Asian Journal of Chemistry Vol. 21, No. 8 (2009), 5989-5993

Numerical Techniques for Methane Modeling During the Warm-Up of Converters

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Numerical simulation is carried out for reducing the concentration of polluting methane during the warm-up period of the converter. A comparison between two numerical techniques namely the quasi steady state model (QSSM) and the unsteady state model (USSM) was carried out.

Key Words: Catalytic oxidation, Methane, Quasi steady state, Unsteady state.

INTRODUCTION

Methane is emitted from gasoline, diesel, ethanol, LPG, natural gas internal-combustion-engine vehicles and from gas turbines. These emissions occur predominantly due to incomplete fuel combustion. There is hardly any industrial process where methane is not emitted and considered as a pollutant[1].

Methane combustion yields lowest amount of CO_2 per unit of produced energy[2]. Due to less emission of CO_2 to atmosphere, makes the natural gas even more attractive as a fuel for purpose of energy.

A considerable amount of methane is released during the warm-up period from cold start of catalytic converter, as the converter takes some time to reach its operating temperature. Two different numerical methods the quasi steady state model (QSSM) and the unsteady state model (USSM) are studied during this period to bring about a reduction in its concentration. The QSSM consists of equations comprising of both ordinary differential equations (ODEs) as well as partial differential equation (PDE)[3]. The USSM analysis consists of a set of PDEs. A comparison between the results derived using the two models found them to be in agreement.

REACTION KINETICS AND MODELING

The oxidation of methane is given by the following reaction[2].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H = -192 \text{ Kcal mol}^{-1}$$

The rate expression for the above heterogeneous reaction is given by[4]:

$$(-r)_{cat}(C_s, T_s) = k_{cat} \exp^{(-E_{cat}/RT_s)} C \tag{1}$$

where, activation energy (E_{cat}) is taken as 1.59×10^5 J/g mol and rate constant (k_{cat}) is taken as 3.10×10^9 m/s.

A simple one-dimensional model was formed taking into account the gas-solid heat and mass transfer, the axial heat conduction in the catalyst and the chemical reaction on the wall of a cylindrical channel of the converter.

Some major assumptions made during modeling include: • Catalyst does not deactivate. • The noble metal concentration is kept constant. • Diffusion in washcoat is neglected, as washcoat is very thin[5]. • Negligible axial diffusion of mass and heat transfer in gas phase. • Heat transfer by radiation within channels and heat exchange between the substrate and the surroundings at both inlet and outlet faces of the monolith are neglected.

QUASI STEADY STATE MODEL (QSSM)

Accumulation of mass and energy in the gas phase is neglected *i.e.*,

$$\frac{\partial C_g}{\partial t} = 0 \qquad \frac{\partial T_g}{\partial t} = 0 \tag{2}$$

Mass balance for the gas:

$$v\left(\frac{\partial C_g}{\partial x}\right) + k_g S\left(C_g - C_s\right) = 0 \tag{3}$$

Mass balance for the solid:

$$a(-r)_{cat}\left(C_s, T_s\right) = k_g S\left(C_g - C_s\right) \tag{4}$$

Energy balance for the gas:

$$-v\rho_g Cp_g\left(\frac{\partial T_g}{\partial x}\right) - hS\left(T_g - T_s\right) = 0 \tag{5}$$

Energy balance for the solid:

$$\lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}\right) + hS\left(T_g - T_s\right) + a(-\Delta H)(-r)_{cat}\left(C_s, T_s\right) = \rho_s Cp_s\left(\frac{\partial T_s}{\partial t}\right) \tag{6}$$

Initial conditions:

$$C_g(0,t) = C_g^0, \quad T_g(0,t) = T_g^0, \quad T_s(x,0) = T_s^0 \tag{7}$$

Boundary conditions:

$$\left(\frac{\partial T_s}{\partial x}\right)_{x=0} = 0, \quad \left(\frac{\partial T_s}{\partial x}\right)_{x=L} = 0 \tag{8}$$

In QSSM equations (3) and (5) are ODEs whereas (6) is a PDE. They are solved in dimensionless form using the following expressions:

$$C = \frac{C_g}{C_g^0}, \quad T_g^{'} = \frac{T_g}{T_g^0}, \quad T_s^{'} = \frac{T_s}{T_s^0}, \quad z = \frac{x}{L}, \quad t^{'} = \frac{t}{t_0} \tag{9}$$

UNSTEADY STATE MODEL (USSM)

Mass balance for gas:

$$v\left(\frac{\partial C_g}{\partial x}\right)+k_g S\left(C_g - C_s\right)=\left(\frac{\partial C_g}{\partial t}\right) \tag{10}$$

Mass balance for solid:

$$a(-r)_{cat}\left(C_s, T_s\right)=k_g S\left(C_g - C_s\right) \tag{11}$$

Energy balance for gas:

$$-v\rho_g Cp_g\left(\frac{\partial T_g}{\partial x}\right)-hS\left(T_g - T_s\right)=\rho_g Cp_g\left(\frac{\partial T_g}{\partial t}\right) \tag{12}$$

Energy balance for solid phase:

$$\lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}\right)+hS\left(T_g - T_s\right)+a(-\Delta H)(-r)_{cat}\left(C_s, T_s\right)=\rho_s Cp_s\left(\frac{\partial T_s}{\partial t}\right) \tag{13}$$

In USSM equations (10), (12) and (13) are PDEs. Initial and boundary conditions for the converter remain the same as given by (7) and (8) also following new boundary conditions are included:

$$\left(\frac{\partial C_g}{\partial x}\right)_{x=L}=0 \qquad \left(\frac{\partial T_g}{\partial x}\right)_{x=L}=0 \tag{14}$$

All above equations are first converted to dimensionless form and then descretised. The ODEs are solved using Runge-Kutta method and PDEs by Backward Implicit scheme[3].

RESULTS AND DISCUSSION

The variation in the gas concentration, the gas temperature and the solid temperature along the length of the converter for the two models is shown by Figs. 1-3. Results are analyzed for decrease in dimensionless concentration upto 0.1000 with respect to dimensionless time.

Fig. 1 shows the comparison of results obtained for concentration of methane along the converter length with respect to time for QSSM and USSM models. By using the methods of solution, insignificant changes in concentration are found. At dimensionless time 12.00 the concentrations are 0.9729 and 0.9348 by QSSM and 0.9734 and 0.9365 by USSM at axial lengths 0.40 and 1.00 respectively. At dimensionless time 14.30 the concentration is 0.6874 and 0.4117 by QSSM and 0.6997 and 0.4131 by USSM at axial distances 0.04 and 1.00. Both methods are giving almost similar results.

Fig. 2 shows the comparison of results for variation of gas temperature along the axial length with respect to time for an inlet gas temperature of 540 ºC. Gas

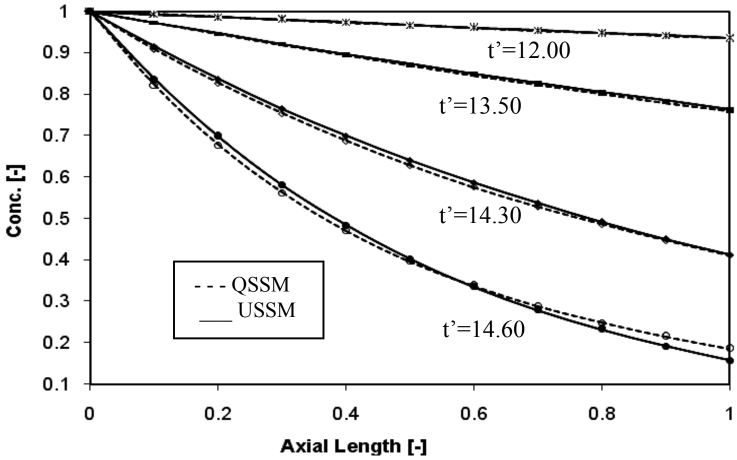

Fig. 1. Variation of the gas concentration along the axial length for quasi steady state (QSSM) and unsteady state (USSM) models

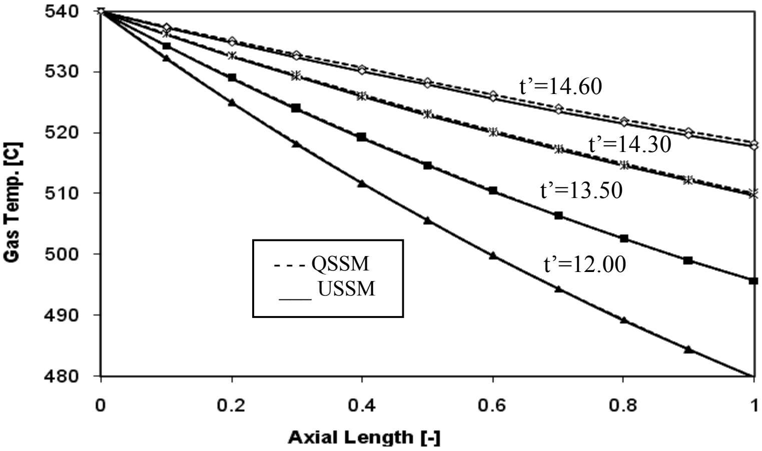

Fig. 2. Variation of the gas temperature along the axial length for quasi steady state (QSSM) and unsteady state (USSM) models

temperatures calculated in axial direction with variation of time show insignificant change in temperatures by using both the methods. At dimensionless time 13.50 the gas temperature are 519.24, 506.48, 495.71 ºC by QSSM and 519.11, 506.35, 495.65 ºC by USSM at axial lengths 0.40, 0.70 and 1.00, respectively, clearly show both methods giving similar results.

Fig. 3 shows the comparison of results obtained for solid temperature along the length. At dimensionless time 13.50 the solid temperatures are 444.34, 443.47, 442.99 ºC by QSSM and 443.11, 442.25 and 441.77 ºC by USSM at axial lengths 0.20, 0.60 and 0.90, respectively, indicating both methods of solution giving almost similar results.

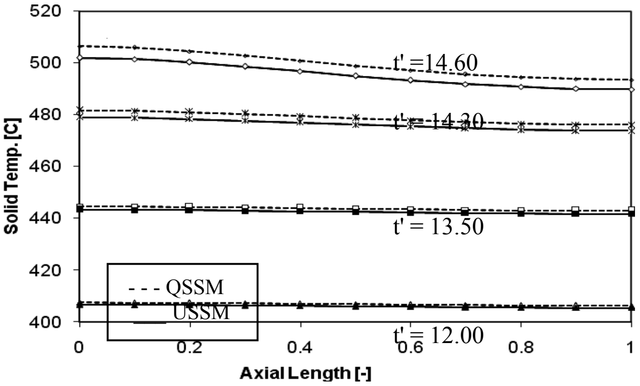

Fig. 3. Variation of the solid temperature along the axial length for quasi steady state (QSSM) and unsteady state (USSM) models

Nomenclature

a	Catalytic surface area per unit reactor volume, $cm^2\ cm^{-3}$
C	Concentration of the methane, gmol cm^{-3}
C_p	Specific heat, cal $g^{-1}\ K^{-1}$
h	Heat transfer coefficient, cal $cm^{-2}\ s^{-1}\ K^{-1}$
$-\Delta H$	Heat of reaction, cal $gmol^{-1}$
k_g	Mass transfer coefficient, cm s^{-1}
L	Length of monolith, cm
S	Geometric surface area per unit reactor volume, $cm^2\ cm^{-3}$
T	Temperature, K
t	Time, s
v	Gas velocity, cm s^{-1}
x	Axial coordinates, cm
z	Dimensionless axial coordinates
λ	Thermal conductivity, cal $cm^{-1}\ s^{-1}\ K^{-1}$
ρ	Density, g cm^{-3}

ACKNOWLEDGEMENT

The author thanks Prof. V. K. Srivastava (Academy of Business & Engineering Sciences, Vijay Nagar, Ghaziabad) for his invaluable inputs and advice.

REFERENCES

1. A. Janbey, W. Clark, E. Noordally, S. Grimes and S. Tahir, *Chemosphere*, **52**, 1041 (2003).
2. D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle and A. Datya, *Catal. Rev.*, **44**, 593 (2002).
3. S. Chauhan and V.K. Srivastava, *Comp. Mathematics Appl.*, **55**, 319 (2008).
4. B. Liu, R.E. Hayes, M.D. Checkel, M. Zheng and E. Mirosh, *Chem. Eng. Sci.*, **56**, 2641 (2001).
5. S.T. Kolaczkowski, *Catal. Today*, **47**, 209 (1999).

(*Received*: 28 August 2008; *Accepted*: 21 May 2009) AJC-7571