



MODELING THE EFFECT OF TEMPERATURE ON VOLATILE ORGANIC COMPOUND (VOC) CONVERSION IN A MONOLITHIC CONVERTER

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Abstract

The catalytic converter has been widely used all over the world to enhance air quality. Monolithic catalytic converters are used to convert the harmful pollutants like VOCs into less harmful pollutants. These monolithic converters are very active and efficient in the reduction of air pollution when they are warmed up. To warm up the catalyst, it requires some time and during that time period a significant amount of air pollutants, particularly VOCs, are released into the atmosphere. A one-dimensional model for the VOC ethane was developed using mass and heat transfer between the catalyst surface, catalytic reactions and exhaust gas. A set of a partial differential equation (PDEs) is formed which are solved by backward difference and implicit scheme. The effect of variation in the initial catalyst temperatures and the gas temperature on ethane conversion was investigated.

1. Introduction

Motor vehicles are a significant source of urban air pollution [1]. Catalysts used in catalytic combustion reactions are usually noble metals or transition metal oxides that are supported on a substrate [2]. Platinum-based catalysts are highly active for oxidative removal of small amounts of hydrocarbon from gaseous or liquid streams [3]. Catalytic converters are being extensively used to reduce such emissions from the vehicular exhaust. catalytic reactions are found to be more suitable in combustion for low concentration of HCs [4, 8].

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At the start of the operation, the cold converter is exposed to polluting gas entering at elevated temperatures and it gets gradually heated by the incoming hot gas [5]. With passage of time the converter is heated to its operating temperature and thereafter the catalytic reaction begins. The heat released due to highly exothermic catalytic reaction causes the reaction rate to increase thereby causing a decrease in the concentration of the polluting gas.

During this warm-up period of the catalyst, about 60 to 80% of the emissions are released untreated to the atmosphere [6]. The untreated VOCs form a major part of these emissions. VOCs are very harmful to the environment and living organism. They are major contributor to formation of ozone and photochemical smog [7]. Hence, in order to further reduce emissions, the time needed for the catalyst to reach the operating temperature needs to be reduced [9]. A one-dimensional model is used to simulate the thermal and conversion characteristics of the converter operating under warm-up conditions. In order to initiate the combustion reaction at a lower temperature as compared to gas phase reactions, platinum is used as the catalyst.

2. Rate Kinetics

The reaction of ethane oxidation to form a less harmful gas carbon dioxide is being considered:



The presence of catalyst helps in lowering the activation energy of the reaction and makes it proceed at a lower temperature. Rate expression for catalytic reaction is given as:

$$(-r)_{\text{ethane}} = k P_{\text{C}_2\text{H}_6}^\alpha P_{\text{O}_2}^\beta [10]$$

here $k = k_0 e^{-E/RT}$.

Values used are:

$$k = 6.457 \cdot 10^{13} \text{ mol/cm}^2 \cdot \text{h.KPa}^{\cdot 5}; (-\Delta H) = -372.78 \text{ cal/gmole}; \alpha = 1.1, \beta = -0.6.$$

3. Assumptions for the one-dimensional Model

Some major assumptions made during modeling include [11, 12]:

- axial diffusion of mass and heat transfer in the gas phase is negligible.
- Diffusion in washcoat is neglected as washcoat is assumed to be very thin.
- The concentration of noble metal catalyst was kept constant and the solid catalyst does not deactivate.
- Monolith is cylindrical with circular cross-section channels
- Gas-phase concentration, gas temperature, gas velocity, and the solid temperature are uniform across the monolith cross-section at any axial position.
- The heat released due to the catalytic reactions inside the wash coat was totally transported to the gas phase by convective heat transfer.
- Heat transfer due to the radiation inside the channels and heat exchange between the substrate and the surroundings at both inlet and an outlet face of the monolith is ignored.
- Non-uniform flow distribution inside the catalytic converter is neglected because the entire monolith is represented as one single channel.

4. Mass and Energy balance equations for catalytic reactions

Table 1. Mass and energy balance equations for catalytic reactions.

Mass and energy balance	Modeling equations
Mass balance in the gas phase	$v\left(\frac{\partial C_g}{\partial x}\right) + Sk_g(C_g - C_s) = \left(\frac{\partial C_s}{\partial t}\right)$
Mass balance in solid phase	$((-r)_{VOG})a = Sk_g(C_g - C_s)$
Energy balance in gas phase	$-Cp_g v\rho_g\left(\frac{\partial T_g}{\partial x}\right) - Sh(T_g - T_s) = \rho_g Cp_g\left(\frac{\partial T_s}{\partial t}\right)$
Energy balance in solid phase	$Cp_s\rho_s\left(\frac{\partial T_s}{\partial t}\right) = (-\Delta H)s(-r)_{VOG} + Sh(T_g - T_s) + \lambda_s\left(\frac{\partial^2 T_s}{\partial x^2}\right)$
Dimensionless Equations	
Dimensionless mass balance equation	$\left(\frac{\partial C'}{\partial z}\right) = -\left(\frac{\partial C'}{\partial t'}\right)\delta_1 - \{(-r_{c2H6})\}\psi_1$
Dimensionless energy balance equation for gas phase	$\left(\frac{\partial T'_g}{\partial z}\right) = -(T'_g - T'_s)\delta_{22} - \left(\frac{\partial T'_g}{\partial t'}\right)\delta_2$
Dimensionless energy balance equation for solid phase	$\left(\frac{\partial^2 T'_s}{\partial z^2}\right) = -\{(-r_{VOG})\}\psi_2 + (T'_s - T'_g)\alpha_1 + \left(\frac{\partial T'_s}{\partial t'}\right)\delta_3$
<p>$\psi_1, \delta_1, \psi_2, \alpha_1, \delta_3, \delta_{22}$ and δ_2 are dimensionless number and their values are given by:</p> $\delta_1 = \frac{L}{vt_0}; \psi_1 = \frac{aLK_0(C_{g0})^{-0.5}(RT)^{0.5}}{v}; \psi_2 = \frac{a(-\Delta H)k_0(C_{g0}^{0.5})(RT)^{0.5}L^2}{\lambda_s T_{g0}}; \alpha_1 = \frac{ShL^2}{\lambda_s};$ $\delta_3 = \frac{L^2 Cp_s \rho_s}{\lambda_s t_0}; \delta_{22} = \frac{SLh}{Cp_g v \rho_g}; \delta_2 = \frac{L}{vt_0}.$	

5. Initial and Boundary Conditions

Initially, the converter is at ambient temperature and is suddenly exposed to hot incoming gas from the engine.

Entering ethane concentration at all times $C_g(0, t) = C_g^0$

Entering gas temperature at all times $T_g(0, t) = T_g$

Solid catalyst temperature at the start $T_s(x, 0) = T_s^0$

At the converter entrance: $x = 0, \frac{\partial T_s}{\partial x} = 0$

At the converter exit: $x = L, \frac{\partial T_s}{\partial x} = 0; \frac{\partial C_g}{\partial x} = 0; \frac{\partial T_g}{\partial x} = 0$

Dimensionless initial conditions and boundary conditions

The dimensionless gas concentration of ethane at entry at all times:
 $C'(0, t') = 1.0$

The dimensionless gas temperature at entry at all times: $T'_g(0, t') = \frac{T_g}{T_g^0}$

The dimensionless solid temperature at the start: $T'_s(0, t') = \frac{T_s}{T_s^0}$

Also At $z = 0, \frac{\partial T'_s}{\partial z} = 0; At z = 1, \frac{\partial T'_s}{\partial z} = 0; At z = 1, \frac{\partial c'}{\partial z} = 0; At z = 1, \frac{\partial T'_g}{\partial z} = 0.$

Dimensionless equations are coupled pdes which are solved using implicit schemes using backward and centred difference formula with the help of Matlab [13].

6. Results and Discussion

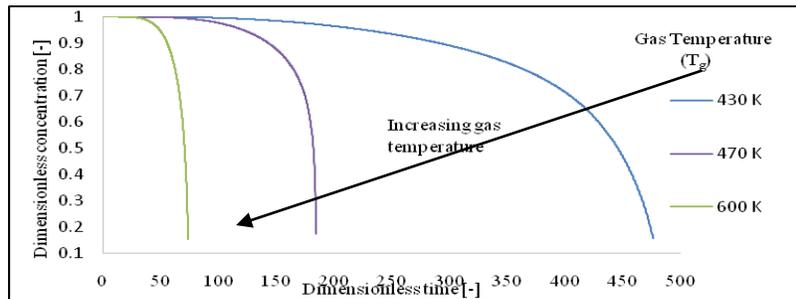


Figure 1. Exit concentration variation of ethane with time for different values of inlet gas temperatures over a solid catalyst initially at 298K.

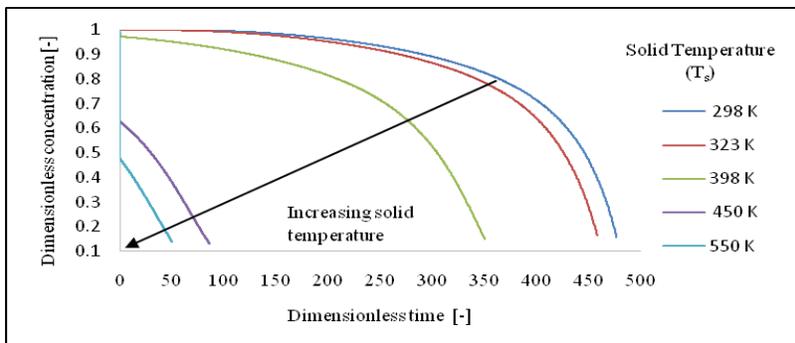


Figure 2. Exit Concentration variation of ethane at 430K with time for different preheated Solid Catalyst Temperatures.

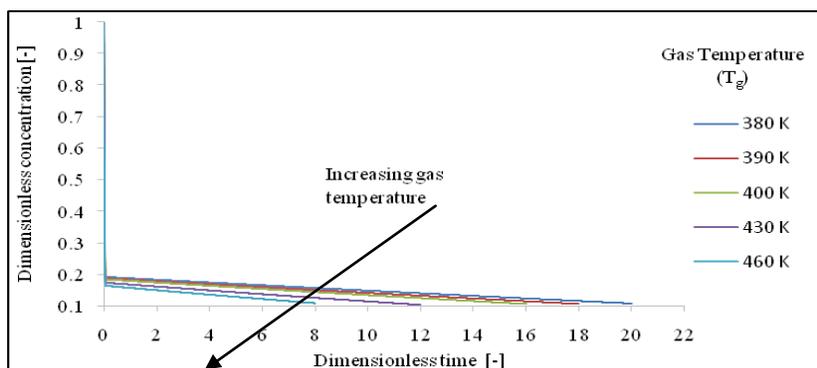


Figure 3. Exit concentration variation of ethane in a preheated Converter at 480K with time for different Inlet Gas Temperatures.

Figure 1, shows the variation of exit ethane concentration with respect to time for different inlet gas temperatures of 430K, 470K, and 600K respectively. At dimensionless time 25.00 the exit concentrations of ethane are 0.9999, 0.9998, and 0.9982 for inlet gas temperatures of 430K, 470K, and 600K respectively. With the increase of time, the effect of rise in inlet gas temperature on the conversion of ethane becomes more obvious. At dimensionless time 73.70 the concentrations of ethane are 0.9984, 0.9928, and 0.1555 for inlet gas temperatures of 430K, 470K, and 600K respectively. With rise in inlet gas temperature conversion is also increased, due to the fact that at higher gas temperatures more heat is transferred from the gas by convection to the solid surface the conversion of ethane takes shorter span of time because solid surface gets heated faster.

Figure 2, shows the effect of initial converter temperature of 298K and 323K, and preheated solids at temperatures of 398K, 450K and 550K on the conversion of ethane gas entering at 430K and 39ppm [14] concentration. The preheated solids show faster conversion of ethane as compared to solids catalyst present at the ambient temperature as shown in Figure 3. Initially at dimensionless time 10.00 the exit concentrations of ethane are 0.9999, 0.9998, 0.9689, 0.5900 and 0.4168 for preheated solid temperatures of 298K, 323K, 398K, 450K, and 550K, respectively. The results show that for a preheated solid catalyst above 398K, the catalytic reaction gets started almost immediately as the gas enters the catalytic converter. As at dimensionless time 40.00 the exit concentrations are 0.4418 and 0.2082 for preheated solid temperatures of 450K and 550K respectively. Though, with preheated solids at lower temperature of 398K, dimensionless time 342.00 is required for the ethane exit concentration to reach values of 0.2180 respectively. Therefore, higher initial solid temperatures show a notable effect on the conversion of ethane.

Figure 3, shows the exit concentration of ethane gas at different inlet gas temperatures of 380K, 390K, 400K, 430K, and 460K over an initially preheated solid catalyst at 480K. It is observed that because of high temperature of the solid catalyst at 480K, the conversion of ethane gas is exceeding fast. From the start to dimensionless time 0.10 the ethane concentration is not seen to be much dependent on the incoming heated gas temperature and values are 0.1914, 0.1875, 0.1837 and 0.1635 for different inlet gas temperatures of 380K, 390K, 400K, 430K and 460K respectively. However, beyond the dimensionless time 0.10, the variation in inlet gas temperatures is seen to have a noteworthy effect on the ethane conversion. For inlet gas temperatures of 380K, 390K, 400K, 430K and 460K the dimensionless times taken for the concentration of ethane to become 0.1077, 0.1062, 0.1062, 0.1033 and 0.1088 are 20.00, 18.00, 16.00, 12.00 and 8.00 respectively. Due to higher initial solid temperature of 480K, the ethane conversion is extremely fast and an increase in the temperature of the inlet gas further increases the conversion.

7. Conclusion

At ambient conditions, the ethane oxidation is not considerable during the warm up period of the catalytic converter. Some time is required to

preheat the catalytic converter to reach it to operating temperature due to low initial temperature. In order to get a faster conversion of the VOC ethane, the warm up period can be reduced by either initially preheating the catalytic converter or by introducing gas at higher temperature. The catalytic reactions start much earlier for preheated converter as compared to the catalytic converter is at ambient temperatures which converts ethane much faster. Also, when the temperature of incoming gas is increased, the conversion of ethane is extremely fast. So, these results show the intense effect of solid preheating and higher inlet gas temperature in decreasing the warm up period.

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