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Modeling and Simulation for Propylene Present in Exhaust Gas using a Monolithic Catalytic Converter

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Numerical simulation is carried out for reducing the concentration of hydrocarbon propylene present in exhaust. Catalytic converter monoliths are used to bring a faster reduction of propylene at a much lower temperature. Model equations are proposed to calculate the concentration and temperature of the gas, along with catalyst temperature during the warm-up period.

Key Words: Modeling, Catalytic converter, Propylene, One dimensional.

INTRODUCTION

Vehicular transport forms an essential part of lifestyle, both for industrial as well as personnel use. Its extensive use has led to an increase in air pollution due to the harmful gases released from the exhaust of the automobiles. Catalytic converters are designed to reduce the pollutants discharged from the exhaust.

Monolithic converters one piece construction offers attrition free operation in vibrating and pulsating atmosphere[1] and also offers a great deal of design flexibility due to variety of geometrical configurations which could not be achieved earlier when packed beds were used as converters.

There are many hurdles that the developer of a mathematical model of a catalytic converter has to encounter due to a number of areas that have not been addressed adequately by researchers over the last few years. For some of these areas solutions exist, whilst others require a long-term research. Reliable and efficient numerical simulations help in reducing the number of experiments and help in interpreting more detailed effect of some parameters otherwise neglected[2-4].

In this paper, one dimensional model is used to determine the reduction of propylene during cold start period. During cold start conditions the converters temperature being low the untreated hydrocarbon emissions are high[5,6]. These converters are effective in reducing pollution only after they are heated up to the desired operating temperature[7]. The change in concentration of the gas as it passes through the converter channel along with the corresponding gas and solid temperature in the assembly is analyzed during this period.

KINETICS AND MODELING

Propylene is a relatively fast oxidizing hydrocarbon[8]. Its oxidation reaction is given by:

$$C_3H_6 + 4.5O_2 \longrightarrow 3CO_2 + 3H_2O$$

Platinum used as catalyst for the reaction, causes it to proceed at a much lower temperature. Various kinetic parameters taken for the catalytic oxidation reaction[9] are given in Table-1.

TABLE-1
RATE EXPRESSION FOR PROPYLENE OXIDATION BY CATALYTIC REACTION

$$(-r)_{cat}(C_s T_s) = k_{cat} \exp^{\left(\frac{E_{cat}}{RT_s}\right)} C_{C_3H_6}$$

k_{cat} : 9.14 × 10^4 cm s^{-1} E_{cat} : 12,000 cal g mol^{-1}

A one-dimensional model that takes into account variation in concentrations and temperatures along the axial gradients is considered. During the warm up period the parameters taken into account include the gas-solid heat and mass transfer, the axial heat conduction in the catalyst and the chemical reactions as shown in Fig. 1.

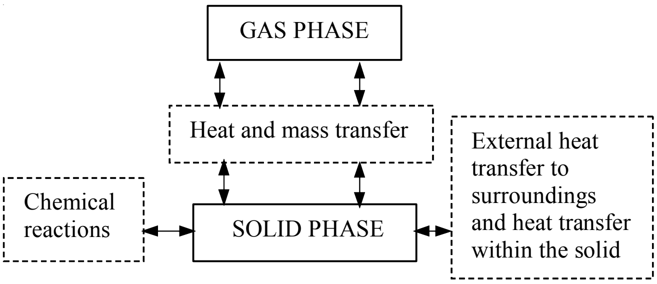

Fig. 1. Process interaction within a typical catalyst

Assumptions made during modeling:

- Monolith is cylindrical with circular cross-section channel.
- A channel of the monolith is assumed to be the representative of the whole monolith.
- Catalyst does not deactivate.
- Diffusion in wash coat is neglected.
- Heat transfer by radiation within channels is neglected.
- Heat exchange between the substrate and the surroundings at both inlet and outlet faces of the monolith is neglected.
- Non-uniform flow distributions inside the converter are neglected.

At quasi steady state.

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

Mass balance in gas phase:

$$v\left(\partial C_g / \partial x\right) + k_g S\left(C_g - C_s\right) = 0 \tag{2}$$

Mass balance in solid phase:

$$a\left(-r\right)_{cat}(C_s, T_s) = k_g S\left(C_g - C_s\right) \tag{3}$$

Energy balance in gas phase:

$$-C_{pg} v \rho_g \left(\partial T_g / \partial x\right) - hS\left(T_g - T_s\right) = 0 \tag{4}$$

Energy balance in solid phase:

$$C_{ps}\rho_s\left(\partial T_s / \partial t\right) = \lambda_s\left(\partial^2 T_s / \partial x^2\right) + hS\left(T_g - T_s\right) + a\left(-\Delta H\right)\left(-r\right)_{cat}(C_s, T_s) \tag{5}$$

Initial conditions:

$$C_g\left(0, t\right) = C_g^0 \quad \text{(entering gas concentration)} \tag{6}$$

$$T_g\left(0, t\right) = T_g^0 \quad \text{(entering gas temperature)} \tag{7}$$

$$T_s\left(x, 0\right) = T_s^0 \quad \text{(solid catalyst temperature at the start)} \tag{8}$$

Boundary conditions:

$$\text{at } x = 0, \left(\partial T_s / \partial x\right) = 0 \quad \text{(lagging solid catalyst at entry)} \tag{9}$$

$$\text{at } x = L, \left(\partial T_s / \partial x\right) = 0 \quad \text{(lagging solid catalyst at exit)} \tag{10}$$

Equations 2-10 are solved in dimensionless form using the following expressions:

$$C = C_g / C_g^0,\ T_g^{'} = T_g / T_g^0,\ z = x / L,$$

$$T_s^{'} = T_s / T_s^0,\ t^{'} = t / t_0 \tag{11}$$

Dimensionless equation for combined mass balance becomes:

$$\left(\frac{dC^{'}}{dz}\right) = -\chi\ C^{'} e^{\left(-E_{cat} / RT_s^{'}\right)} \tag{12}$$

Dimensionless equation for energy balance for gas phase:

$$\left(\frac{dT_g^{'}}{dz}\right) = \phi\ \left(T_s^{'} - T_g^{'}\right) \tag{13}$$

Dimensionless equation for energy balance for solid phase:

$$\left(\frac{dT_s^{'2}}{dz^2}\right) = -\gamma\ C^{'} e^{\left(-E_{cat} / RT_s^{'}\right)} + \alpha\ \left(T_s^{'} - T_g^{'}\right) + \delta\left(\frac{dT_s^{'}}{dt^{'}}\right) \tag{14}$$

where, χ, ϕ, γ, α and δ are dimensionless numbers as shown in Table-2.

TABLE-2
DIMENSIONLESS NUMBERS AND THEIR CORRESPONDING VALUES

Dimensionless numbers	Mathematical values
$\chi = \frac{Lak_{cat}}{v}$	2.95×10^{5}
$\phi = \frac{4Lh}{v\rho_g Cp_g d}$	56.77
$\alpha = \frac{4hL^2}{\lambda_s d}$	23296.78
$\delta = \frac{\rho_s Cp_s L^2}{\lambda_s t_0}$	159880.60
$\gamma = \left(C_g^0\right)\frac{aL^2(-\Delta H)k_{cat}}{\lambda_s T_g^0}$	1.46×10^{8}

Dimensionless initial conditions:

$$C'(0,t') = 1.00\,,\quad T_g'(0,t') = \frac{T_g}{T_g^0}\,,\quad T_s'(z,0) = \frac{T_s}{T_s^0} \tag{15}$$

Dimensionless boundary conditions:

$$\text{at } z = 0.0,\ \frac{dT_s'}{dz} = 0 \tag{16}$$

$$\text{at } z = 1.0,\ \frac{dT_s'}{dz} = 0 \tag{17}$$

The ordinary differential eqns. 12 and 13 have been solved by using Runge-Kutta method for determining the gas concentrations and temperature. The partial differential eqn. 14 is used for calculation of solid catalyst temperature. Backward Implicit scheme is used for solving it. Effect of grid sizes has been studied.

RESULTS AND DISCUSSION

In this work propylene oxidation in the presence of a catalyst during warm up period of the converter is considered. Discussion has been done with help of Fig. 2 representing variation in concentration of the gas and Figs. 3-5 representing temperatures of the exhaust gas and the solid catalyst along the length of the converter. Computation is done using dimensionless equations. Results are analyzed for decrease in dimensionless concentration upto 0.2000 with respect to dimensionless time.

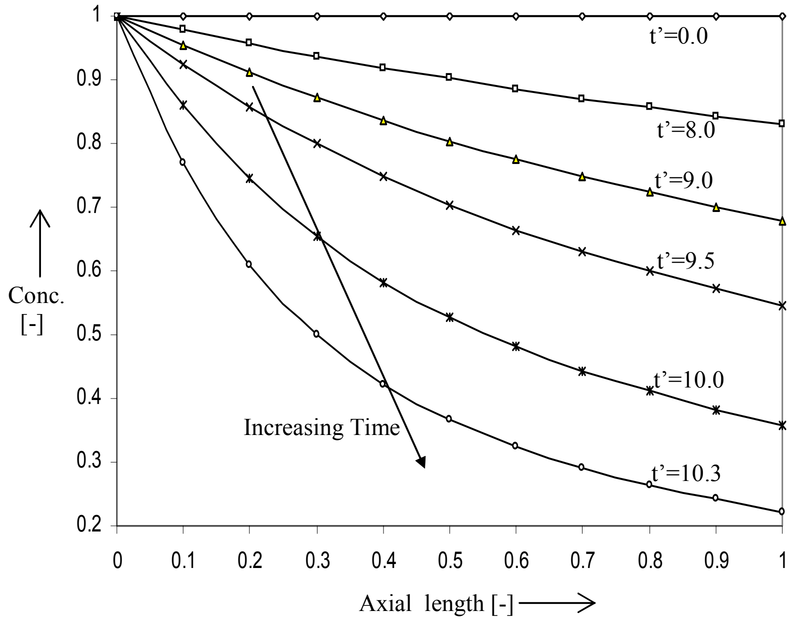

Fig. 2. Exit conversion variation along axial length for propylene (1900 ppm) in the exhaust gas.

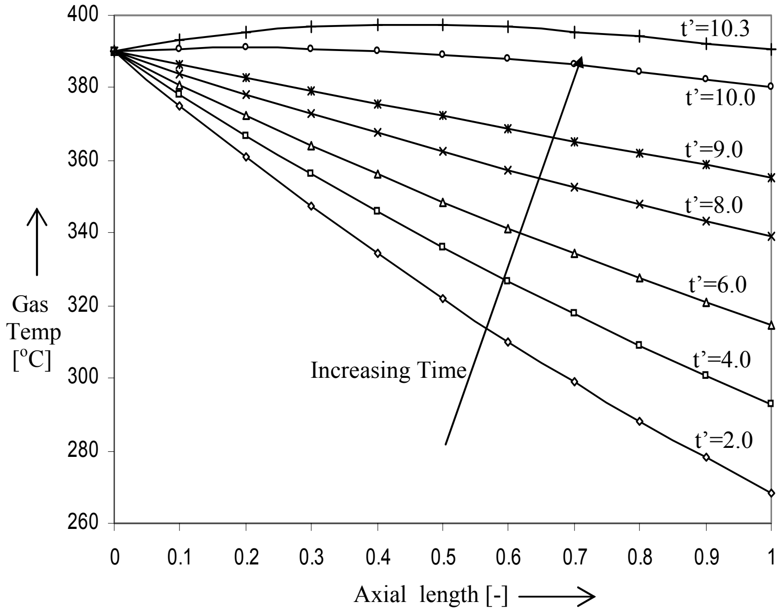

Fig. 3. Gas temperature variation along axial length for propylene in the exhaust gas

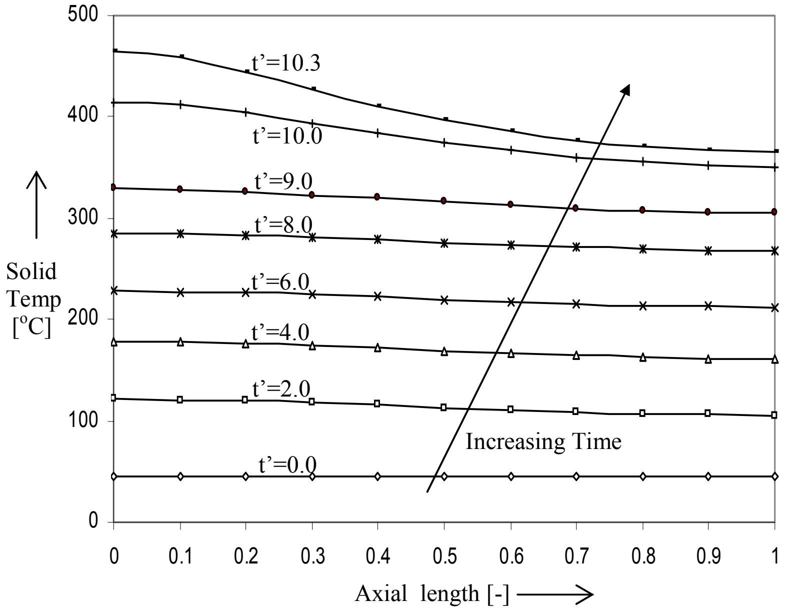

Fig. 4. Solid temperature variation along axial length for propylene in exhaust gas

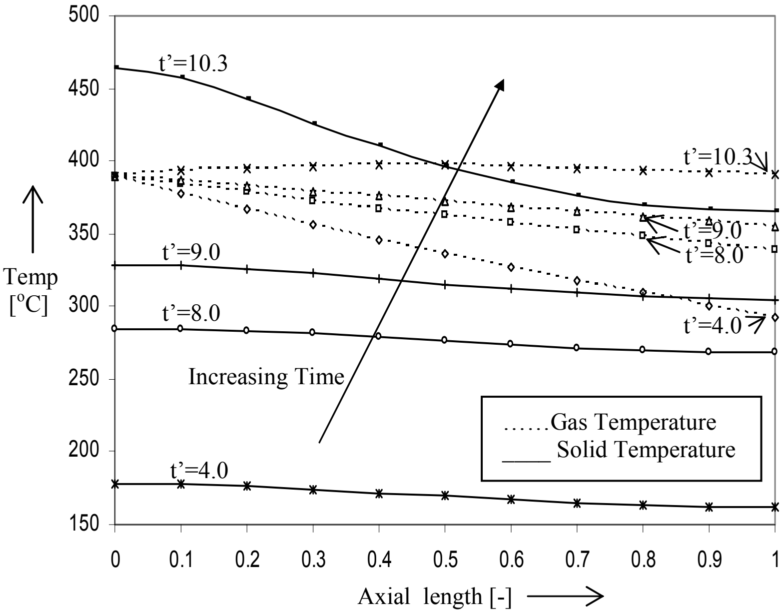

Fig. 5. Gas and solid temperature variation along axial length for propylene in exhaust gas

Fig. 2 shows variation in axial direction concentration for propylene present in the exhaust at the time of the start of the converter. Propylene (1900 ppm) at 390 ºC enters a relatively cooler converter, initially maintained at 45 ºC. Initially there is hardly any change in the values of the concentration of the gas. With increase of time appreciable difference in concentration is observed towards the later part of the converter. At time 9.00 the concentrations are 0.9541, 0.8361, 0.7479 and 0.6786 at axial distances 0.10, 0.40, 0.70, 0.90 and 1.00, respectively. At axial length 7.00 the concentrations are 0.8706, 0.7479, 0.6309, 0.4432 and 0.2915 for times 8.00, 9.00, 9.50, 10.00 and 10.30, respectively. This is due to the fact that at a particular location as time increases the catalyst reaction increases due to increase of catalyst temperature and more conversion of the gas takes place thereby decreasing its concentration.

Fig. 3 represents gas temperature in axial direction with respect to time. Gas is introduced in the system at 390 ºC. It is observed that the gas temperature is more near the entry but less near the exit. This is due to loss of heat from the gas as it flows along the length of the converter to the catalyst surface initially at a much lower temperature (45 ºC). At time 6.00 the temperatures are 372.26, 348.51, 327.46 and 314.89 ºC at axial distances 0.20, 0.50, 0.80 and 1.00, respectively. As time increases the catalyst gets heated up and after catalytic reactions start a stage is reached where heat is transferred from heated solid to the gas. Hence the gas temperature starts rising all through the converter length. At time 10.30 the gas temperatures are 395.34, 397.39, 394.02 and 390.61 at axial distances 0.20, 0.50, 0.80 and 1.00, respectively.

Fig. 4 represents the solid temperature in axial direction with respect to time. Initially the solid is at 45 ºC as time increases the solid temperature increases, initially due to heat supplied by the gas and later on due to onset of catalytic reactions. It is observed that at lower values of time although the temperature of entire converter increases but not much temperature variation is observed in the axial direction. As more time passes solid temperature rises further and a difference in its inlet and exit values along the converter length is observed. At time 4.00 the solid temperatures at axial distances 0.00, 0.30 and 1.00 are 177.87, 174.16 and 161.45 ºC, respectively. Whereas at time 10.00, the solid temperatures at axial distances 0.00, 0.30 and 1.00 are 414.68, 394.08 and 351.10 ºC, respectively. In this case the solid temperatures becoming higher than that of the inlet gas indicate the presence of catalytic reactions in the converter.

Fig. 5 represents the solid and gas temperature in axial direction with respect to time. The comparison is shown in axial direction for timings 4.00, 8.00, 9.00 and 10.30. Already their effects have been discussed in Figs. 3 and 4, respectively. Also from Fig. 5 it is observed that at later values of time the solid temperature at the entrance is higher than the gas temperature due to catalytic reactions taking place on solid surface. However towards the exit gas temperature is higher than the solid temperature, which is a favourable condition due to gas taking away excess heat from the solid surface and thereby preventing the sintering of solid.

Nomenclature

a	Catalytic surface area per unit reactor volume (cm^{2} cm^{-3})
b/a	Ratio of stoichometric coefficients for oxygen and propylene.
C	Concentration of the propylene (g mol cm^{-3})
C_p	Specific heat (cal g^{-1} K^{-1})
d	Hydraulic diameter (cm)
E_{cat}	Activation energy for the catalytic reaction (cal gmol^{-1})
h	Heat transfer coefficient (cal cm^{-2} s^{-1} K^{-1})
$-\Delta H$	Heat of reaction (cal g mol^{-1})
k_g	Mass transfer coefficient (cm s^{-1})
k_{cat}	Rate constant for catalytic reaction (cm s^{-1})
L	Length of monolith (cm)
M	Ratio of incoming oxygen and propylene.
R	Gas constant (cal g mol^{-1} K^{-1})
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})

Superscript:

o	Initial conditions
'	Dimensionless quantities

Subscript:

s	Solid
g	Gas

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