PARAMETER SENSITIVITY ANALYSIS ON MATHEMATICAL MODEL OF METHANE OXIDATION USING REVERSE FLOW REACTOR WITH PERIODICALLY PERTURBED FEED GAS

A Nuryaman[*], L Zakaria and S Suharsono

Department of Mathematics, Faculty of Mathematics and Natural Sciences, Universitas Lampung

[*]Corresponding author email : aang.nuryaman@fmipa.unila.ac.id

Abstract

In this paper, we investigate the effect of operation parameters to dynamic of dependent variables for catalytic oxidation reaction using reverse flow reactor (RFR). Here, we consider a 1-D pseudo-homogeneous model for RFR with cooling through the wall and periodically perturbed feed gas. By using finite difference method to the model, we construct numerical schemes. The simulations are conducted for various value of period of gas feeding, switching time, cooling capacity and superficial velocity.

1. Introduction

Methane is the second largest greenhouse gas whose global warming potential about 20 times greater than carbon dioxide and it is a wasted energy resource if not used. Methane include the gas whose low and unstable concentration, about 1 vol %, and the most difficult of the hydrocarbons to react whose adiabatic combustion temperature about 1900 ^{o}C in the traditional combustion mode [1]. Therefore, auto-thermal operation is difficult to attain a valuable without pre-heating the feed. Thus, conversion of methane to carbon dioxide will give two advantages those are reduction of global warming effect and utilization of the heat output from the reaction to pre-heat the feed. The other hand, a catalyst is required to accelerate the conversion and to carry out stable combustion for low concentrations.

A concept successfully used in methane combustion is catalytic reverse flow reactor (RFR). This concept was first proposed by Frank-Kamenetski[2] and was reviewed by Matros and Bunimovich [3]. RFR is a packed-bed reactor in which the flow direction is periodically reversed to trap a hot zone within the reactor. With reverse flow, reactions that are not normally auto-thermal may be run and sustained at lower inlet temperatures and higher conversions than possible in a direct flow adiabatic reactor.

There are some methods in previous research to investigate dynamics of feed gas in RFR. In [4-17] shown generally there are three methods to investigate this problem, those are experimental, analytical and numerical or computational approaches. The last two methods are usually considered mathematical models that describe the dynamics of feed gas dynamics in RFR.

Various models were proposed to describe the dynamic behavior of the RFR. For example: Khinast et.al [4] and Salomon et al [5] have used a one-dimensional pseudo-homogeneous model, while [6] proposed a one-dimensional heterogeneous model, and [7] used a two-dimensional

heterogeneous model. These models assumed that the temperature and concentration of feed gas are constant along time.

In [11]-[12], authors proposed an analytical approach to solve singular perturbation poblem that derived from 1-D pseudo-homogeneous model in steady state condition under some assumptions. By using same model but at unsteady state condition, an analytical solution using homotopy perturbation method was studied [16]. Furthermore, Wibowo et.al [15] have reported solution unique existence of mathematical model of reverse flow reactor especially in the parabolic and hiperbolic equations.

Meanwhile the study of feed gas dynamics in RFR through numerical simulation approaches were reported in [8], [10] and [14]. Budhi et.al have investigated RFR stability for constant and oscilating feed concentration [10]. With the same topic, Nuryaman et.al [14] have studied the impact of changes in operating parameter values to RFR dynamics for constant temperature and periodic concentration of feed gas.

In this paper, we explorate the previous research in [14] with considering constant temperature and concentration of feed gas is periodically perturbed like trigonometry function. Here we consider one-dimensional pseudo homogenous model that describing cooled RFR behavior. By numerical simulation approach we analyze the parameter sensivity to RFR stability.

This paper is organized as follows. In Section 2, a mathematical model for the dynamic of methane temperature and concentration and numerical scheme are described. In Section 3, numerical simulation is presented to describe the dynamic behavior of methane in reverse flow reactor. Conclusions are written in the last section.

2. Mathematical Modeling and Numerical Scheme

In mathematical modeling of the RFR, we adopt 1D-pseudo homogeneous model for the cooling RFR consists of one panel in Khinast et. al [4] as follow

$$\left((1-\epsilon)\left(\rho c_p\right)_s + \epsilon\left(\rho c_p\right)_g\right)\frac{\partial T}{\partial t} = \lambda_{ax}\frac{\partial^2 T}{\partial z^2} - u\left(\rho c_p\right)_g\frac{\partial T}{\partial z} + (-\Delta H)g(T)C - U_w a_w(T - T_c) \quad (1)$$

$$\epsilon\frac{\partial C}{\partial t} = \epsilon D\frac{\partial^2 C}{\partial z^2} - u\frac{\partial C}{\partial z} - g(T)C \quad (2)$$

where $g(T) = \frac{\eta k_\infty k_c a_v \exp(-E_a/RT)}{k_c a_{v+\eta k_\infty}\exp(-E_a/RT)}$ which correspond to reaction rate. Here $T = T(z,t)$ and $C = C(z,t)$ respectively denote the temperature (K) and feed concentration (mol/m^3) of feed gas at position z and time t. Equations system (1) - (2) be equipped with bondary conditions for flow to the right as follow

$$-\frac{\lambda_{ax}}{u\left(\rho c_p\right)_g}\frac{\partial T}{\partial z} = T_{in} - T, \; -\frac{\epsilon D}{u}\frac{\partial C}{\partial z} = C_{in} - C, \quad \text{at } z = 0 \quad (3)$$

$$\frac{\partial T}{\partial z} = 0, \; \frac{\partial C}{\partial z} = 0, \qquad \text{at } z = L. \quad (4)$$

In Eq. (3) and (4), parameters T_{in} and C_{in} respectively denote temperature and concentration of feed gas those enter into RFR from left/right side o f reactor. In this article we assume temperature of feed gas is constant along time and concentration of feed gas is periodically perturbed function like

$C_{in} = A + \varepsilon \sin \omega t$ where ω corresponding with period for every time interval before the flow direction is reversed.

To describe the dynamic behavior of methane in reverse flow reactor, we use numerical approach since the model is nonlinear form. Many numerical methods can be used to simulate the behavior of methane which is modeled by equation (4)–(7). For example: finite difference method, finite volume method, Runge – Kutta method and others. Here we used finite difference method with forward difference for derivative respect to time variable and central difference for second derivative and backward difference for first derivative respect to space variable. So we get numerical schemes as below

$$T_j^{n+1} = T_j^n + a_1\left(T_{j+1}^n - 2T_j^n + T_{j-1}^n\right) - b_1\left(T_j^n - T_{j-1}^n\right) + c_1 g\left(T_j^n\right)C_j^n - d_1\left(T_j^n - T_C\right) \quad (5)$$

$$C_j^{n+1} = C_j^n + a_2\left(C_{j+1}^n - 2C_j^n + C_{j-1}^n\right) - b_2\left(C_j^n - C_{j-1}^n\right) - d_2 g\left(T_j^n\right)C_j^n \quad (6)$$

Where

$$a_1 = \frac{\lambda_{ax}\Delta t}{\left((1-\epsilon)(\rho c_p)_s + \epsilon(\rho c_p)_g\right)\Delta z^2}, \qquad a_2 = \frac{D\Delta t}{\Delta z^2}$$

$$b_1 = \frac{u(\rho c_p)_g \Delta t}{\left((1-\epsilon)(\rho c_p)_s + \epsilon(\rho c_p)_g\right)\Delta z}, \qquad b_2 = \frac{u\Delta t}{\epsilon \Delta z}$$

$$c_1 = \frac{(-\Delta H)\Delta t}{\left((1-\epsilon)(\rho c_p)_s + \epsilon(\rho c_p)_g\right)}$$

$$d_1 = \frac{U_w a_w \Delta t}{\left((1-\epsilon)(\rho c_p)_s + \epsilon(\rho c_p)_g\right)}, \qquad d_2 = \frac{\Delta t}{\epsilon}$$

Here $T_j^n = T(z_j, t_n)$, $C_j^n = C(z_j, t_n)$, $\Delta z = L/N_z$ and $\Delta t = t/N_t$ with N_z and N_t denote the number of spatial and time coordinate partitions, respectively. Parameter values that be used in our simulations are given in Table 1.

Table 1. Parameter values, [4]

Parameters	Value	Descriptions
ϵ	0.69	void fraction
$(\rho c_p)_s$	904.55 kJm^{3}K^{-1}	volumetric heat capacity of solid
$(\rho c_p)_g$	0.508 kJm^{3}K^{-1}	volumetric heat capacity of gas
λ_{ax}	5.64 kW m^{-1}K^{-1}	effective axial heat conductivity
u	0.3 ms^{-1}	Superficial gas velocity
U_w	0.1377 kW m^{-1}K^{-1}	Heat transfer coefficient at reactor wall
a_w	272 m^{-1}	Specific reactor wall surface
T_C	323 K	Coolant temperature
$(-\Delta H)$	802000 kJ/kmol	Heat of reaction
D	6.52x10^{-6} m^{2}s^{-1}	Gas diffusion coefficient
E_a	9.629 x 10^4 kJ/kmol	Activation energy
R	8.3145 kJ/kmol/K	Universal gas constant

k_∞	7.34 x 10^7 s^{-1}	Frequency factor
k_c	0.115 ms^{-1}	Mass-transfer coefficient
a_v	2000 m^{-1}	Specific particle surface area
η	1	Effectiveness factor
L	0.26 m	Reactor length
t_f	60 s	Switching time

3. Results

In this section we show some numerical simulations to analyze the sensitivity of operating parameters by means the effect of changing the parameter values on RFR stability or the continuation of the oxidation process.

Parameter sensitivity analysis of feed gas period

First case for constant feed gas, the behavior of temperature and concentration of feed gas are shown in Figure 1. Furthermore, if we investigate until six times reversed, we have Figure 2.

In the start up condition, when the concentration of the feed gas is constant, the temperature around the left end of the reactor decreases. This is due to the diffusion effect so that the temperature of the feed gas entering the reactor decreases. Mathematically, it can be seen from the form of the boundary conditions at the left end of RFR. Gradually to the right the temperature rises then drops again. This is due to the effect of heat energy released when the feed gas reacts inside the reactor. In the middle position of the reactor to the right end the temperature decreases due to the cooling process and reduced heat of the reaction because the reactant gas has run out of reaction.

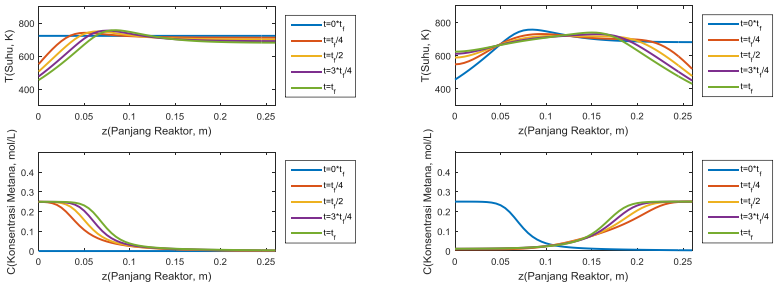

Figure 1. Dynamics of temperature and concentration of feed gas for some time values t with $\boldsymbol{A = 0.25, \varepsilon = 0.05}$ **and** $\boldsymbol{\omega = 0}$. Left figure, for flow from left to right and right figure after reversed.

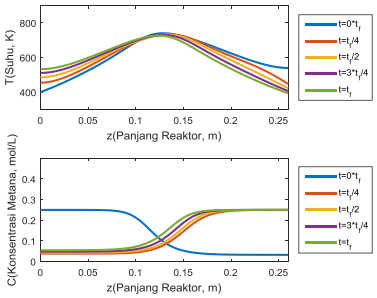

Figure 2. Dynamics of temperature and concentration of feed gas for some time values t with $\boldsymbol{A = 0.25, \varepsilon = 0.05}$ **and** $\boldsymbol{\omega = 0}$ after six times reversed.

From Figure 2, when the feed gas flow is reversed several times, the highest temperature is in the reactor center position. This is caused around the end of the reactor where the feed gas enters, the temperature is still low so that only a small amount of feed gas reacts. While around the end of the reactor where the remaining feed gas or the reaction product comes out, the temperature drops again

due to the same thing as in the start up conditions.

Next step, we simulate the impact of changing the period parameter $\boldsymbol{\omega}$ that shown in Figure 3 as follow.

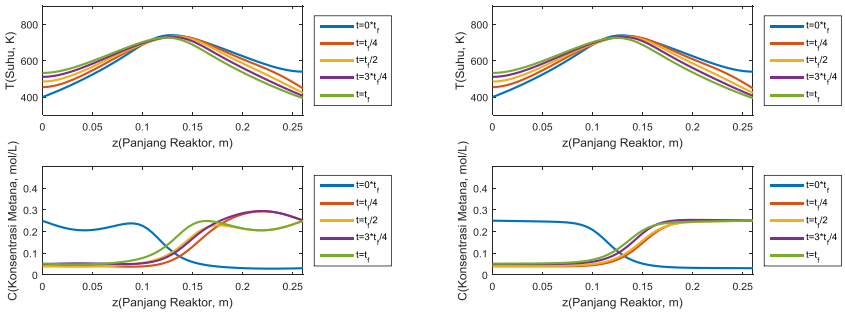

Figure 3. Dynamics of temperature and concentration of feed gas for some times t value with $\boldsymbol{A = 0.25, \varepsilon = 0.05}$ after six times reversed. Left figure, for $\boldsymbol{\omega = 5\pi}$ and right figure $\boldsymbol{\omega = \frac{\pi}{5}}$.

In the case of feed gas being disturbed periodically, the parameters of the feed gas period affect the presence of waveforms in the plot of feed gas. The concentration of the feed gas which oscillates periodically has little effect on the temperature dynamics of the feed gas in the reactor. The existence of waveforms on the dynamics plot of feed gas concentration occurs for a large period. The similar conditions to constant feed gas concentrations occur when the feed gas period is small. In general, the size of the feed gas period does not make the reactor go out. This is indicated by the dynamic plot shape of the feed gas temperature in the reactor like shown in Figure 3.

Parameter sensitivity analysis of switching time

Switching time is one of important factor in RFR operation. Figure 4 and Figure 5 show the effect of switching time to dynamics of feed gas along RFR.

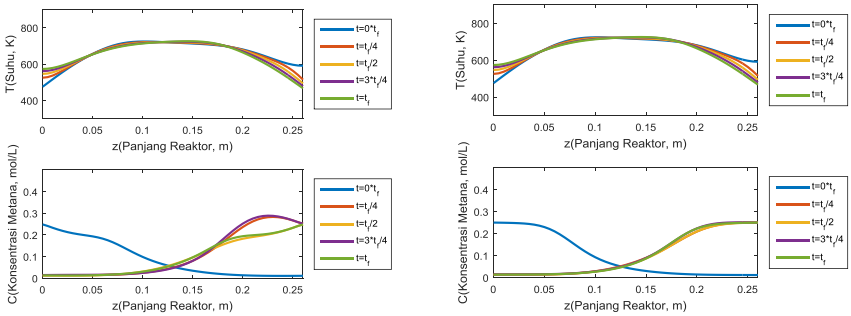

Figure 4. Dynamics of temperature and concentration of feed gas for some times t value with $\boldsymbol{A = 0.25, \varepsilon = 0.05, t_f = 20s}$ after six times reversed. Left figure, for $\boldsymbol{\omega = 5\pi}$ and right figure $\boldsymbol{\omega = \frac{\pi}{5}}$.

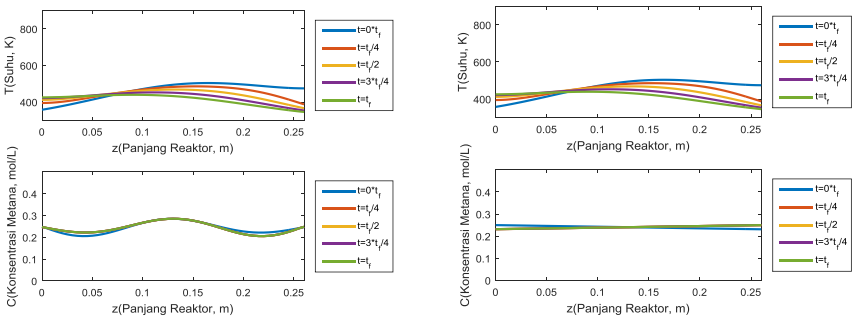

Figure 5. Dynamics of temperature and concentration of feed gas for some times t value with $\boldsymbol{A = 0.25, \varepsilon = 0.05, t_f = 120s}$ after six times reversed. Left figure, for $\boldsymbol{\omega = 5\pi}$ and right figure $\boldsymbol{\omega = \frac{\pi}{5}}$.

The choice of the duration of reversal (switching time) is very influential on the stability of the RFR in operation. From Figure 4 and Figure 5, it is indicated that the reversal time that is too short (case $\boldsymbol{t_f = 20s}$) or too long (case $\boldsymbol{t_f = 120s}$) will make the RFR go out. This situation is shown by the dynamics of temperature which decreases closer to the feed gas temperature. It shows there is no reaction in the reactor. This result is in agreement with the results that reported in [10] and [17].

Parameter sensitivity analysis of superficial gas velocity

In Figure 6 and Figure 7, we show effect of supervicial gas velocity value to dynamics of feed gas along RFR. When in the operation of the RFR, the feed gas flow velocity is small, it is indicated that the reactor will eventually go out. A slow feed gas flow rate will cause more feed gas to act in the reactor end position where the feed gas enters. Thus getting to the end of the reactor, there is no additional heat from the reaction product. Simultaneously the contribution of reactor cooling continues. As a result, over time the overall temperature becomes low and eventually goes out. The opposite condition occurs when the feed gas flow rate is increased as shown in Figure 7.

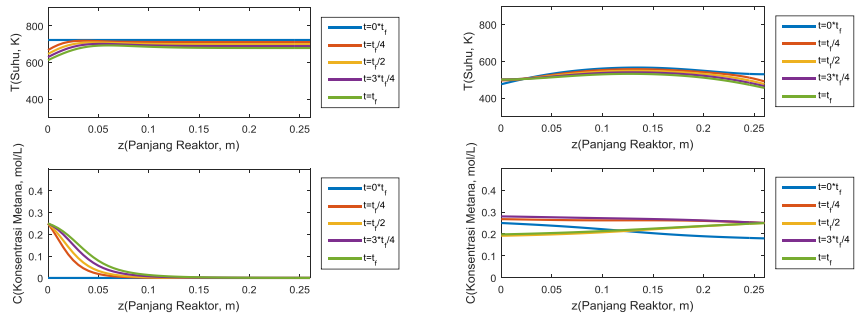

Figure 6. Dynamics of temperature and concentration of feed gas for some times t value with $\boldsymbol{A = 0.25, \varepsilon = 0.05, u = 0.1}$ after six times reversed. Left figure, for $\boldsymbol{\omega = 5\pi}$ and right figure $\boldsymbol{\omega = \frac{\pi}{5}}$.

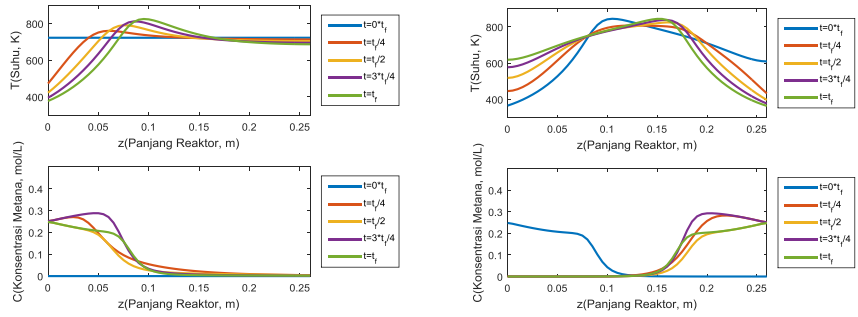

Figure 7. Dynamics of temperature and concentration of feed gas for some times t value with $\boldsymbol{A = 0.25, \varepsilon = 0.05, u = 0.7}$.

4. Conclusion

RFR stability investigations have been shown for the oxidation process with periodically disturbed feed gas. The parameter sensitivity analysis process through a numerical approach is carried out to see the effect of the feed gas period, switching time, and superficial gas velocity. The results of the analysis show that the choice of switching time and superficial gas velocity greatly influences the sustainability and stability of RFR operations.

Acknowledgements

This research was supported by Lembaga Penelitian dan Pengabdian Kepada Masyarakat (LPPM) Universitas Lampung via Program Penelitian Unggulan DIPA BLU Unila with grant no 2237/UN26.21/PN/2019.

References

[1] Wang, Y., Man, C., and Che, D., Catalytic combustion of ventilation air methane in reverse flow reactor, *Energy Fuels* 24, (2010), pp 4841 – 4848.

[2] Frank-Kamenetskii, D. A., Diffusion and Heat Transfer in Chemical Kinetics, Princeton Univ. Press, Princeton, NJ, 1955.

[3] Matros, Y.S., and Bunimovich, G., Reverse flow operation in fixed bed catalytic reactors. *Catalysis Reviews-Science and Engineering* **38**(1), (1996), pp 1-68.

[4] Khinast, J., Jeong, Y.O., and Luss, D., Dependence of Cooled Reverse-Flow Reactor Dynamics on Reactor

Model. *AIChE Journal*. **45**(2) (1999), pp. 299-309.

[5] Solomons, S., Hayes, R.E., Poirier, M. and Sapoundjiev, H. Flow reversal reactor for the catalytic combustion of lean methane mixture. Catalysis Today. (2003) 83, pp 59-69.

[6] Bhatia, S.K., Analysis of catalytic reactor operation with periodic flow reversal. *Chem. Eng. Sci*., (1991), 46 (1), pp 361–367.

[7] Balaji, S., Lakshminarayanan, S., Heat Removal from Reverse Flow Reactors used in Methane Combustion. *Can. J. Chem. Eng*, (2005), **83** (4), pp 695-704.

[8] Gosiewski, K., Effective approach to cyclic steady state in the catalytic reverse-flow combustion of methane. *Chemical Engineering Science*, (2004), 59, pp. 4095-4101.

[9] Litto, R., Hayes, R.E., and Liu, B. Catalytic Combustion for Reduction of Fugitive Methane Emissions From Natural Gas Compressor Stations. *Greenhouse Gas Control Technology*, (2005), **1**(7), pp. 329-336.

[10] Budhi, Y.W., Effendy, M., Bindar, Y., and Subagjo. Dynamic behavior of reverse flow reactor for lean Methane Combustion. Journal of Engineering and Technological Sciences (2014), **46**(3), pp. 299-317.

[11] A. Nuryaman, A. Y. Gunawan, K. A. Sidarto, and Y. W. Budhi, A Singular Perturbation Problem for Steady State Conversion of Methane Oxidation in a Reverse Flow Reactor, *ITB Journal of Science*, (2012), **44A** (3), pp. 275-284. doi:10.5614/itbj.sci.2012.44.3.7.

[12] A. Nuryaman and A. Y. Gunawan, A Singular Perturbation Problem in Steady State of Methane combustion using Reverse Flow Reactor, *Far East Journal of Mathematical Sciences*, (2017), **102**(9), pp. 2069-2079. http://dx.doi.org/10.17654/MS102092069

[13] A. Nuryaman, Simulasi Numerik Model Matematika Dinamika Reaksi Oksidasi dengan Konsentrasi Gas Umpan Periodik, Prosiding Seminar Nasional Sains Matematika Informatika dan Aplikasinya IV, Bandar Lampung, (2016), **4**(4), pp. 139-145.

[14] A Nuryaman, R Riyanto, and S Saidi, Dynamics of Temperature and Concentration on Oxidation Reaction using Reverse Flow Reactor with Periodic Feed Gas Like Square Wave Function: a Numerical Approach, *J. Phys.: Conf. Ser*. **1338**, (2019), 012040. https://doi.org/10.1088/1742-6596/1338/1/012037

[15] Edy Wibowo, R., Suzuki, T., & Takahashi,R., A Mathematical Study on the System of Partial Differential Equations Describing Reverse-Flow Reactor, *Mathematical Modeling and Analysis*, (2016), 21(4), pp 550-568. https://doi.org/10.3846/13926292.2016.1186756.

[16] A Nuryaman, An Analytical Solution of 1-D Pseudo Homogeneous Model for Oxidation Reaction using Homotopy Perturbation Method, *Journal of Research in Mathematics Trends and Technology (JoRMTT)*, (2019), 1(1), pp 7-12.

[17] Kurniawan, T., Budhi, Y.W., and Bindar, Y., Reverse Flow Reactor for Catalytic of Lean Methane, *World Chemical Engineering Journal*, (2018), 2(1), pp 21-26.