nonlinear dynamic models for a methanol reforming process, where the key control points of the unit were identified. Following the above progress, aim of this study is to present a dynamic model for the simulation of a methanol reformer that incorporates both time and spatial variations. Under this model, a model predictive control scheme is applied in order to control both the reformer temperature and hydrogen production and is compared with the performance of conventional PID controllers. In this regard, the structure of the paper is the following: section 2 describes the operating features of a methanol reformer and the respective mass and energy dynamic models along with the necessary adaptation and assumptions. Next, section 3 performs a sensitivity analysis on the main variables that affect the performance of the steam reformer. Finally, section 4 presents the control analysis of MPC and conventional (PID) control schemes and their application to the reformer.

2. Description of the Methanol Reformer and Dynamic Model Development

2.1. Methanol Reformer Characteristics

The methanol steam reformer includes two streams as inputs (assumed that are preheated at the reactor's operating temperature): a) the methanol-water mixture and b) the air stream as shown in Fig. 1. For this study, we consider a packed bed reactor/reformer modeled as a pseudo-homogeneous 1D system that describes only axial profiles of radially averaged temperatures and concentrations [13]. As the fluid enters the reactor tubes, it comes into contact with the catalyst (CuO-MnO) which is in the form of particles. The catalyst is in a fixed position with respect to the flow of the main fluid and the following reactions take place are [5], [13]:

Steam Reforming (R1)
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ $\Delta H_{R,298} = 49$ kJ/mol
Partial Oxidation (R2)
$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2$ $\Delta H_{R,298} = -193$ kJ/mol
Methanol Cracking/Decomposition (R3)
$CH_3OH \rightarrow CO + 2H_2$ $\Delta H_{R,298} = 90.1$ kJ/mol
Water Gas Shift Reaction (R4)
$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H_{R,298} = -41.2$ kJ/mol

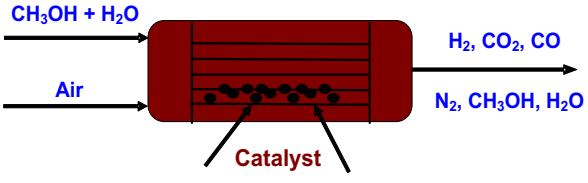


Fig. 1. Steam reformer reactor principles [5], [14]

2.2. Methanol Reformer Dynamic Modeling

The mathematical model includes a) mass and energy balances in the form of partial differential equations (PDEs), b) validated reaction kinetics (Arrhenius type) taken from earlier group studies [5], [13] and c) algebraic equations mainly concerning state equations. The necessary discretization was carried out using the method of orthogonal collocation for the time dimension and forward difference for the spatial dimension. More details regarding assumptions, model parameters and related information can be retrieved from [5], [13].

Feed Section at the Reformer

$$F_{H2O} = F_{CH3OH} \cdot (S/M\ Ratio) \quad (1a)$$

$$F_{O2} = F_{CH3OH} \cdot (O/M\ Ratio) \quad (1b)$$

$$\frac{dF_i^{'}}{dt} = \frac{Q_{in}}{V_{feed}} \cdot (F_i - F_i^{'}) \quad (2)$$

where F_i and F_i, are the theoretical and the actual (time delayed) flowrates of component i in mol/s respectively, *S/M* and *O/M* ratios refer to the steam/methanol (H_2O/CH_3OH) and oxygen/methanol (O_2/CH_3OH) feed ratios, Q_{in} is the volumetric flow of the gaseous component mixture at the theoretical inlet of the feed in m³/s, V_{feed} is the theoretical volume in which the components are considered to be mixed in m³, t is the time in s.

Essentially, the ratio Q_{in}/V_{feed} represents the inverse residence time (units s^{-1}), according to which the response of the components feed resembles a realistic operation.

PDEs related to concentration and temperature variation

$$\frac{\partial C_i}{\partial t} + \frac{\partial (u \cdot C_i)}{\partial z} - \varepsilon_{cat} \cdot D_z \frac{\partial^2 C_i}{\partial z^2} = \rho_{cat} \cdot \sum_{i=1}^{N} \sum_{j=1}^{R} \nu_{i,j} \cdot R_j \quad (3)$$

$$\rho_f \cdot Cp_f \cdot \frac{\partial T}{\partial t} + \rho_f \cdot Cp_f \cdot \frac{\partial (u \cdot T)}{\partial z} - k_z \frac{\partial^2 T}{\partial z^2} = \rho_{cat} \cdot \sum_{j=1}^{R} R_j \cdot \Delta H_{R,T,j} \quad (4)$$

For z=0 (reactor inlet) / For z=L (reactor end)

$$C_i = C_{i,in} \ and \ T = T_{in} \ / \ \frac{\partial C_i}{\partial z} = 0 \ and \ \frac{\partial T}{\partial z} = 0 \quad (5)$$

$$P_i = C_i \cdot R_g \cdot T \quad \text{and} \quad F_i = C_i \cdot Q_o \quad (6)$$

$$Q_o = u \cdot S = \frac{\sum F_{i,in} \cdot R_g \cdot T_{in}}{P_{reactor}} \quad (7)$$

where z is the reactor length in m, u superficial fluid velocity in m/s, ε_{cat} the catalyst void fraction, D_z the axial diffusivity in m²/s, $\nu_{i,j}$ the component's *"i"* coefficient in reaction j (*R1-R4*), R_j the reaction rate in mol/kg, ρ_{cat} the catalyst density in kg/m³, ρ_f the fluid density in kg/m³, Cp_f the fluid heat capacity in J/K·kg, T the reformer's operation temperature in K, k_z the axial thermal conductivity in W/m·K, $\Delta H_{R,T,j}$ the enthalpy of reaction j (*R1-R4*) at the reactor's operation temperature T in

J/K·mol, P_i and F_i the component's *"i"* partial pressure and flowrate in bar and mol/s respectively, R_g the ideal gas constant in bar·m³/mol·K, Q_o the volumetric flowrate in m³/s (taken at the inlet feed temperature T_{in}), S the cross sectional area in m² and $P_{reactor}$ the reactor operating pressure in bar.

3. Simulation Results

The two main variables that require continuous control during methanol reforming are: a) the operating temperature (in K) and b) the hydrogen production (in lt/min). Based on the mathematical simulation model that was presented in Section 2, it is concluded that only the input flows of the reactants (methanol, water and air) and the temperature of the input stream can be grouped as potential manipulated variables. Based on the above, we performed a dynamic (open loop) simulation in order to observe the effect of the *"manipulated-to-be variables"* to the reformer operation. The reference conditions are:

T_{in} =300°C, S/M=1.5, O/M=0.15 and CH_3OH_{in}=19.2 g/min.

Fig. 2 shows the effect of the S/M (H_2O/CH_3OH) ratio on the hydrogen production and reformer temperature after steady-state levels have been achieved. As can be seen, increasing the S/M ratio causes a decrease on the reformer's temperature due to the enhancement of the endothermic reforming reactions (see Section 1 for the reactions) and consequently the reformer's heat demand. At the same time, a small decrease in hydrogen production is observed for ratios >1.5. The effect is insignificant and associated with the decrease in methanol conversion due to a decrease in the residence time of the reactants in the reactor.

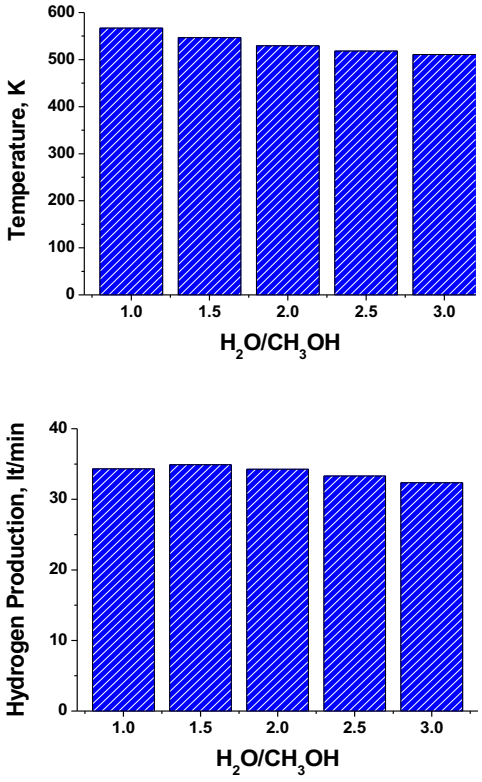
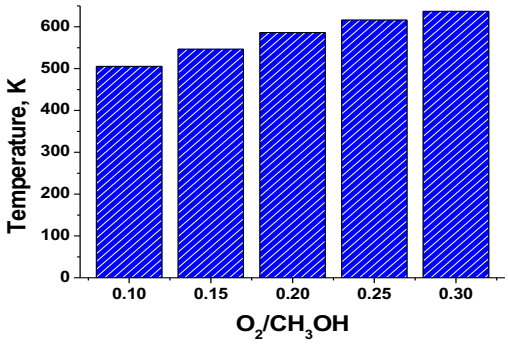


Fig. 2. Effect of S/M ratio on the reformer temperature and the hydrogen production

Next, Fig. 3 presents the effect of the O/M ratio on the same process variables. An increase in the ratio causes an enhancement of the exothermic oxidation (see Section 1 for the reactions) resulting in a relatively high temperature increase. Regarding the hydrogen production, an increase is observed for ratios >0.1 (almost complete conversion) and then an insignificant small decrease due to residence time reduction. Continuing the analysis, Fig. 4 presents the effect of the inlet feed temperature (423-537K), where it can be seen that increasing this temperature, a clearly beneficial effect on methanol conversion (and direct increase in hydrogen production) is observed. Furthermore, the operating temperature increases, as expected.



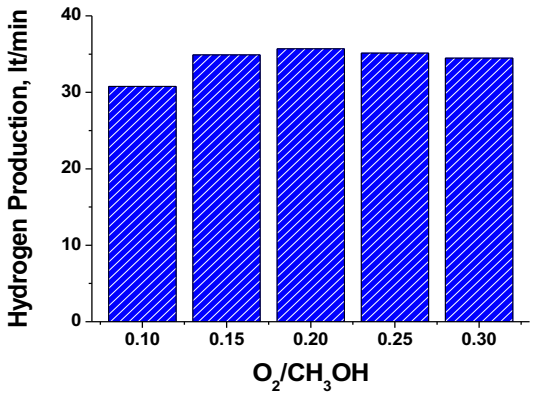
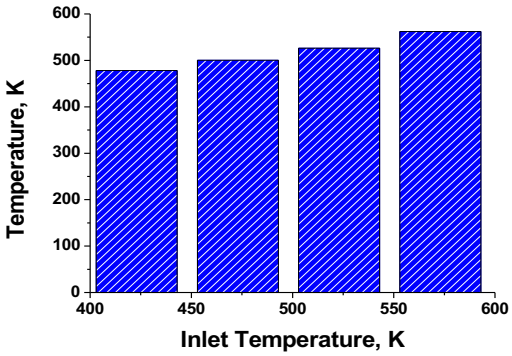


Fig. 3. Effect of O/M ratio on the reformer temperature and the hydrogen production



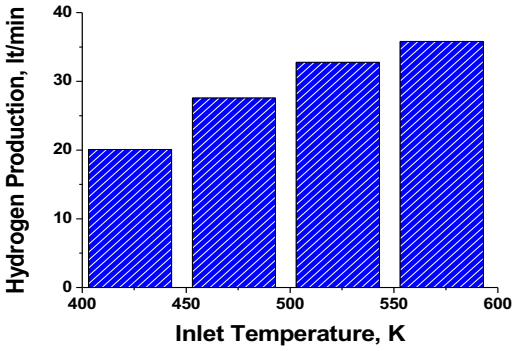
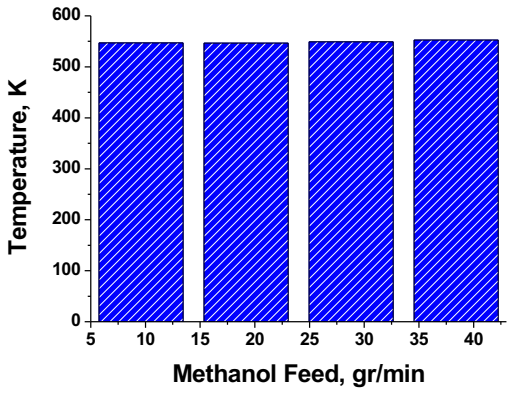


Fig. 4. Effect of the feed temperature on the reformer temperature and the hydrogen production

Finally, Fig. 5 shows the effect of methanol feed (9.6-38.4g/min) where only hydrogen production is affected (e.g. doubling the methanol the hydrogen production is nearly doubled).



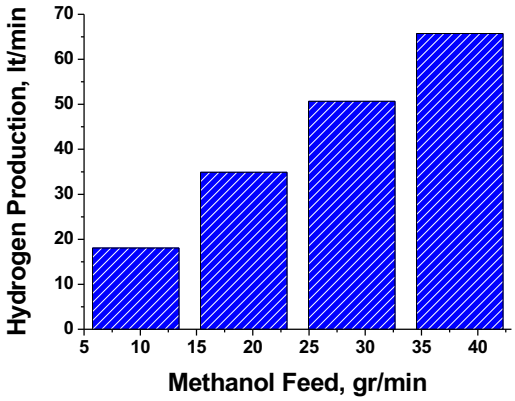


Fig. 5. Effect of the methanol feed on the reformer temperature and the hydrogen production

Based on the above open loop sensitivity analysis, it appears that methanol feed flow is considered to be the most suitable manipulated variable for controlling hydrogen production. Regarding the control of the reactor's operating temperature, it is reported that the O/M ratio is a better option than S/M. A typical control scheme is illustrated in Fig. 6.

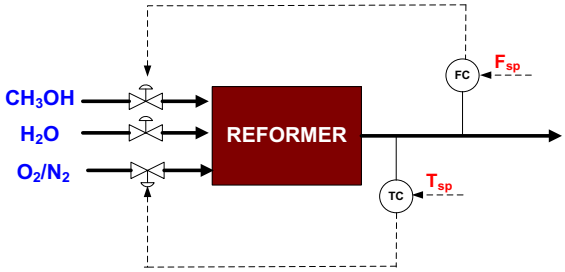


Fig. 6. A simplified structure based on feedback control

4. Control Analysis

After ensuring the capabilities of the mathematical model, a control analysis is applied in order to study the possibility of the autonomous reformer/reactor operation. Two control structures are analyzed and compared: a) two conventional PID controllers for the individual control of hydrogen production and reformer temperature and b) a model predictive controller. Regarding PID controllers a detailed analysis has been presented in earlier group studies [5], [15]. The typical PID controller equation is shown in Eq. 7 and followed in Table 1 by the respective parameters tuned

via Ziegler-Nichols methodology. We also included a fine tuning to ensure a more realistic approach and found that the "D" term might be optional).

$$c(t) = c_s + K_c \cdot e(t) + \frac{Kc}{\tau I} \cdot \int_0^t e(t)dt + K_c \cdot \tau_D \cdot \frac{de(t)}{dt} \quad (7)$$

Table 1. PID Controller parameters

	K_c	t_I	t_D
Hydrogen Control	$1e^{-2}$	10	<2
Temperature Control	$1.7e^{-4}$	15	<2

In order to apply the MPC, the following objective function (equally weighted at 0.5) was implemented and includes the quadratic deviations of the controlled variables (reformer temperature "$T_{reformer}$" and hydrogen production "F_{H2}" in discrete state) from their set-points (*sp*). Moreover, it includes the deviations (based on two consecutive time periods) of the manipulated variables (O/M ratio and methanol feed rate). The control horizon was taken at ~1/3 of the prediction horizon (where steady-state is achieved and is accurately capturing system dynamics). Typically, no constraints were added to the problem since the simulation is performed away from boundaries related to the upper/lower limit of the manipulated variables:

$$\min J = W_{1,y}(T_{reformer} - T_{sp})^2 + W_{2,y}(F_{H_2} - F_{H_2,sp})^2 + W_{1,u}(\Delta[O/M])^2 + W_{2,u}(\Delta[F_{CH_3OH}])^2 \quad (8)$$

4.1. Reference Control (Constant Set-Point)

Fig. 7 shows the reformer temperature profile following a typical reference signal (constant set-point at 550K) along with the variations on the manipulated variable (O/M ratio).

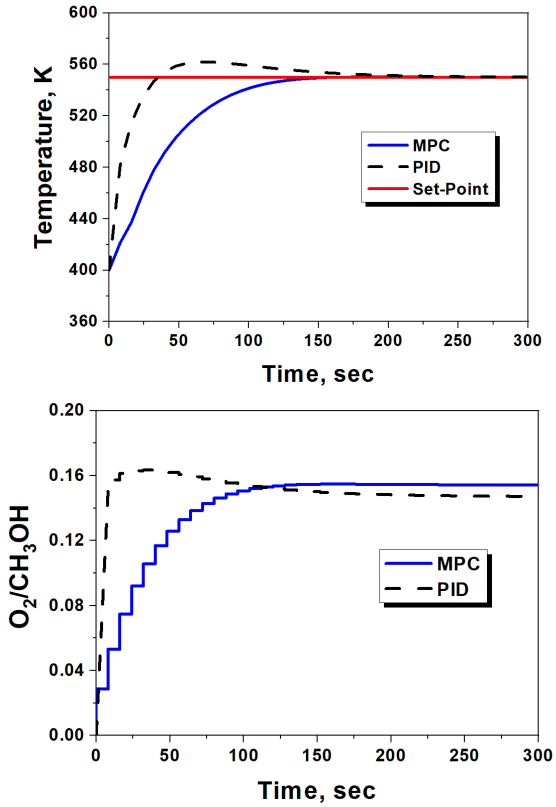


Fig. 7. Variation on the reformer temperature (controlled variable) by manipulating the O/M ratio

As can be seen, the MPC control scheme provides a slower, but with no overshoots trajectory, towards achieving the set-point. Meanwhile, PID control shows a faster action at the start of the operation, but reports the same settling time (~150s) and a minor ~10K overshoot. The superiority of the MPC is mostly assessed at the variations of the O/M ratio that follow a gradual and more smooth settling, while in the case of the PID controller, sharp actions are observed during the first 20-30s of operation.

Similarly, Fig. 8 shows the controllers' comparison regarding hydrogen production. Similar to the previous analysis, the MPC provides a more robust regulation, whereas the conventional PID controller leads to an oscillatory behavior with an extreme (>130%) overshoot. This operation may pose a risk regarding the strict limits of the variables (controlled and manipulated) that may be prone to saturation or reach upper limits (constraints). Regarding the manipulation of methanol feed it is observed that MPC provides certain control actions, while in the case of the conventional PID a risky variation occurs as methanol feed reaches high enough values during the first 20s of operation. This means that PID controllers would lead to increased methanol consumption for the same operation as compared to the MPC.

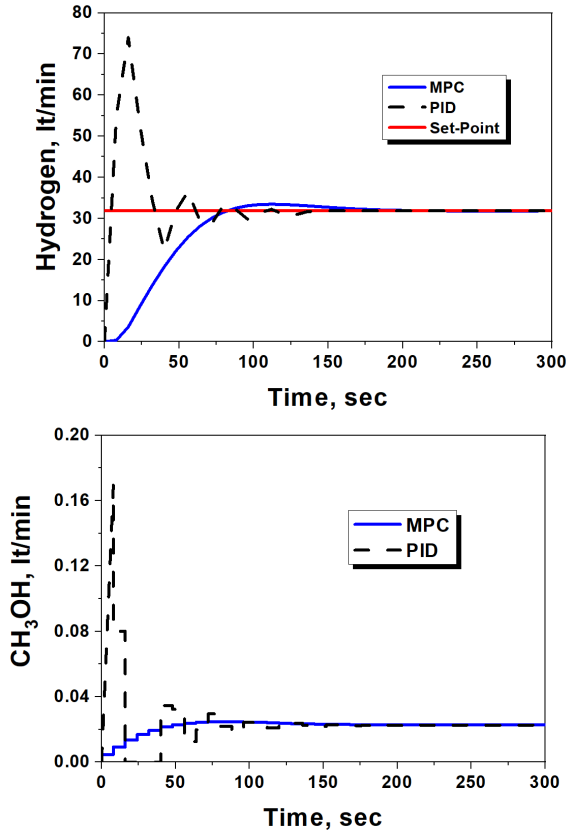


Fig. 8. Variation on the hydrogen production (controlled variable) by manipulating methanol feed

4.2 Disturbance rejection

Fig. 9 shows the reformer's temperature profile under the influence of a disturbance (increase in the S/M ratio from 1.5 to 2 at t=400sec). As can be seen, the increase in steam causes the promotion of endothermic reactions and thus, a temperature decrease is observed. This change forces both control systems (PID and MPC) to increase the O/M ratio (manipulated variable) in order to return the reformer's temperature to the desired set-point. In particular, the MPC returns to the reference signal slightly faster than in the case of the PID controller. The emerged disturbance does not cause any significant effect on the hydrogen production and thus, excluded from the analysis.

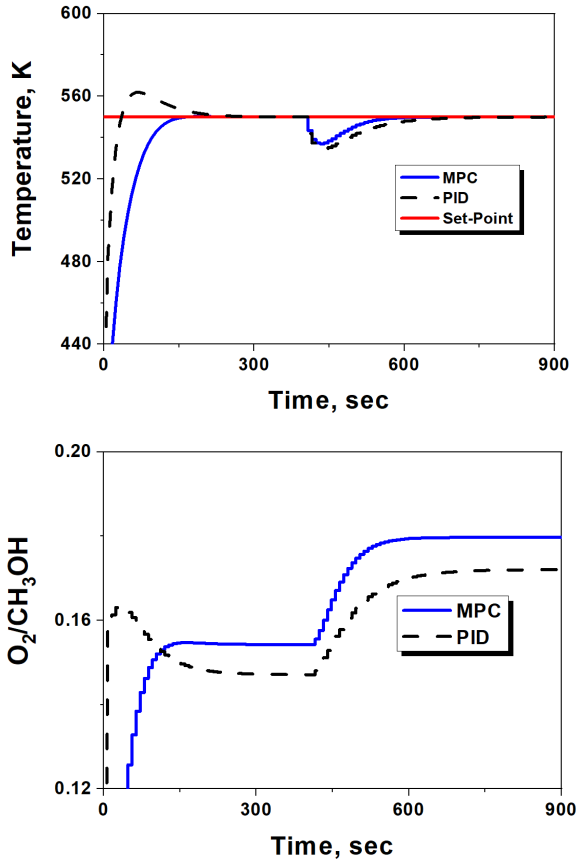


Fig. 9. Variation on the reformer temperature (controlled variable) by manipulating the O/M ratio

5. Conclusion

In this paper a control-oriented model for a methanol steam reformer towards hydrogen production was presented. The dynamic model was developed on the basis of including basic mass and energy principles that take place during the operation of the catalytic reactor. In this sense, partial differential equations described the concentration and temperature time variation by including a validated reaction scheme from a previous study. Next, open loop simulations (at the absence of a controller) revealed that oxygen/methanol ratio significantly affects reformer temperature, whereas the methanol feed rate affects hydrogen production. Both these variables were used at the subsequent control analysis that involved a model predictive control scheme and two individual PID controllers. Both control schemes showed a satisfactory implementation, with the MPC to gain attention due to the lower overshoots and the smoother manipulation of the sensitive process variables. Such an analysis can form the basis in control-oriented advanced schemes that can lead to the efficient production of hydrogen in vehicular applications (fuel cell-based) fed by alternative fuels.

Nomenclature

Cp_f	fluid heat capacity, J/K·kg,
D_z	axial diffusivity, m²/s
F_i	component's 'i' fowrate in bar, mol/s
k_z	axial thermal conductivity, W/m·K
P_i	component's 'i' partial pressure, bar
$P_{reactor}$	reactor operating pressure, bar
Q_o	volumetric flowrate, m³/s
R_j	reaction rate, mol/kg (j: reaction)
Rg	ideal gas constant, bar·m³/mol · K
S	cross sectional area, m²
T	reformer's operation temperature, K
u	superficial fluid velocity, m/s
z	reactor length, m

Greek Symbols

$\Delta H_{R,T,j}$	enthalpy of reaction j at the reactor's operation temperature T, J/K·mol
ε_{cat}	catalyst void fraction
$\nu_{i,j}$	component's "*i*" coefficient in reaction *j*
ρ_{cat}	catalyst density, kg/m³
ρ_f	fluid density, kg/m³

Subscripts

i	Components CH_3OH, O_2, N_2, H_2O, CO, CO_2, H_2

References

[1] J. D. Holladay, J. Hu, D. L. King, and Y. Wang, "An overview of hydrogen production technologies," 2009. doi: 10.1016/j.cattod.2008.08.039.

[2] A. Larminie, James; Dicks, *Fuel Cell Systems Explained*. 2003. doi: 10.1002/9781118878330.

[3] G. Pantoleontos *et al.*, "Dynamic modeling, simulation and optimization of the partially-autothermal reforming of biogas in coated monolith channels," *Chemical Engineering Journal Advances*, vol. 16, p. 100539, Nov. 2023, doi: 10.1016/j.ceja.2023.100539.

[4] J. Jurado, F. Trejo, J. Ancheyta, A. Elyshev, and A. Zagoruiko, "A comprehensive analysis of kinetic models for methane autothermal reforming reactions," *Fuel*, vol. 386, p. 134136, Apr. 2025, doi: 10.1016/j.fuel.2024.134136.

[5] D. Ipsakis, M. Ouzounidou, S. Papadopoulou, P. Seferlis, and S. Voutetakis, "Dynamic modeling and control analysis of a methanol autothermal reforming and PEM fuel cell power system," *Appl Energy*, 2017, doi: 10.1016/j.apenergy.2017.09.077.

[6] S. Savvopoulos, M. N. Hussain, H. Hatzikirou, and I. Janajreh, "A computational approach in automating the continuous sonicated biodiesel production," *Sustainable Energy Technologies and Assessments*, vol. 60, p. 103509, Dec. 2023, doi: 10.1016/j.seta.2023.103509.

[7] S. V. Savvopoulos, S. S. Voutetakis, S. Kuhn, and D. Ipsakis, "Theoretical Feedback Control Scheme for the Ultrasound-Assisted Continuous Antisolvent Crystallization of Aspirin in a Tubular Crystallizer," *Ind Eng Chem Res*, vol. 60, no. 17, pp. 6221–6234, May 2021, doi: 10.1021/acs.iecr.1c00227.

[8] S. V. Savvopoulos, M. N. Hussain, J. Jordens, S. Waldherr, T. Van Gerven, and S. Kuhn, "A Mathematical Model of the Ultrasound-Assisted Continuous Tubular Crystallization of Aspirin," *Cryst Growth Des*, vol. 19, no. 9, pp. 5111–5122, Sep. 2019, doi: 10.1021/acs.cgd.9b00466.

[9] Q. Li, Y. Hao, F. Weng, and L. Sun, "Dynamic modelling and characteristics analysis of methanol steam reforming solid oxide fuel cell system," *Renew Energy*, vol. 241, p. 122187, Mar. 2025, doi: 10.1016/j.renene.2024.122187.

[10] T. Hos, G. Sror, and M. Herskowitz, "Autothermal reforming of methanol for on-board hydrogen production in marine vehicles," *Int J Hydrogen Energy*, vol. 49, pp. 1121–1132, Jan. 2024, doi: 10.1016/j.ijhydene.2023.08.315.

[11] T. Zheng, D. Zhou, Y. Zhan, and Y. Xu, "Integration design optimization of self-thermal methanol steam reforming microreactor for hydrogen production," *Int J Hydrogen Energy*, vol. 48, no. 84, pp. 32642–32653, Oct. 2023, doi: 10.1016/j.ijhydene.2023.05.013.

[12] A. T. Stamps and E. P. Gatzke, "Dynamic modeling of a methanol reformer-PEMFC stack system for analysis and design," *J Power Sources*, vol. 161, no. 1, pp. 356–370, 2006, doi: 10.1016/j.jpowsour.2006.04.080.

[13] M. Ouzounidou, D. Ipsakis, S. Voutetakis, S. Papadopoulou, and P. Seferlis, "A combined methanol autothermal steam reforming and PEM fuel cell pilot plant unit: Experimental and simulation studies," *Energy*, vol. 34, no. 10, 2009, doi: 10.1016/j.energy.2009.06.031.

[14] D. Ipsakis, S. Voutetakis, S. Papadopoulou, and P. Seferlis, "Optimal operability by design in a methanol reforming-PEM fuel cell autonomous power system," *Int J Hydrogen Energy*, vol. 37, no. 21, 2012, doi: 10.1016/j.ijhydene.2012.02.134.

[15] D. Ipsakis, T. Damartzis, S. Papadopoulou, and S. Voutetakis, "Dynamic modeling and control of a coupled reforming/combustor system for the production of H2 via hydrocarbon-based fuels," *Processes*, 2020, doi: 10.3390/pr8101243.