Effect of intraparticle diffusion-reactions at reverse flow reactors. Cases study: Methane catalytic oxidation

M Effendy1*, E Y Wardhono2, Soeryanto1 and I M Arsana1
1 Universitas Negeri Surabaya, Jl. Ketintang Surabaya, 60231, Indonesia
2 University of Sultan Ageng Tirtayasa, Jl. Jenderal Sudirman km 3 Cilegon, 42435, Indonesia.

*Email: mohammadeffendy@unesa.ac.id

Abstract. Reverse Flow Reactor (RFR) is a fixed bed reactor whose direction of flow changes at a certain time periodically. To obtain an overview of the flow direction changing on the RFR effect on the reaction rate, the intraparticle diffusion reaction factor needs to be assessed. The flow that changes in RFR causes the value of tortuosity to behave dynamically so that the reaction rate also changes dynamically. The model approach that involves intraparticle diffusion reactions is to determine the effectiveness factor. The procedure used is to estimate the effectiveness of the simulated reaction, which allows obstacles due to intraparticle diffusion to be considered at each point of the reactor without using numerical integration of the diffusion equation in the pellet (catalyst). The results obtained show that the conversion of methane gas changes over time. This change can be approached by assuming the total reaction rate in bulk is constant, but the total reaction rate in the catalyst varies depending on the intraparticle diffusion reaction, which is indicated by the value of effectiveness factor. The dynamic effectiveness factor behaviour can be approximated by the 6th degree polynomial equation as follows: 6.38e-13*t6 + 3.23e-10*t5 – 5.84e-8*t4 + 4.34e-6*t3 – 9.91e-5*t2 – 0.0004*t + 0.1781

1. Introduction
In recent years, the concern about reverse flow catalytic reactors has been increasing, especially in the process of reducing the impact of greenhouse gases due to unidentified industrial gas leakage and oxidation of volatile organic compounds (VOC) for waste gas purification [1]. This is because the dynamic catalytic reactor makes it possible to run in an auto-thermal at low feed concentration [2], can control the maximum temperature in the case of high inlet concentrations [3], and can handle the varied inlet flow composition and velocity [4].

One of several causes of researcher interest to explore the reverse flow catalytic reactor is; process performance resulted can increase or deteriorate as a result of the dynamic conditions caused. For example, a study of trickle bed reactors [5] and Fischer-Tropsch synthesis [6] have shown improvements in process performance using periodic operations. Gulari et al. have reviewed the research outcome of carbon monoxide catalytic oxidation and it shows an increasing of the catalytic system performance under periodic operation [7]. Ramirez et al. stated that dynamic conditions have impact to efficiency changing in the diffusion reaction process so that it can provide higher productivity, conversion, selectivity and efficiency, and increase catalyst activity [8].

In order to facilitate the revelation of the reaction rate in catalyst particles, it is assumed that the reaction rate occurs under conditions of surface / bulk multiplied by the effectiveness factor. As a
functional factor, the effectiveness factor provides some information about the effectiveness of a single catalyst particle and also the effectiveness factor can be seen as an indicator of the effective use of the catalyst particle space. So far, the concept of effectiveness factors has been used in steady state conditions [9]. This is because the practical chemical reaction system is intended to operate in steady state conditions.

Based on the information above, there are important things that must be considered in the operation of reverse flow catalytic reactors, the performance of the reaction diffusion sometimes improves so the performance is getting better than steady state conditions. Therefore the study of the diffusion reaction that occurs during the operation of reverse flow reactor is an interesting research subject that methodological design is required.

It should be mentioned that, the introduction of dynamic effectiveness factors has been carried out by Ramirez et al. [8] which states that the dynamic effectiveness factor is a scale factor between two reaction rate functions, they are the dynamic reaction rate in the boundary (surface / bulk) condition and dynamic level function in the reaction in the catalyst particles conditions. Motivated by Ramirez et al.’s research, the objective of this paper is to apply the concept of dynamic effectiveness factors to the operation of reverse flow methane oxidation reactors. So it will provide an answer to why the process performance of the methane oxidation reverse flow catalytic reactor can be increasing or decreasing.

2. Methodology
2.1. Material
The material required in this study is a commercial catalyst Pt / γ-Al2O3 3% -weight. Pt / γ-Al2O3 is used as a reaction catalyst for methane oxidation. The gas used is CH4 and compressed air, which are as feeding for the methane oxidation reaction. Alumina in the reactor is as an inert material to make the reactant flow approach the plug-flow. Mesh will also be used as a catalyst holder in the reactor.

2.2. Equipment
Quartz fixed bed reactors (2 cm inside diameter, 35 cm long) were used in all experiments (see Figure 1). It is equipped with a control panel switch, heating temperature control, methane gas detector which is connected to the computer.

2.3. Experiment Steps
Methane and air are flowed through a bubble soap meter to obtain the desired flow rate. The methane concentration read on the methane gas detector has to be 1%. The gas mixture passes through the catalyst inside the reactor at a predetermined temperature. The catalyst and inert are held by quartz wool. Gas products that leave the reactor will pass through the methane gas detector before disposed. The conversion of methane gas is calculated based on the equation as follows:

$$X_{CH4} = \frac{Inlet\ Cons - Outlet\ Cons}{Inlet\ Cons} \times 100\%$$  \hspace{1cm} (1)

In order to create a reverse flow condition, at certain times valve numbers 2 and 4 are closed while valve numbers 1 and 3 are opened. Next time valve numbers 1 and 3 are closed and valve numbers 2 and 4 are opened. Valve openings changing are carried out periodically, the period of changing is named as switching time. Setting the switching time is done by the switch control valve (see Figure 1).

2.4. Product Analysis
To find out the concentration of methane in the mixture, methane gas detector with TGS 2611 Figaro type sensor is used. Figaro TGS 2611 has a sensing element consisting of a semiconductor metal oxide layer, formed on an alumina substrate together with integrated heater. With the presence of gas detected, the conductivity of the sensor increases depending on the concentration of gas in the air. A simple electrical circuit can convert conductivity changing to an output signal that is in accordance with the concentration of gas (methane gas detector). Calibration of the methane gas detector is done.
using the Beland's method [10]. The correlation between sensor resistance and gas concentration follows the equation below:

\[ R_s = A \times [C]^{\alpha} \]  

(2)

where:
- \( R_s \): sensor resistance that is read by gas detector.
- \( C \): gas concentration from Gas Cromatograph result.
- \( \alpha \): slope of sensor resistance.
- \( A \): a constant that is affected by sensor type.

---

**Figure 1.** Scheme of reverse flow reactor for methane oxidation.

2.5. **Catalyst Characteristic**
BET analysis of Pt / Al2O3 catalyst specific area was obtained using Quantachrome Nova 3200e of surface area and porosity analysis. N2 absorption in isothermal conditions was obtained at a temperature of -195.7°C through various relative pressures on the sample before the gas exited at 300.0°C for 11 hours. The area obtained from the BET analysis is 167.468 m² / gram with total empty volume of 0.8034 cc / gram.

2.6. **Data and Analysis**
This stage serves as the main experiment where the results obtained will be used to determine the effectiveness factor. In determining the effectiveness factor there are two main steps:

a. Obtain the conversion of methane gas under dynamic conditions.

b. Determination of the value of the time function effectiveness factor of the reverse flow reactor experimental data.

2.7. **Simulation**
In design and/or simulation of heterogeneous model requirement, which involve distributed parameters (for example, partial differential equations (PDEs) for gases and catalyst particles) provide fairly good accuracy. But this model is rarely used for design and/or simulation purposes because of the difficulty to find computational solutions [11].

A common approach to avoid the disadvantages of heterogeneous models is by using the concept of effectiveness factors [9, 12]. The idea is: to assume the reaction rate in the catalyst particles in the
condition of the surface / bulk multiplied by the functional factor: the effectiveness factor. So use a pseudo-homogeneous model is enough.

The reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$  \hspace{1cm} (3)

The mass balance of pseudo-homogeneous model used in reverse flow reactors under isothermal conditions is as follows:

$$\frac{\partial C_{CH4}}{\partial t} = D_{eff} \varepsilon_{bed} \frac{\partial^2 C_{CH4}}{\partial z^2} - u_s(t) \frac{\partial C_{CH4}}{\partial z} - \rho_{cat} \eta \ r_{CH4}$$  \hspace{1cm} (4)

$$\frac{\partial C_{O2}}{\partial t} = D_{eff} \varepsilon_{bed} \frac{\partial^2 C_{O2}}{\partial z^2} - u_s(t) \frac{\partial C_{O2}}{\partial z} - \rho_{cat} \eta \ 2 \ r_{CH4}$$  \hspace{1cm} (5)

Where:

$$u_s(t) = U_s \ k(t)$$

$$U_s = linear \ flow \ rate \ (\frac{m}{detik})$$

$$k(t) = +1 \ or \ -1, \ depends \ on \ flow \ direction$$

3. Result and Discussion

3.1. Methane gas detector calibration

Figure 2 shows the correlation of the magnitude of resistance read in the methane gas detector using the TGS 2611 sensor with the concentration of methane gas read from Gas Chromatography (GC).

![Figure 2. Correlation of resistance read by TGS 2611 sensor vs Methane Concentration read by GC.](image)

Based on Figure 2, it can be obtained constant $A$ is 6.53 and $\alpha$ is 0.066. The equation below is applied to obtain the concentration of methane gas based on the reading of the methane gas detector.

$$[C] = \left( \frac{R_s}{6.52} \right)^{0.066}$$  \hspace{1cm} (6)

3.2. Experiment

In chapter of the experiment step, it has been explained to obtain reverse flow condition, valve opening changing are carried out periodically, and the changing period is called as the switching time.

In this experiment, the variation used was switching time of 1 minute and 3 minutes at 540oC with a flow rate of 10 ml/sec and the concentration of 1% methane. Figure 3 shows the experimental results obtained in the above conditions.

Based on Figure 3, there are certain times that the performance of the reverse flow reactor (RFR) provides better performance compared to steady state conditions. However, the calculation of the average conversion during a certain time at 1-minute switching time (ST) provides worse performance compared to steady state conditions. On ST 3 minutes, RFR performance is almost the same with
steady state. Result difference due to ST variation indicates different reaction rate, which is caused by the formation of dynamic conditions as impacted by reversal of the feed gas direction. Reaction rates changing by the time indicates the reaction-diffusion phenomenon in the catalytic oxidation system of methane gas in non-steady state condition. The behaviour of intraparticle diffusion reaction can be observed from the value changing of the effectiveness factor.

3.3. Dynamic Effectiveness Factor Determination

Modeling and simulation are implemented to predict the value of the effectiveness factor by trial and error. The model used refers to Equations 1 and 2. The parameters and physical properties to complete the mathematical model are obtained from measurements and calculations.

The model and kinetics parameters of oxidation reaction of the 3% - weight Pt / Al₂O₃ methane catalyst commercial were carried out previously. The best model tested based on the assumption of of the Langmuir-Hinshelwood (LH) reaction mechanism is based on the assumption of the controlling stage of methane adsorption, which is stated as follows:

$$ r = \frac{k_1 C_{CH_4}}{1 + \sqrt{K_2 C_{O_2}}} $$

with:

$$ k_1 = 1488.72 \times \exp\left(-\frac{82245.41}{RT}\right) $$
$$ K_2 = \exp\left(-\frac{8373.61}{R} + \frac{44640.9}{RT}\right) $$

Figure 4 shows effectiveness factor changing when ST is 3 minute.
dynamically. The reason is the effectiveness factor can be seen as the transformation of the total reaction rate in bulk into the total reaction rate in the catalyst particles.

\[ \eta : r_{T,\text{bulk}} \to r_T \]  \hspace{1cm} (8)

The results in laboratory scale (Figure 3) shows that the conversion of methane gas obtained changes over time. This change can be approached by assuming the total reaction rate in bulk is constant, but the total reaction rate in the catalyst varies depending on the intraparticle diffusion reaction, which is indicated by the value of effectiveness factor (see Figure 4). The dynamic effectiveness factor (DEF) behaviour in Figure 4 can be approximated by the 6th degree polynomial equation as follows:

\[ \text{DEF} = 6.38e^{-13}t^6 + 3.23e^{-10}t^5 - 5.84e^{-8}t^4 + 4.34e^{-6}t^3 - 9.91e^{-5}t^2 - 0.0004t + 0.1781 \]  \hspace{1cm} (9)

Where:

\[ t = \text{time (second)} \]

4. Conclusion

The process of reversing the flow direction of the feed gas which is applied to the fixed bed reactor provides performance behaviour that is not the same as steady state condition. The performance behaviour is influenced by the disrupted intraparticle reaction-diffusion due to the reversal of flow direction. The dynamic of the intraparticle diffusion reaction process can be approximated by the effectiveness factor value that changes at any time. Specifically, in the current study, dynamic changing in effectiveness factors cannot lead to performance improvement compared to steady state conditions. However, it provides an overview of the possibility to obtain the better performance, at certain times a higher conversion is obtained compared to steady state conditions. This really depends on the selection of switching time.

5. Reference

[1] Cittadini, M, Vanni M and Barresi A.A 2002 Chem. Eng. Process 41 437-443.
[2] Sapundzhiev C, Grozev G and Elenkov D 1991 Chem. Eng. Technol. 14 209 – 212.
[3] Sapundzhiev C, Chaouki J, Guy C and Klívana, D 1993 Chemical Engineering Communications 125 171–186.
[4] Cittadini M, Vanni M, Barresi A.A and Baldi G 2001 Chem. Eng. Process 40 255–262.
[5] Turco F, Hudgins R R, Silveston P L, Sicardi S, Manna L and Banchero M 2001 Chem. Eng. Sci. 56 1429-1434.
[6] L.Guillou, V. Le Courtois, S. Paul 2015 Fischer-Tropsch Synthesis Under Periodic Operation in a Microstructured Reactor (Salt Lake City, UT: AICHE Annual Meeting).
[7] Gulari E, Zhou X and Zse, 1995 Catalysis Today 25 145-157.
[8] Ramirez J A, Ochoa-Tabaj A and Valdez-Parada F J 2005 The Journal of Physical Chemistry B 109 11058-11064.
[9] S.S. E. H. Elnashaie and S. S. Elshishini 1993 Modeling, Simulation and Optimization of Industrial Fixed Bed Catalytic Reactors (Amsterdam: Gordon and Breach Science)
[10] Beland M 2002 Sterilisable Probe for Extraction of Volatile Compounds in Liquids and Their Quantitative Determination W.O. 03/069314 A1.
[11] H.C. Rodrigues, J. Herskovits, C.M. Mota Soares, J.M. Guedes, A.L. Araujo & J.O. Folgado, F. Moleiro & J.F.A. Madeira 2014 Proceeding of The International Conference on Engineering Optimization (Lisbon-Portugal: CRC Press/Balkema) p 347
[12] Aris R 1975 The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts Vol 1 (Oxford University Press: Oxford).