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MODELING AND SIMULATION OF CATALYTIC CONVERTERS FOR OXIDATION OF HYDROCARBON POLLUTANT ETHYLENE

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ABSTRACT

Environmental degradation due to release of pollution from both industrial and transport sector is a major concern presently. This has led to adverse effects of not only human life but also for plants and vegetables as polluting gases like unburnt hydrocarbons, carbon monoxide and oxides of nitrogen release from the transport sector have increased immensely over the past few years, thereby, bringing faster degradation of the atmosphere. In this paper, one dimensional modeling for reduction of hydrocarbon ethylene from vehicular exhaust was carried out using metal oxide catalyst. Modeling equations for mass and energy balance for the gas and solid phase formed in an adiabatic monolith operating under warm-up conditions. The response of the catalytic converter during this warm-up period in the converter was analyzed.

Keywords: Backward Implicit Scheme, Catalytic Converter, Ethylene, One-Dimensional, Modeling, Warm Up Period

I. INTRODUCTION

Increasing air pollution is posing to be a major problem for the environment. Among the pollutants, petroleum hydrocarbons gain importance due to their high toxicity and carcinogenicity. The origin of petroleum hydrocarbons in the air is due to combustion of natural gas, coals, fuels oil, forest and exhausted gas from vehicles. The hydrocarbons are released into atmosphere as burned/changed and not burned/unchanged forms [1].

Air pollution has remained a foremost health concern in India. In the past decades, several studies highlighted, the important contribution of ambient air pollution to excess morbidity and mortality [2,3]. In particular, exposure to particulate air pollution has been found to be associated with increase in hospital admissions for cardiovascular and respiratory disease and mortality in many countries [4,5] including India [6,7,8]. Epidemiologic studies also showed a close link between air pollution and asthma and diseases due to allergies [9].

Health impact of air pollution depends on the pollutant type, its concentration in the air, length of exposure, other pollutants in the air, and individual susceptibility. Poor and starving people, young and old, and people with pre-existing respiratory diseases and other ill health are more at risk [10].

The main sources of air pollution are the flue gases, emission from refineries, factories exhaust emissions from vehicles [11].

Emission from vehicles particularly automobiles is responsible for about two third of air pollution in the urban area. The major pollution contaminants emitted by motor vehicles including carbon monoxide (CO), oxides of nitrogen (NOx), sulfur oxides, (SO), hydrocarbons (HC), lead (Pb) and suspended particulate matter, have harmful effects on both human health and ecology. The internal combustion engines require a mixture of air and fuel to burn and generate energy to propel the vehicle. These burnt gases which come out from the exhaust are responsible for pollution. In petrol engines, the gases comprise a mixture of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons. If these gases are in excess quantities, vehicular pollution is instigated. Emissions from diesel vehicles comprise of CO and unburnt hydrocarbon in the diesel exhaust are rather low, both of which are compensated by high concentration of CO_2 and NOx, there are smoke particles and oxygenated hydrocarbon, including aldehydes and odor-producing compounds [11].

Ethylene is a ubiquitous industrial gas that is produced and used in very large quantities in the United State and elsewhere. Ethylene is also emitted by a wide variety of biogenic and anthropogenic sources so the opportunity for exposure is widespread. Despite these attributes there have been few formal or informal attempts at characterizing human inhalation exposure in different subpopulations. Although a tremendous amount of information is available on airborne concentrations under a variety of conditions, the data has not been compiled or assembled in a manner that allows a systematic examination of the overall burden from inhalation [12].

Normally, as the gas concentration increases, so does the degree of damage. Ethylene can originate from several sources. Living sources include plant constituents (vegetative and reproductive tissue and fruit) that are ripening or decomposing. The most important nonliving sources of ethylene include: improperly adjusted or uncleansed greenhouse heating units, leaky gas lines, and exhausts from combustion engines [13].

Modeling is a good way of analyzing the physico-chemical processes while considering the initial warm-up period of an automobile from cold start [14]. In this paper catalytic combustion of ethylene is studied. Using a one-dimensional unsteady state model mass and energy balance equations for the gas and the solid phase are formed. These equations are solved using Backward Implicit Scheme Method.

II. REACTION KINETICS

The catalytic oxidation of ethylene is taking place by the reaction:

$$C_2H_4 + O_2 \rightarrow 2CO_2 + 2H_2O \quad \ldots . \Delta H = -1.411\times 10^6 J/mol \quad (1)$$

The rate expression for the reaction is given by [15]:

$$-r_{C2H4} = k_0 \exp(E_a/RT)\, C_{C2H4} \quad (2)$$

Here, the surface reaction is assumed to be irreversible, first order with respect to ethylene and zero order with respect to oxygen, as oxygen present in excess.

Parameter values [15] for PdO catalyst are:

Pre exponential factor, k_0 = 19,000 cm/s

Activation energy , E_a = 48,200 J/mol

The rate expression is used in the one-dimensional model to account for the conversion taking place due to the catalytic reaction.

III. ONE-DIMENSIONAL MODELING

The converter is operating under warm-up conditions and the processes taken into account include gas-solid heat and mass transfer, axial heat conduction in the catalyst and the chemical reaction in presence of a catalyst.
Some major assumptions made during modeling include catalytic concentration is kept constant, catalyst does not deactivate, monolithic is cylindrical and a single circular cross-section channel is considered, diffusion in wash coat is neglected, as wash coat is assumed to be very thin, monolith is assumed to be adiabatic and heat exchange between the substrate and the surroundings at both inlet and outlet faces of monolithic are neglected as there is lagging present at the inlet and the outlet faces of the monolith.

3.1 Modeling Equations

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 while solving mass and energy balance equations.

3.2 Mass balance equation:

Net convective transport of gas in the axial direction (x) + reaction term = accumulation

$$v\left(\frac{\partial C}{\partial x}\right) + a(-r_{C2H4}) = \left(\frac{\partial C}{\partial t}\right) \qquad (3)$$

3.3 Energy balance equation for gas phase

Net convective transport of gas in the axial direction – Heat transfer from the gas to solid wall = Net accumulation of heat in the gas phase

$$-v\rho_g C_{pg}\left(\frac{\partial T_g}{\partial x}\right) - hS\,(T_g - T_s) = \rho_g C_{pg}\left(\frac{\partial T_g}{\partial x}\right) \qquad (4)$$

3.4 Energy balance equation for solid phase:

Heat conduction in the wall in the axial direction + Heat transfer from gas to wall + Heat released due to chemical reaction = Net accumulation of heat in the solid wall

$$\lambda_s\left(\frac{\partial^2 T_s}{\partial T^2}\right) + hS\,(T_g - T_s) + a(-\Delta H)(-r_{C2H4}) = \rho_s C_{ps}\left(\frac{\partial T_s}{\partial t}\right) \qquad (5)$$

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3.5 Initial and boundary conditions

Initially the converter is at room temperature and is suddenly exposed to incoming hot gases from the engine.

C_2H_4 concentration at the entrance for all times

$$C_g(0,t) = C_g^0 \qquad (6)$$

Gas temperature at the entrance at all times

$$T_g(0,t) = T_g^0 \qquad (7)$$

Solid temperature initially along the converter length

$$T_s(x,0) = T_s^0 \qquad (8)$$

At the converter entrance:

$$x = 0 \ , \frac{\partial T_s}{\partial t} = 0 \qquad (9)$$

At the converter exit:

$$x = L \ , \quad \frac{\partial T_s}{\partial x} = 0 \qquad (10)$$

$$x = L \ , \quad \frac{\partial C_g}{\partial x} = 0 \qquad (11)$$

$$x = L \ , \quad \frac{\partial T_g}{\partial x} = 0 \qquad (12)$$

Making above equations dimensionless using the following expressions:

$$C' = \frac{C_g}{C_g^0} \ , \quad T'_g = \frac{T_g}{T_g^0} \ , \quad T'_s = \frac{T_s}{T_s^0} \ , \quad z = \frac{x}{L} \ , \quad t' = \frac{t}{t_0} \qquad (13)$$

IV. DIMENSIONLESS EQUATIONS

4.1 Dimensionless mass balance equation

Mass balance equation (3) reduces to

$$\left(\frac{\partial C'}{\partial z}\right) = -\delta_1 \left(\frac{\partial C'}{\partial t'}\right) - \psi_1 C' \exp\left(-\frac{E_s}{RT_s}\right) \qquad (14)$$

Here δ_1 and ψ_1 are dimensionless numbers and their values are determined using following expressions:

$$\delta_1 = \frac{L}{vt_0} \qquad (15)$$

$$\psi_1 = \frac{La k_0}{v} \qquad (16)$$

4.2 Dimensionless Energy Balance equation for gas phase

Energy balance equation (4) for gas phase reduces to

$$\frac{\partial T'_g}{\partial z} = -\delta_2 \frac{\partial T'_g}{\partial t'} - \delta_{22}(T'_g - T'_s) \quad (17)$$

Here δ_2 and δ_{22} are dimensionless numbers and are given by following expressions:

$$\delta_2 = \frac{L}{vt_0} \quad (18)$$

$$\delta_{22} = \frac{hSL}{vp_g C_{pg}} \quad (19)$$

3.2.3 Dimensionless Energy balance equation for solid phase:

Energy balance equation (5) for solid phase reduces to

$$\frac{\partial^2 T'_s}{\partial z^2} = -\delta_3 \frac{\partial T'_s}{\partial t'} - \psi_2 C' \exp\left(-\frac{E_a}{RT_s}\right) + \alpha_1(T'_s - T'_g) \quad (20)$$

Here δ_3, ψ_2 and α_1 are dimensionless numbers and they are given by following expressions

$$\delta_3 = \frac{(\rho_s C_{ps}) L^2}{\lambda_s t_0} \quad (21)$$

$$\psi_2 = \frac{C_g^0 aL^2 (-\Delta H) k_0}{(\lambda_s T_g^0)} \quad (22)$$

$$\alpha_1 = \frac{ShL^2}{\lambda_s} \quad (23)$$

4.3 Dimensionless initial and boundary conditions

$$C'(0, t') = 1.0 \quad (24)$$

$$T'_g(0, t') = \frac{T_g}{T_g^0} \quad (25)$$

$$T'_s(z, 0) = \frac{T_s}{T_g^0} \quad (26)$$

$$\text{At, } z = 0, \frac{\partial T'_s}{\partial z} = 0 \quad (27)$$

$$z = 1.0, \frac{\partial T'_s}{\partial z} = 0 \quad (28)$$

$$z = 1.0, \frac{\partial C'}{\partial z} = 0 \quad (29)$$

$$z = 1.0, \frac{\partial T'_g}{\partial z} = 0 \quad (30)$$

The coupled PDEs (14), (17) to (20) along with the initial and boundary conditions specified in Equations (24) to (30) are used for calculation of the gas concentrations, the gas temperature and the solid catalyst temperature using the Backward implicit finite difference numerical scheme [16].

V.RESULTS AND DISCUSSIONS

Exhaust gas containing 160 ppm of hydrocarbon ethylene at an inlet temperature of 280°C was introduced in a converter initially at 25°C. The hot incoming gas raises the temperature of the converter by transferring heat to it. Catalytic reaction takes place on the wall of the monolith channel. The catalytic reaction starts once the converter has attained the operating temperature. Due to this reaction a decrease in the concentration of ethylene is observed. The inlet concentration of ethylene (160 ppm) has a dimensionless value of 1.0000 and the results are obtained and analyzed for decrease in the dimensionless concentration up to 0.2000. Results obtained in Table 1 and Figure 1 show the effect of reaction temperature on conversion.

Table 1- Modeled results of effect of temperature on conversion of ethylene gas

Calculated values from modeling	
Temperature (°C)	Conversion (-)
25	0.012
147.45	0.0201
201.10	0.0971
232.62	0.1972
295.36	0.4939
337.62	0.6905
369.59	0.8064
413.34	0.916
450.3	0..9695
470.68	0.9857

Table 1 represents the conversion of ethylene gas with respect to the average solid catalyst temperature. During the initial period as seen from the graph almost no conversion of gas occurred till solid catalyst attained its operational temperature of 159.86°C. Once the solid reaches to its operational temperature the exothermic catalytic reactions get initiated and due to heat released by these reactions the rate of reaction increases. 50% conversion is obtained at approximately 295.36°C and for almost 70% conversion of solid temperature of about 337.62°C is required

Table 2 Experimental results of effect of temperature on conversion of ethylene gas [17]

Experimental Values	
Temperature (°C)	Conversion (-)
116.00	0.0
223. 00	0.1
251. 00	0.2
270.00	0.3
286.00	0.4
301.00	0.5
315.00	0.6
329.00	0.7
347.00	0.8
366.00	0.9

Table 2 represents the experimentally determined conversion of ethylene gas with respect to the average solid catalyst temperature [17]. During the initial period as seen from the graph almost no conversion of gas occurred till solid catalyst attained its operational temperature of 224°C. Once the solid reaches to its operational temperature the exothermic catalytic reactions get initiated and due to heat released by these reactions the rate of reaction increases. 50% conversion is obtained at approximately 301°C and for almost 70% conversion of solid temperature of about 329°C is required.

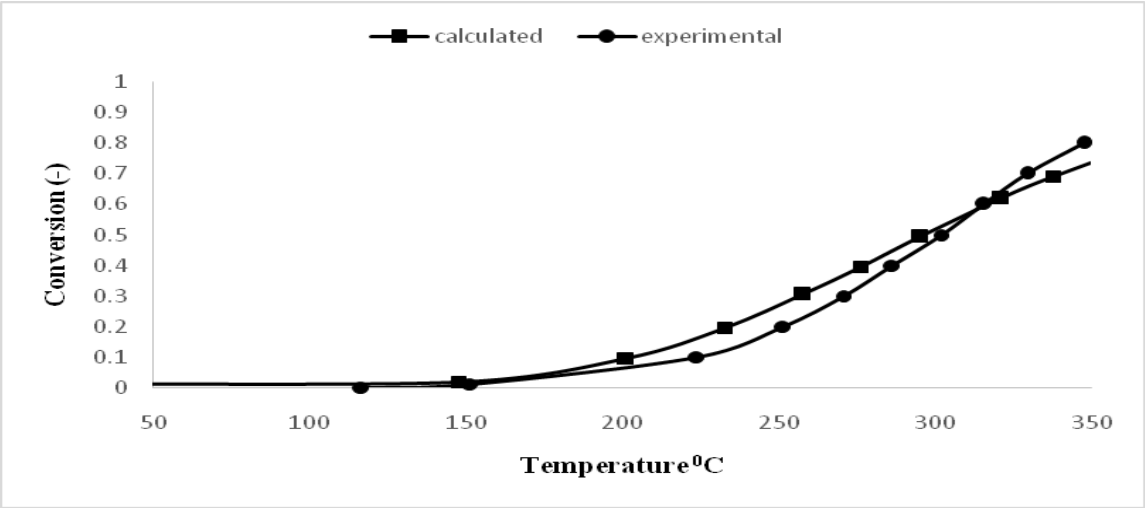

Figure 1- Comparison of reaction temperature on conversion of ethylene gas modeled and experimental

Figure 1 represents the comparison of the reaction temperature on conversion of ethylene gas calculated and experimental. Ethylene gas is introduced into the catalytic converter, coated with a particular catalyst, i.e. PdO, and study the behavior of conversion with respect to increased temperature. This study was carried by designing model equation of mass transfer, energy transfer for both solid and gas phases. The results so obtained were compared with experimental values taken from a research paper [17] forcomplete oxidation of ethylene. When these two were compared on a single graph 50% conversion is obtained at about295.36°C and 301°C for modeled and experimental values respectively and the results shown by them are in agreement.

VI. CONCLUSIONS

Modeling and simulation was carried out for hydrocarbon ethylene's oxidation in a monolithic converter assembly to bring about its reduction to less harmful pollutants CO_2 and H_2O by using PdO catalyst. A one-dimensional model was formed taking into account the heat and mass transfer effects and chemical reaction in a channel of the monolith converter. This study helps to analyzing the behavior of the converter during the warm up period by analyzing the change in both gas concentration and solid temperature with respect to time. The modeled results are found to be in agreement with the experimental ones existing in literature.

Nomenclature

A : catalytic surface area per unit reactor volume, cm^2/cm^3
C_g : concentration of ethylene in bulk gas phase, $gmol/cm^3$
C_g^0 : concentration of ethylene in inlet gas phase, $gmol/cm^3$
C_s : concentration of ethylene in solid phase, $gmol/cm^3$
C_{pg} : specific heat of gas, cal/gm°C
C_{ps} : specific heat of solid, cal/gm°C
E : activation energy for catalytic reaction, cal/gmol
h : heat transfer coefficient, $cal/cm^2s°C$
$-\Delta H$: heat of reaction, cal/gmol
k_0 : pre-exponential factor for catalytic reaction, cm/s
L : length of monolith, cm
R : gas constant, cal/gmol°C
S : geometric surface area per unit reactor volume, cm^2/cm^3
T_g : gas temperature, °C
T_g^0 : inlet gas temperature, °C
T_s : solid temperature, °C
T_s^0 : inlet solid temperature, °C
t : time, s
v : gas velocity, cm/s
x : axial coordinates, cm
r_{C2H4} : rate of reaction, $gmol/cm^2$ s

Greek Symbols

ρ : density, g/cm^3

λ : thermal conductivity, cal/cm s °C

Dimensionless

C′ : dimensionless concentration

T'_g : dimensionless gas temperature

T'_s : dimensionless solid temperature

z : dimensionless axial coordinates

t′ : dimensionless time

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