

## Reverse Flow Reactor for Catalytic Oxidation of Lean Methane

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## ABSTRACT

Methane as a potential greenhouse gases contributor which gives 21 GWP has to be mitigated to diminish the global warming effect. High concentration methane can be easily converted into CO<sub>2</sub> by mean oxidation. However lean methane can only be oxidized in the catalytic reaction system as the catalyst lowers the reaction temperature up to 400 °C. Nevertheless, this is still high temperature to achieve by low concentration and low-temperature feed. It still needs preheating the feed until its reaction condition reached which can be supplied outside or within the system called auto thermal. One of promising auto thermal reactor is reverse flow reactor which is the reactor that its feed flow periodically switches to make the heat trapped inside the reactor. In this work, we have designed a reverse flow reactor by one-dimensional model, pseudohomogeneous for mass and heterogeneous for energy to burn lean methane from a station compressor. The critical parameter of switching time on the system of periodical reversal is also presented.

**Keywords:** lean methane, catalytic oxidation, reverse flow reactor, design, switching time.

## 1. INTRODUCTION

The increase of earth temperature caused by greenhouse gases, better known as global warming, has been threatening the life of humankind as well as the environment. The greenhouse gases are carbon dioxide, methane, nitrous oxide, and halocarbon synthetics. It has been known that methane contribution to the global warming 21 times more powerful than carbon dioxide (Forster et al., 2007). The methane emissions come from various sectors, such as agriculture (44%), landfills and biomass (22%), coal (12%), and the oil and gas industry (15%) (Moore et al., 1998). One of emission comes from the oil and gas industry is fugitive methane from compressor building with very lean concentration 0.1-1%-v CH<sub>4</sub>. Methane can be reduced by oxidation reaction to become carbon dioxide. This methane oxidation decreases the global warming effect by 87% (Hayes, 2007).

Methane in concentration range 5-16%-v is easily burned with air (Hayes and Kolaczowski, 1997). However, methane with a concentration below 5%-v

can only burn on the catalyst. Catalytic oxidation allows the methane oxidation occurred in the larger range of concentration (Lee and Trimm, 1995). Various catalysts for methane oxidation are generally derived from a class of noble metals (Pd, Rh, and Pt) with the support of alumina (Al<sub>2</sub>O<sub>3</sub>) (Otto, 1989; Lee and Trimm, 1995; Hayes et al., 2001). We can use fixed bed reactor for catalytic methane oxidation.

Fixed bed reactor for lean methane oxidation reactions needs to be designed in a different way both for the reactor construction and the operation conditions to get the auto-thermal reactor. Auto thermal conditions in fixed bed reactor can be achieved by designing a fixed bed reactor with heat exchange type of recuperative or regenerative (Kolios et al., 2000). The maximum efficiency of the regenerative type is 95%, while the maximum efficiency of the recuperative type is only 75% (Baressi et al., 2007). Reverse flow reactor (RFR) (Figure 1) is one of fixed bed reactor with regenerative one. The auto-thermal reaction achieves in RFR despite the temperature reaction and the adiabatic temperature is small. This phenomenon occurs because of the ends

position of catalyst or inert act as a type of regenerative heat exchanger (Eigenberger and Nieken, 1989).

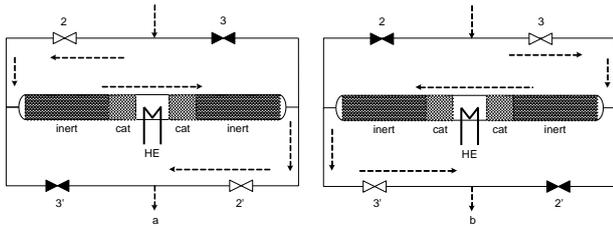


Fig. 1. The illustration of Reverse flow reactor.

RFR operation offers many advantages associated with dynamic conditions that occur during the reaction. Dynamic conditions for concentration and temperature on the RFR are produced by way of change of the feed direction. The flow of the feed that comes from left to right changed periodically to be from right to left within a particular time cycle. Matros and Bunimovich (1996) explain that the dynamic conditions will increase the conversion, selectivity, and temperature in a reactor.

Many researchers report that lean methane has been succeeding to be oxidized at ambient temperature with RFR (Sapoundjiev and Aube, 1999; Salomons et al., 2003; Kushwaha et al., 2004; Hayes, 2004; Kushwaha et al., 2005). The results showed besides reducing the greenhouse gas effect, the heat can be extracted from the catalytic oxidation of lean methane in RFR (Sapoundjiev and Aube, 1999; Kushwaha et al., 2005). The performance of the RFR for the catalytic oxidation of lean methane is affected by feed concentration, switching time (ST), and velocity (Salomon et al., 2003).

One-dimensional (1D) pseudo-homogeneous model of catalytic oxidation of methane by considering the axial dispersion rates and eliminate the dynamic term mass balance shows a respectable agreement profile that corresponds with the experimental data (Eigenberger and Nieken, 1988). Heterogeneous models for energy balance developed by Gawdzik and Rakowski (1989) without involving the dispersion term. Heterogeneous model by incorporating the term dispersion is described by Matros and Bunimovich (1996). Heterogeneous model simplification can be done by ignoring the dynamic term in the balance gas (Gawdzik and Rakowski, 1989; Matros and Bunimovich, 1996).

The paper presents the comparison between the fixed bed conventional one flow performances with the reverse flow reactor by one-dimensional modeling and simulation. The effect of switching time on the system of periodical reversal is also examined

## 2. METHODS

### 2.1 Model

The global reaction of methane oxidation is as follow.

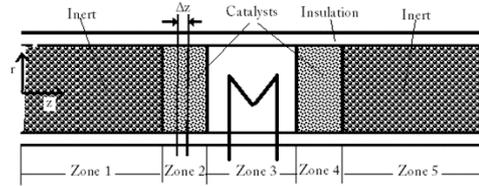
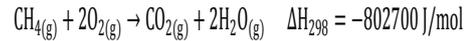


Fig. 2. Zones distribution and volume element for mathematical modelling.

The rate of reaction for methane oxidation using catalyst Pt/Al<sub>2</sub>O<sub>3</sub> is as follow (Bosomiu et.al, 2008).

$$r_M = 2.24 \times 10^7 \exp\left(\frac{-98324}{RT}\right) C \quad (1)$$

Data properties and operating conditions are available in Table 1.

Table 1. Reactor dimension, catalyst, and inert properties

Diameter	0.108 m
Reactor length	0.26 m
Overall heat transfer coefficient	131 W/(m <sup>2</sup> .K)
Inert zone	
Inert length each segment	0.1 m
Material of inert	Alumina
Average diameter of inert particle	0.003 m
Catalyst zone	
Catalyst length each segment	0.01 m
Material of catalyst	Pt/Al <sub>2</sub> O <sub>3</sub>
Average diameter of catalyst particle	1 x 10 <sup>-5</sup> m
Specific area of catalyst	2000 m <sup>2</sup> /m <sup>3</sup>
density	1082 kg/m <sup>3</sup>
Length of heat extraction zone	0.04 m
Void fraction of bed, ε	0.36
Void fraction of catalyst particle, ε <sub>p</sub>	0.451
Number of tube	726

One dimension pseudo-homogeneous model for mass balance and one-dimension heterogeneous model for energy balance.

Mass balance

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - W_{(x,T_s)} \quad (2)$$

Energy balance for gas phase

$$\epsilon \rho_g c_g \frac{\partial T_g}{\partial t} = -u \rho_g c_g \frac{\partial T_g}{\partial z} - \alpha_0 a_v (T_g - T_s) - \frac{4U_{overall}}{d} (T_g - T_{amb}) - Q_{extract} \quad (3)$$

Energy balance for solid phase

$$[(1 - \epsilon) \rho_p c_p c_s + \epsilon_s \rho_s c_s] \frac{\partial T_s}{\partial t} = k_{eff} \frac{\partial^2 T_s}{\partial z^2} + \alpha_0 a_v (T_g - T_s) + (-\Delta H) W_{(x,T_s)} \quad (4)$$

Boundary conditions:

$$C = C_{input}, \quad T_g = T_{g,input}, \quad (5)$$

Left side

$$T_{s,inert} = T_{s,inert} 0, \quad T_{s,catalyst} = T_{s,catalyst} 0$$

Right side

$$T_{s,inert} = T_{s,inert} 0, \quad T_{s,catalyst} = T_{s,catalyst} 0$$

Boundary conditions for each zone:

Zone 1 (left side inert)  
At  $z = z_0$ ,

$$D_{eff} \frac{dC}{dz} = \frac{(1 + K_{(t)})}{2} uL(C - C_{imp}) \quad (6)$$

$$k_{eff} \frac{dT_g}{dz} = \frac{(1 + K_{(t)})}{2} u c_g \rho_g (T_g - T_{g,imp}) \quad (7)$$

$$\frac{dT_s}{dz} = 0 \quad (8)$$

At  $z = z_1$ ,

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0 \quad (9)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (10)$$

Zone 2 (left side catalyst)  
at  $z = z_1$ ,

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0, \quad (11)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (12)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (13)$$

at  $z = z_2$ ,

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (14)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (15)$$

Zone 3 (heat extract)  
at  $z = z_2$ ,

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0 \quad (16)$$

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0 \quad (17)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (18)$$

at  $z = z_3$ ,

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (19)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (20)$$

Zone 4 (right side catalyst)  
at  $z = z_3$ ,

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0 \quad (21)$$

$$\frac{dT_s}{dz} = 0, \frac{dT_g}{dz} = 0, \frac{dC}{dz} = 0 \quad (22)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (23)$$

at  $z = z_4$ ,

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (24)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (25)$$

Zone 5 (right side inert)  
at  $z = z_4$ ,

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (26)$$

$$\frac{dT_s}{dz} = 0, \frac{dC}{dz} = 0 \quad (27)$$

at  $z = z_5$ ,

$$D_{eff} \frac{dC}{dz} = \frac{(1 - K_{(t)})}{2} uL(C - C_{imp}) \quad (28)$$

$$k_{eff} \frac{dT_g}{dz} = \frac{(1 - K_{(t)})}{2} u c_g \rho_g (T_g - T_{g,imp}) \quad (29)$$

$$\frac{dT_s}{dz} = 0 \quad (30)$$

$K_{(t)} = +1$  forward and  $-1$  for backward

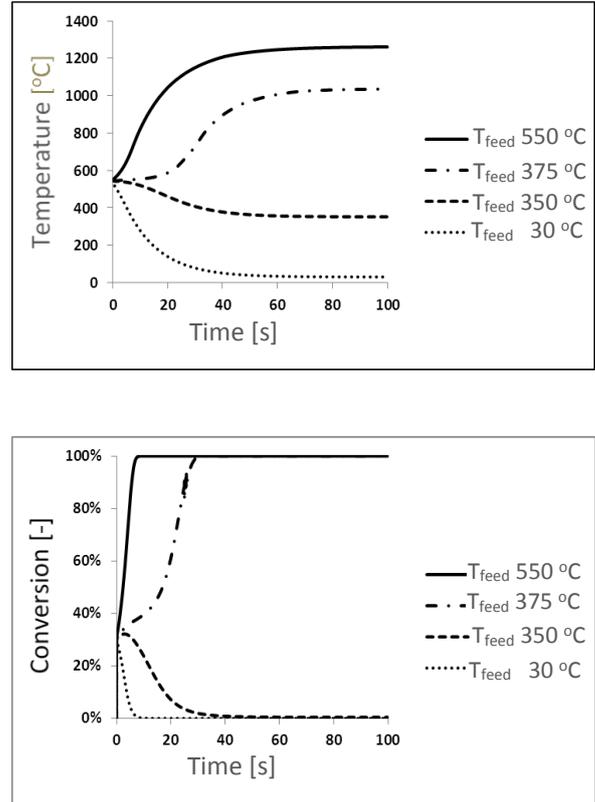
RFR operates auto thermally only if the catalytic oxidation generates sufficient heat for heating the feed. Thus, one of the issues in this study is to examine the effect of switching time on the stability of the oxidation reaction. The RFR model developed based on a one-dimension pseudohomogeneous model for mass balance and heterogeneous model for energy balances with methane as a model component. The simulation was conducted using a software package FlexPDE student version with constant feed methane concentration (1%-v) and preheating the left part of RFR as an initiation of the reaction.

### 3. RESULTS AND DISCUSSION

#### 3.1 One way flow (Fixed Bed)

Methane oxidation is impossible occurred with the one-way flow with a concentration of 1%-v methane at ambient temperature unless the catalyst was first heated up to 550 °C temperature. The methane oxidation reaction can take place with one-way flow operation to achieve 100% conversion whenever the feed heated up to temperatures above 375 °C with the initial temperature catalyst 550 °C (Figure 3.a). This means the reaction on a one-way flow of reactor operation requires initial catalyst temperature 550 °C with feed must constantly be heated to a temperature

of at least 375 °C for the reaction is not extinct. At steady state, the reactor temperature achieved 1000 °C and 1200 °C for feed temperature 375 °C and 550 °C subsequently. The heat resulted from reaction will be carried by the flow of gas out of the reactor in a reactor operating in this one-way direction



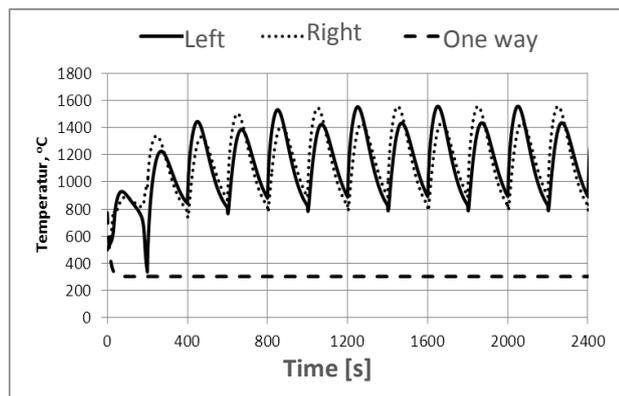
**Fig. 3.** Effect of feed temperature on (a) catalyst temperature and (b) conversion of the initial temperature of 550 °C catalyst for the one-way flow reactor.

Time achievement of steady-state conditions and 100% conversion in one-way operation is influenced by the temperature of the feed. As the feed temperatures higher, the time to reach steady-state conditions and the complete reaction was getting faster. Whenever the feed temperature heated at 375 °C the steady-state temperature is reached at 70 s and full conversion at 30 seconds. Meanwhile, the steady temperature and complete reaction reached at 50 and 8 seconds with the feed flow heated at 550 °C.

#### 3.2 Reverse flow reactor

Simulation a reverse flow reactor (RFR) was conducted with the feed 1%-v methane at a temperature of 30 oC with the left side inert and catalyst preheating temperature up to 500 oC. Simulation results are presented reverse flow operation together with one way flow operation under the same conditions (Figure 4). One direction flow reactor operation was not able to establish oxidation at a low concentration and temperature of feed methane, while reverse flow reactor able to achieve pseudo-steady state and auto-thermal. The total conversion for one way can only reach 0.01%, much smaller

compared to the reverse flow reactor that reached 99.6%.



**Fig. 4.** Comparison of dynamic temperature profiles reverse flow reactor and one-way flow on the feed temperature of 30 °C, the temperature initially inert and catalyst 500 °C and switching time (ST) 200 seconds for reversal operation.

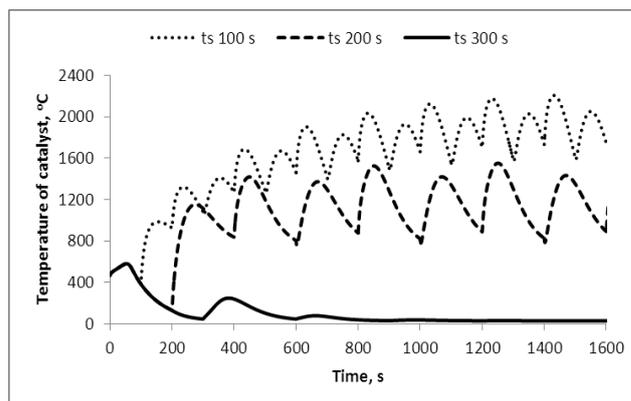
Dynamic profile on the left side of the catalyst temperature RFR after pseudo-steady state is reached indicates a pattern of a high-low hill with a full line. High hill means of heat generated from the reaction on the left catalyst will be carried by the flow to heat the catalyst on the right side which indicated by the dotted line. In other words, a high hill means the reaction has occurred. Whenever the feed flow direction reversed, now from the right, the left RFR catalyst creates a small hill which indicates that the heat generated from the reaction on the right catalyst carried by the flow and heated the left part of RFR.

### 3.3 Effect of Switching Time (ST) on the Heat Extinction in RFR

Preheating of the left side of the inert and catalyst sections at a temperature of 500 °C able to create the auto-thermal conditions in the reactor especially for ST 100 and 200 seconds (Figure 4). The ambient temperature feed which comes from left side heated by the inert so that the feed ready to react on the catalyst. Meanwhile, the right side inert will absorb the heat from the reaction. As reaction time goes by, the left inert temperature will further decrease. This required reversal of the feed direction to sustain the auto-thermal condition. Switching time plays an important role in ensuring the RFR in auto-thermal condition. The simulation showed that a large ST will make the reaction extinguished, as in the ST 300 seconds (Figure 5). The maximum switching time for RFR with preheating left part of RFR at temperature 500 °C and 1%-v methane is 230 s. switching time more than 230 s will make the reaction extinct.

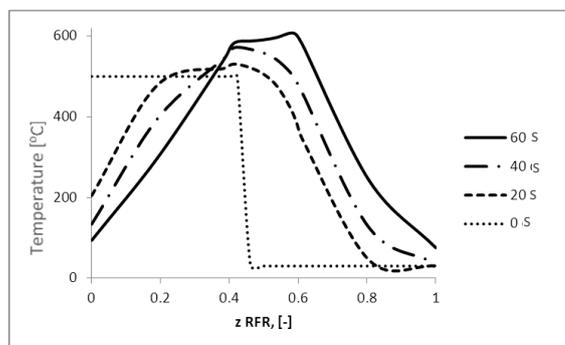
The shorter ST the longer time to achieve the pseudo-steady state. The shorter ST mean RFR more often get disturbances. At ST 200 s, the pseudo-steady state condition is reached in time 1000 s. While for shorter ST 100 s, the temperature profile still looks the

tendency of increasing up to 1600 seconds of time (Figure 5). Other information obtained from the simulations indicates there is a minimum ST required for maintaining RFR in an auto-thermal condition. At this simulation, the ST minimum is 60 s.



**Fig. 5.** The dynamic temperature profile of RFR for ST 100, 200, and 300 s.

Simulations show that for ST less than 60 seconds RFR will be extinguished. During the first few tens of seconds, the reaction will occur by utilizing the heat from the preheated left catalyst and inert (Figure 7). The complete conversion occurs in almost 80 seconds (Figure 8a). The left side inert temperature will decrease due to the heat transfer to the feed, but the right side of the inert temperature will increase due to heat transfer from the gases of reaction from the left catalyst. If the feed flow direction is reversed in a short time, then the amount of heat absorbed in the inert part of the right side will not be enough to heat the feed (Figure 6). The less amount of heat correlated with methane that has not converted perfectly on the first few tens of seconds (Figure 7). This situation will make the reaction fail to achieve auto thermal condition. Thus, there is a minimum ST required in order to make auto thermal RFR can be achieved at a given initial concentration and temperature.



**Fig. 6.** Dynamic temperature profile along the RFR at the beginning of a few tens of seconds

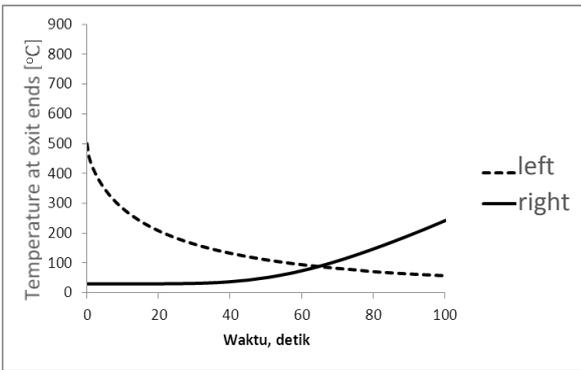
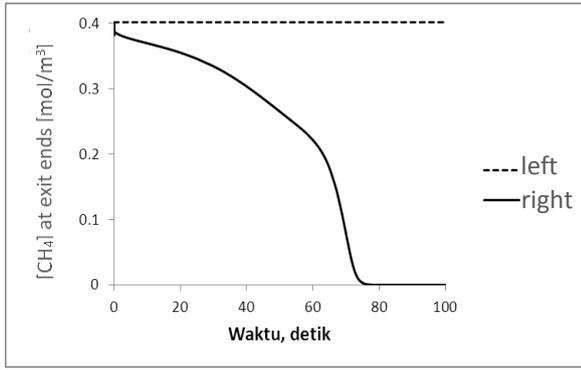


Fig. 7. dynamic concentration profile (a) and temperature (b) at the ends of the hose RFR first 100 seconds.

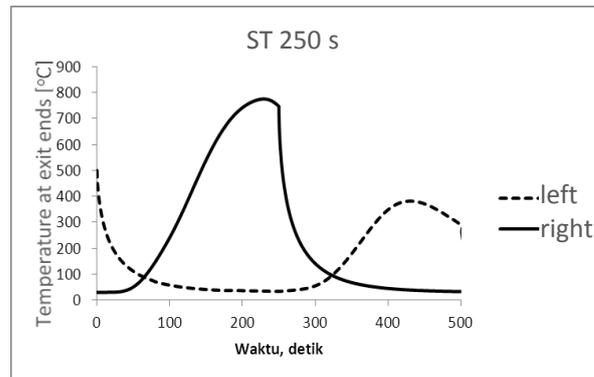
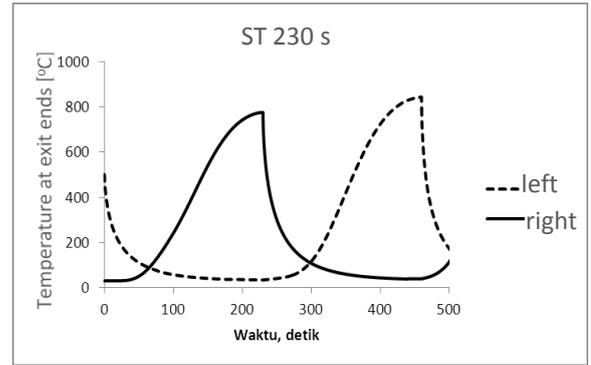


Fig. 8. dynamic profile of temperature on: (a) ST 230 seconds and (b) ST 250 seconds at the ends of the reactor.

If the switching time (ST) is too large, then the heat will be shifted to the right so that the reaction finally extinct (Eigenberger and Nieken, 1989; van de Beld et al., 1994). In agreement with the researchers, the ST 230 seconds RFR can still achieve auto thermal conditions (Figure 8a), but the ST 250 seconds RFR no longer be auto thermal (Figure 8b). In ST 250 seconds, the ability to store heat from the right side inert already passed the point of maximum, so that when the feed reversed, it will not react due to its low temperature. The movement of the temperature profile along the reactor until the RFR extinguished which is at ST 250 seconds is shown in Figure 9.

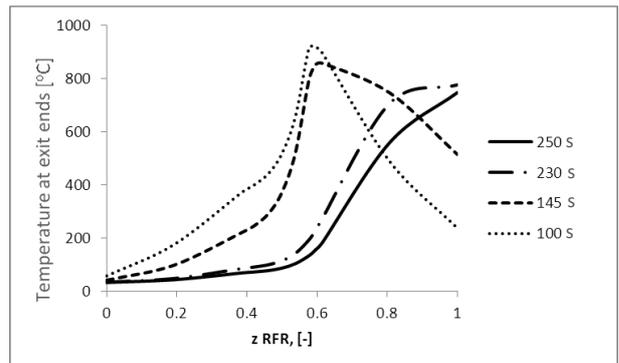


Fig. 9. Dynamic temperature profile along the reactor.

#### 4. Conclusions

The reverse flow reactor (RFR) has shown some advantages compare to one-way flow when applying to low temperature and concentration feed flow. The role of switching time is very important in determining the extinction of oxidation reaction, the temperature of reactor, conversion and time for reaching the pseudo-steady state. Conversion of methane achieves 99 % in RFR for ST 200 second. There is a range of switching time from minimum to maximum for auto-thermal condition operation.

## 5. Nomenclature

### Symbols

$a_v$  = specific interfacial area [ $m^2/m^3$ ]  
 $c_g$  = heat specific of gas phase [ $J/(kg.K)$ ]  
 $c_s$  = heat specific of solid phase [ $J/(kg.K)$ ]  
 $C$  = methane molar density [ $mol/m^3$ ]  
 $D_{eff}$  = axial effective diffusivity [ $m^2/s$ ]  
 $E_A$  = Activation energy [ $J/mol$ ]  
 $k_{eff}$  = heat conductivity [ $W/m.K$ ]  
 $l$  = reactor length [ $m$ ]  
 $Q_{extract}$  = heat extraction [ $J/s$ ]  
 $t$  = time [ $s$ ]  
 $T_g$  = Temperature of gas phase [ $K$ ]  
 $T_{inp}$  = Temperature of input [ $K$ ]  
 $u$  = superficial velocity [ $m^2/s$ ]  
 $W$  = rate of reaction [ $mol/(m^3.s)$ ]  
 $x$  = conversion of methane [-]  
 $z$  = axial direction [ $m$ ]  
 Greek Letters  
 $\alpha_0$  = coefficient of heat transport [ $W/(m^2.K)$ ]  
 $\beta_0$  = coefficient of mass transport [ $m/s$ ]  
 $\Delta H$  = heat reaction [ $J/mol$ ]  
 $\epsilon$  = bed porosity  
 $\epsilon_p$  = void fraction of catalyst particle  
 $\epsilon_s$  = fraction of solid phase

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