Modeling Converters during the Warm-up period for Hydrocarbon Oxidation

Sanchita Chauhan, and V.K. Srivastava

Abstract—Catalytic converters are used for minimizing the release of pollutants to the atmosphere. It is during the warm-up period that hydrocarbons are seen to be released in appreciable quantities from these converters. In this paper the conversion of a fast oxidizing hydrocarbon propylene is analysed using two numerical methods. The quasi steady state method assumes the accumulation terms to be negligible in the gas phase mass and energy balance equations, however this term is present in the solid phase energy balance. The unsteady state model accounts for the accumulation term to be present in the gas phase mass and energy balance and in the solid phase energy balance. The results derived from the two models for gas concentration, gas temperature and solid temperature are compared.

Keywords—propylene, catalyst, quasi steady state, unsteady state.

I. INTRODUCTION

CATALYTIC converters are being extensively used in environmental applications and currently there is a growing interest in their use for catalytic combustion reactions [1]. Earlier converters contained a bed of particulate bead catalysts, but now they have been replaced by monolithic converters as the later exhibit higher conversion of pollutants due to higher geometric surface area and are also lighter weight [2].

The converters are effective in reducing pollution only after they have obtained the desired operating temperature [3]. Initially the converter being at ambient temperature is not able to function due to catalyst being ineffective at low temperatures. However as the incoming exhaust gas is at a much higher temperature, it heats up the converter and the catalytic reaction starts as soon as the operating temperature is achieved. This period is referred to as the warm-up period of the converter. As the reaction starts a considerable decrease in the pollutant hydrocarbon concentration is observed over the period of time.

Experimental testing is relatively expensive and time consuming as compared to modeling [4], [5]. A one-dimensional model can be used to adequately predict the monolith behaviour during the warm up period [6].

Hydrocarbons released during this warm-up period from the converter form a considerable part of the pollutants released untreated to the atmosphere. Different methods have been suggested for their reduction. In the study two models namely quasi steady state and unsteady state models are analysed. The quasi steady state consists of a system of modelled equations comprising of both ordinary differential equations (ODEs) and as partial differential equation (PDE). The unsteady state analysis consists of a set of PDEs. The ODEs are solved using Runge-Kutta method and the PDEs by Backward Implicit Scheme. Finally a comparison is made between the results derived using the two models and we observed that both method are in agreement.

II. MATHEMATICAL MODEL

The catalytic oxidation of a fast oxidizing hydrocarbon propylene in the converter is considered.

$$C_3H_6 + 4.5\,O_2 \rightarrow 3\,CO_2 + 3\,H_2O$$
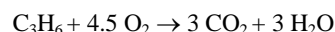
Platinum suspended in alumina washcoat is taken as the catalyst and the rate expression for propylene oxidation reaction [7] is given by:

$$(-r)(C_s, T_s) = k_0 \exp^{(-E/RT_s)} C$$

where, activation energy E is taken as 50,242 J/gmol and pre-exponential factor k_0 is taken as 9.14×10^4 cm/s.

A simple one-dimensional model is formed accounting for the mass and heat transfer in the gas and solid phases, the axial heat conduction in the catalyst and the chemical reaction [8].

A. Assumptions

Some major assumptions made during modeling include:
o Monolith is cylindrical with a circular cross-section channel.
o Gas phase concentration, temperature and velocity and the solid temperature are uniform across the monolith cross-section.
o Uniform properties are assumed for the flowing gas.
o Diffusion in washcoat is neglected, as washcoat is assumed to be very thin.
o Noble metal concentration is kept constant.
o Catalyst does not deactivate.
o The physical properties of monolith are constant and independent of monolith temperature.
o Negligible axial diffusion of mass and heat transfer in gas phase.
o Heat transfer by radiation within channels and heat exchange between the substrate and the surroundings

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at both inlet and outlet faces of the monolith are neglected.

o Non-uniform flow distributions inside the converter are neglected. A single channel as shown in Fig. 1 represents the entire monolith.
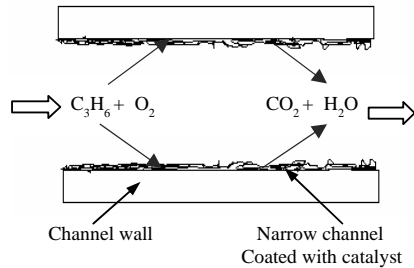

Fig. 1 A channel of the monolith assembly

B. Quasi Steady State Model

The model is operating at a constant inlet temperature under steady flow conditions. For this model the accumulation of mass and energy in the gas phase is neglected.

$$\frac{\partial C_g}{\partial t} = 0 \tag{1}$$

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

where C_g is concentration in bulk gas phase (gmole/cm^3), T_g is gas temperature (K), and t is time (s).

Mass balance for the gas phase:

Includes the net convective transport of gas in the axial direction (x) and the transfer of reactant mass from gas to solid.

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

where k_g is mass transfer coefficient (cm/s), S is the geometric surface area per unit reactor volume (cm^2/cm^3), C_s represent concentration at the solid surface (g mole/cm^3), x is axial length (cm), and v is average velocity (cm/s).

Mass balance for the solid phase:

The rate of reaction taking place at the catalyst surface is taken equal to the mass transfer of the reactant from gas to solid phase.

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

where a is catalytic surface area per unit reactor volume (cm^2/cm^3), and T_s is solid temperature (K).

Energy balance for the gas phase:

The net convective transport of gas in the axial direction results in the heat transfer from the gas to the solid wall.

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

where ρ_g represents gas density (g/cm^3), Cp_g is specific heat of gas (J/g K), and h is heat transfer coefficient (J/cm^{2}s K).

Energy balance for the solid phase:

It accounts for the heat conduction in the solid wall in axial direction, heat transfer between the gas and the solid wall, heat released due to heterogeneous chemical reaction at the wall surface and the net accumulation of heat in the solid wall.

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

where λ_s is thermal conductivity of wall (J/cm s K), Cp_s is specific heat of solid (J/g K), ρ_s is solid density (g/cm^3), and ΔH is heat of reaction (J/gmole).

Initial and Boundary Conditions:

Initially the converter is at the ambient temperature and then it is suddenly exposed to hot exhaust gas from engine.

Propylene concentration at the entrance for all times:

$$C_g(0,t) = C_g^0 \tag{7}$$

Gas temperature at the entrance at all times:

$$T_g(0,t) = T_g^0 \tag{8}$$

Solid temperature initially along the converter length:

$$T_s(x,0) = T_s^0 \tag{9}$$

The boundary conditions for lagging of solid catalyst at:

the converter entrance $x = 0$, $\quad \dfrac{\partial T_s}{\partial x} = 0 \tag{10}$

the converter exit $\quad x = L$, $\quad \dfrac{\partial T_s}{\partial x} = 0 \tag{11}$

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

$$C = \frac{C_g}{C_g^0} \quad, \quad T_g' = \frac{T_g}{T_g^0} \quad, \quad T_s' = \frac{T_s}{T_s^0}$$
$$z = \frac{x}{L} \quad, \text{ and } \quad t' = \frac{t}{t_0} \tag{12}$$

where C, T_g', T_s', z, and t' are all dimensionless. L is converter length (cm) and t_0 is time at start of operation (s).

Dimensionless Equations for Quasi Steady State Model:

Using the dimensionless numbers given by (12) in (3) to (11) to make them dimensionless, following equations are derived:

Combined Mass balance equation:

$$\left(\frac{\partial C}{\partial z}\right) = -\psi_1 Ce^{\left(-E/RT_s\right)} \tag{13}$$

where $\psi_1 = \dfrac{Lak_0}{v}$

Energy balance equation for gas phase:

$$\left(\frac{\partial T_g'}{\partial z}\right) = \delta_1\left(T_s' - T_g'\right) \tag{14}$$

where $\delta_1 = \dfrac{SLh}{v\rho_g Cp_g}$

Energy balance equation for solid phase:

$$\left(\frac{\partial T_s'^2}{\partial z^2}\right) = -\psi_2 Ce^{\left(-E/RT_s\right)} + \alpha_1\left(T_s' - T_g'\right)$$
$$+ \phi_1\left(\frac{\partial T_s'}{\partial t'}\right) \tag{15}$$

where $\psi_2 = \left(C_g^0\right)\dfrac{aL^2\left(-\Delta H\right)k_0}{\lambda_s T_g^0}$,

$\alpha_1 = \dfrac{ShL^2}{\lambda_s}$, and $\phi_1 = \dfrac{\rho_s Cp_s L^2}{\lambda_s t_0}$

Initial and boundary conditions:

$$C\left(0, t'\right) = 1.00 \tag{16}$$

$$T_g'\left(0, t'\right) = \frac{T_g}{T_g^0} \tag{17}$$

$$T_s'\left(z, 0\right) = \frac{T_s}{T_s^0} \tag{18}$$

$$z = 0.0, \quad \frac{\partial T_s'}{\partial z} = 0 \tag{19}$$

$$z = 1.0, \quad \frac{\partial T_s'}{\partial z} = 0 \tag{20}$$

Equations (13) and (14) are ODEs and (15) is a PDE and along with the initial and boundary conditions given by (16) to (20) represent the quasi steady state model in dimensionless form.

C. Unsteady State Model

In the unsteady state model the time derivative terms representing the accumulation for both gas concentrations and gas temperature along with those for solid temperature are taken into account for solving mass and energy balance equations.

Mass balance for gas phase:

$$v\left(\frac{\partial C_g}{\partial x}\right) + k_g S\left(C_g - C_s\right) = \left(\frac{\partial C_g}{\partial t}\right) \tag{21}$$

Mass balance for solid phase:

$$a(-r)\left(C_s, T_s\right) = k_g S\left(C_g - C_s\right) \tag{22}$$

Energy balance for gas phase:

$$-v\rho_g Cp_g\left(\frac{\partial T_g}{\partial x}\right) - hS\left(T_g - T_s\right) = \rho_g Cp_g\left(\frac{\partial T_g}{\partial t}\right) \tag{23}$$

Energy balance for solid phase:

$$\rho_s Cp_s\left(\frac{\partial T_s}{\partial t}\right) = a\left(-\Delta H\right)\left(-r\right)\left(C_s, T_s\right)$$
$$+ hS\left(T_g - T_s\right) + \lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}\right) \tag{24}$$

Initial and Boundary Conditions:

Initial and boundary conditions for the converter remain the same as given by (7) to (11), however new the boundary conditions are included for gas concentration and temperature at the exit of the converter as:

$$x = L, \quad \frac{\partial C_g}{\partial x} = 0 \tag{25}$$

$$x = L, \quad \frac{\partial T_g}{\partial x} = 0 \tag{26}$$

Equations (21) to (26) and (7) to (11) are first converted to dimensionless form using expressions given by (12).

Dimensionless Equations for Unsteady State Model

Combined Mass balance equations:

$$\left(\frac{\partial C}{\partial z}\right) = -\theta_1\left(\frac{\partial C}{\partial t'}\right) - \psi_1 Ce^{\left(-E/RT_s\right)} \tag{27}$$

where $\psi_1 = \dfrac{Lak_0}{v}$, and $\theta_1 = \dfrac{L}{vt_0}$

Energy balance equation for gas phase:

$$\left(\frac{\partial T_g^{'}}{\partial z}\right) = -\theta_2\left(\frac{\partial T_g^{'}}{\partial t^{'}}\right) + \delta_1\left(T_s^{'} - T_g^{'}\right) \qquad (28)$$

where $\theta_2 = \dfrac{L}{vt_0}$, and $\delta_1 = \dfrac{SLh}{v\rho_g Cp_g}$

Energy balance equation for solid phase:

$$\left(\frac{\partial T_s^{'2}}{\partial z^2}\right) = -\psi_2 Ce^{\left(-E/RT_s\right)} + \qquad (29)$$

$$\alpha_1\left(T_s^{'} - T_g^{'}\right) + \phi_1\left(\frac{\partial T_s^{'}}{\partial t^{'}}\right)$$

where $\psi_2 = \left(C_g^0\right)\dfrac{aL^2\left(-\Delta H\right)k_0}{\lambda_s T_g^0}$,

$\alpha_1 = \dfrac{ShL^2}{\lambda_s}$, and $\phi_1 = \dfrac{\rho_s Cp_s L^2}{\lambda_s t_0}$

where ψ_1, ψ_2, θ_1, θ_2, δ_1, ϕ_1, and α_1 are dimensionless quantities and their values are given in Table. 1.

Initial and boundary conditions remain same as given by (16) to (20) and the new dimensionless boundary conditions become:

$$z = 1.0, \quad \frac{\partial C}{\partial z} = 0 \qquad (30)$$

$$z = 1.0, \quad \frac{\partial T_g^{'}}{\partial z} = 0 \qquad (31)$$

Equations (27), (28), and (29) are PDEs along with initial and boundary conditions given by (16) to (20), (30), and (31) represent the unsteady state model in dimensionless form.

III. METHODOLOGY FOR SOLUTION

The ODEs are solved by Runge-Kutta method of fourth order. The PDEs are solved using the Backward Implicit finite difference numerical scheme [9].

As these equations are coupled; hence they are solved at the same time. For the quasi steady state although the time derivative terms do not exist in the ODEs but as it is present in the PDE and the equations being coupled, its effects is therefore introduced in the ODEs.

IV. RESULTS AND DISCUSSION

At the start of the operation, the converter is at 25^0C and the entering exhaust gas at 325^0C, heats the converter. The catalytic reaction starts once the converter has attained the operating temperature. Due to these reactions a decrease in the concentration of propylene is observed. The inlet concentration of propylene (1900ppm) has a dimensionless value of 1.0000 and the results are obtained and analysed for decrease in the dimensionless concentration upto 0.1000. The results presented as two ordinary differential equations and one partial differential equation (2-ODEs and 1-PDE) represent the quasi steady state, whereas the unsteady state system is represented by three partial differential equations only (3-PDEs). Fig. 2, 3 and 4 show the variation in the gas concentration, the gas temperature and the solid temperature along the length of the converter for the two models. Results are derived for dimensionless times 10.00, 12.50, 13.50, 14.00, and 14.70.
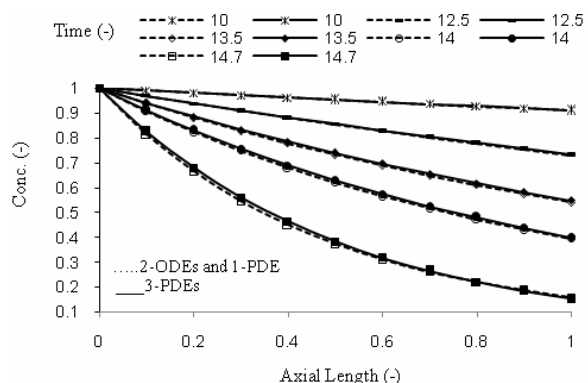

Fig. 2 Propylene concentration variation along the axial length
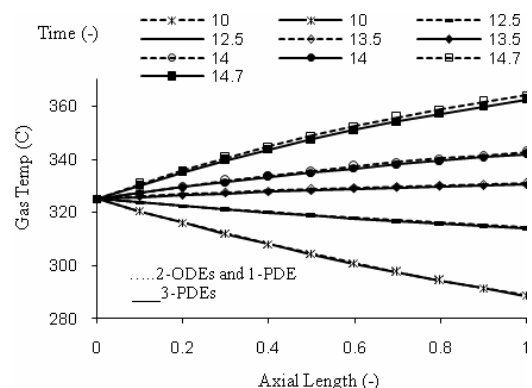

Fig. 3 Gas temperature variation along the axial length.

Fig. 2 shows the comparison of solutions obtained for concentration of propylene along the converter length with respect to time for quasi steady state and unsteady state models. By using the methods of solution, insignificant changes in concentration are found. At dimensionless time 13.50 the concentrations are 0.8288, 0.7327, and 0.5755 by using 2-ODEs and 1-PDE and 0.8343, 0.7399, and 0.5833 by using 3-PDEs at axial lengths 0.30, 0.50, and 0.90 respectively. At dimensionless time 14.70 the concentration is

0.1582 by using 2-ODEs and 1-PDE and 0.1529 by using 3-PDEs at axial distance 1.00. Both methods are giving almost similar results.

Fig. 3 shows the comparison of solutions for variation of gas temperature along the axial length with respect to time for quasi steady state and unsteady state system for an inlet gas at of 325.00^{0}C. Gas 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 temperature are 327.42^{0}C, 328.71^{0}C, and 330.63^{0}C by using 2-ODEs and 1-PDE and 327.05^{0}C, 328.21^{0}C, and 330.01^{0}C by using 3-PDEs at axial lengths 0.30, 0.50, and 0.90 respectively, clearly show both methods giving similar results.
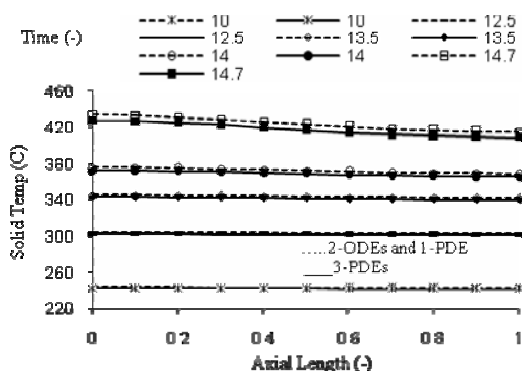

Fig. 4 Solid catalyst temperature variation along the axial length.

Fig. 4 shows the comparison of solutions obtained for solid temperature along the length with respect to time using quasi steady state conditions and unsteady state conditions. At dimensionless time 13.50 the solid temperatures are 344.95^{0}C, 343.90^{0}C, and 342.28^{0}C by using 2-ODEs and 1-PDE and 342.20^{0}C, 341.19^{0}C, and 339.64^{0}C by using 3-PDEs at axial lengths 0.30, 0.5, and 0.9 respectively, indicating both methods of solution giving almost similar results.

V. CONCLUSIONS

In the present study mathematical modeling and numerical simulation for hydrocarbon propylene is carried out using the quasi steady state and the unsteady state models. On analysis of these results we observed that there is an insignificant change in the gas concentration of propylene, the gas temperature and the solid temperature for the two models. So both proposed models represent the physical solution of system equally well and the two numerical methods for solution also give similar results. It is therefore concluded that in the unsteady state model the time derivatives terms for the gas concentration and the gas temperature are very small as compared to that of the solid thermal response, so they do not significantly affect the propylene conversion results. So simpler and easier simulations to get fast and reliable results can be achieved by using the quasi steady state model, where the time derivatives for the gas concentration and the gas

temperature are neglected for predicting the converter behavior.

APPENDIX

TABLE 1
VALUES OF THE DIMENSIONLESS QUANTITIES.

$\psi_1 = 2.95 \times 10^5$	$\delta_1 = 56.77$
$\psi_2 = 1.56 \times 10^8$	$\phi_1 = 159880.60$
$\theta_1 = \theta_2 = 1.20 \times 10^{-1}$	$\alpha_{33} = 23296.78$

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