A FINITE ELEMENT STUDY OF THREE- WAY CATALYTIC CONVERTER FOR NO_X ABATEMENT UNDER TRANSIENT ISOTHERMAL CONDITION

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ABSTRACT

The simulation of catalytic converter system is necessary to characterise the catalyst and to optimise the design of a monolithic reactor for NO_x abatement. The objective of this study is to obtain a quantitative description of NO_x abatement in three-way catalytic converter system of natural gas powered automobile exhaust gas. This work presents a finite element calculation to predict and to evaluate the NO_x abatement in three way catalytic converter. A numerical simulation is carried out using a commercial Finite Element Method (FEM) code, FEMLAB. In this work simulation is done on transient isothermal operation of catalytic converter at temperature of 750 K. The results have shown that the maximum reduction of 99% of NO_x can be achieved using a monolithic reactor with channel dimensions of 1mm radius and 0.4 m length. Specifically, results obtained from the computer modelling exercise have demonstrated that finite element method is capable of modelling the NO_x abatement in TWCC.

***Key words**: Three-Way Catalytic Converter, FEMLAB, NO_x, Kinetics, Monolithic Reactor*

INTRODUCTION

The Environment Protection Agency (EPA) has been regulating nitrogen oxides from automobile sources since 1990. More stringent environmental regulations have resulted in considerable research into ways of reducing harmful manmade exhaust emissions. The ongoing research is leading to innovative applications of new technologies to resolve these environmental issues.

The importance of monolithic reactors has grown rapidly in the last two decades. They serve mainly as tools for environmental protection. The most well known example of a monolithic reactor is the three-way catalytic converter for automobiles. This reactor simultaneously transforms unburned hydrocarbons, carbon monoxide, and nitrogen oxides from the exhaust gases into carbon dioxide, nitrogen, and water.

A monolithic reactor consists of thin parallel straight channels of arbitrary shape, through which the gas, containing the reactants, flows. The walls of the channels are coated with a porous ceramic containing the catalyst layer (Fig. 1). The transition from reactants to products involves transport of the reactants by convective flow in the channels and molecular diffusion towards the channel walls. Simultaneous diffusion and reaction occur inside the porous wash coat whereby the products diffuse back into the gas and are transported out of the reactor. There are obviously a large number of variables in optimizing the reactor performance. Some of the parameters that are important for the general behaviour of the reactor are temperature, channel geometry, flow rate, properties of the wash coat and catalytic activity. The detailed view of monolithic reactor is shown in Figures 1 and 2.

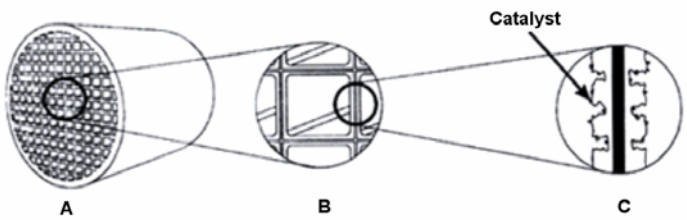


Fig. 1: A) Monolithic reactor, B) Channel wall, C) Porous ceramic (washcoat) with catalyst [1]

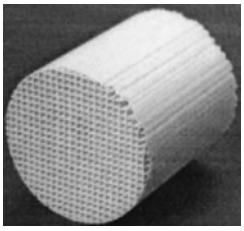


Fig. 2: Monolithic Reactor [2]

AIR QUALITY REGULATION FOR AUTOMOBILE

Table 1 shows the current automobile emissions standard in European countries. It shows that the environmental regulations for NO_x emission are become more stringent. Table 2 shows the comparison of the exhaust emission of different fuels used in passenger cars. It shows that the natural gas powered engine produced the cleanest exhaust gas compared to the diesel and gasoline powered automobiles. However NO_x is the major pollutant in exhaust gases of natural gas powered automobiles. In order to meet future stringent regulation, simulation of catalytic converter is necessary to characterize the catalyst and to optimise the design of monolithic reactor for NO_x abatement.

Table 1: European Union Emission Standards for passenger cars [3]

Standard	Year	HC + NO_x (g/km)	NO_x (g/km)	CO (g/km)	PM (g/km)
Euro I (91/441/EEC)	1992	0.97	-	2.72	-
Euro II (94/12/EC)	1996	0.5	-	2.2	-
Euro II (DI)	1999	0.90	-	1.00	0.10
Euro III	2000	0.56	0.50	0.64	0.05
Euro IV	2005	0.30	0.25	0.50	0.025

Table 2: Exhaust emissions of different engine fuels

	Natural gas*	Diesel ‡	4-stroke spark ignited ‡	4-stroke lean-burn spark ignited ‡	2-stroke spark ignited ‡
NO_x (ppm)	25 – 160	350 - 1000	100 – 4000	1200	100 – 200
SO_x (ppm)	Neg. (0.5 – 20)	10 – 100	15 – 60	20	20
CO_2 (%)	9 (5 – 12)	7	10 – 13.5	11	10 – 13
O_2 (%)	3 – 18	10 – 15	0.2 – 2	4 – 12	0.2 – 2
H_2O (%)	15 (8 – 19)	1.4 – 7	10 – 12	12	10 – 12
HC (ppm)		50 – 330	500 – 5000	1300	20000-30000
CO (ppm)		300 – 1200	0.1 – 6	1300	1 – 3
PM (mg/m^3)		65			

* Ref. [4]
‡ Ref. [5]

THREE-WAY CATALYST (TWC)

The TWC appears to be the most promising solution for NO_x reduction for gasoline direct injected lean-burn engines [6]. TWC involves three steps, which are adsorption (trapping), oxidation and reduction. An alkaline metal oxide trap adsorbs the NO_x in the exhaust gas [7] before further oxidation-reduction reactions occur. The reaction steps of NO abatement shown in Table 4 and * is an alkaline metal oxide trap in TWC.

The rate coefficient of adsorption of species *i* is given by molecular collision theory [8]:

$$k_{a,i} = \sqrt{\frac{RT}{2\pi M_i}} \frac{S_i^o}{L_t} \qquad (1)$$

The rate coefficient of desorption and of a surface reaction is expressed as an Arrhenius type:

$$k_i = A_i e^{-E_{act,i}/RT} \qquad (2)$$

Table 4: Reaction steps considered in the kinetic model

(1)	$NO + * \underset{k_a}{\overset{k_d}{\leftrightarrows}} NO*$
(2)	$NO* + * \overset{k_{diss}}{\rightarrow} N* + O*$

(3)	$NO^* + N^* \xrightarrow{k_{N2,1}} N_2 + O^* + *$	
(4)	$2N^* \xrightarrow{k_{N2,2}} N_2 + 2^*$	

Table 5: Rate expressions and rate parameters for TWC [8]

Rate expression	A_i *or* S_i (s^{-1} or -)	$E_{act,i}$ (kJ/mol)
$r_{a,NO} = k_{a,NO} C_{NO} L_t \theta_v$	0.5	-
$r_{d,NO} = k_{d,NO} L_t \theta_{NO}$	5×10^{13}	108.7
$r_{diss} = k_{diss} \theta_{NO} \theta_v$	3×10^{10}	79.4
$r_{N_{2,1}} = k_{N_{2,1}} \theta_{NO} \theta_N$	2×10^{9}	87.8
$r_{N_{2,2}} = k_{N_{2,2}} \theta_N^2$	3×10^{10}	120

THREE DIMENSION (3D) SIMULATION ON THREE-WAY CATALYTIC CONVERTER (TWCC)

A commercial finite element software, FEMLAB, used in this study is a flexible tool for solving arbitrary systems of partial differential equations (PDEs). It can be used for the transient two- and three-dimensional simulation of catalytic converter system. The simulation is based on the coupling convective flow in the channels and molecular diffusion towards the channel walls. In this study, FEMLAB is used to simulate the catalytic abatement of a NO_x, a contaminant in a waste gas.

The structure consists of hundreds of repetitive unit cells and Figure 4 shows four of these cells. This structure consists of cylindrical channels, allowing free stream flow, within a porous catalyst structure. Transport by diffusion and convection takes place in the channels while diffusion and chemical reactions take place in the porous structure. Due to symmetry, the model domain is reduced to a long prism cutting through a channel and the porous catalyst.

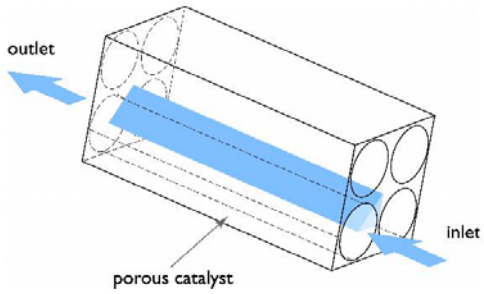


Fig. 4: Monolithic reactor channel

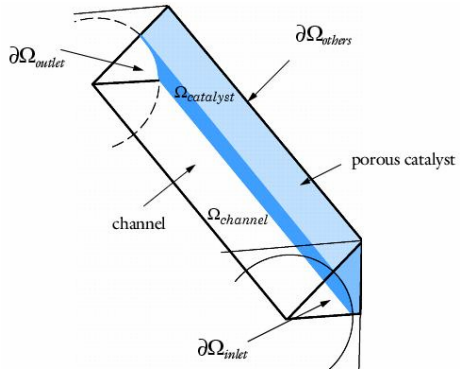


Fig. 5: Portion of analysis

The resulting domain in the model consists of two sub domains, one for the channel and one for the porous catalyst. The model requires a formulation of mass balances for the gas, both in the free gas in the channel and in the gas contained in the porous catalyst. Figure 5 shows the model portions of analysis.

THE DIFFERENTIAL EQUATIONS

The equations are scaled by introducing a new length scale in each direction. Differentiation yields:

$$\partial\, \tilde{x} = \frac{\partial x}{R}; \quad \partial\, \tilde{y} = \frac{\partial y}{R}; \quad \partial\, \tilde{z} = \frac{\partial z}{L} \qquad (3)$$

The selection of the length scales R and L determines the ratio between radius and length in the reactor. Since the concentration gradients are small in the direction of the flow, the scaling can be selected to obtain radius and length dimensions in the same order of magnitude in the scaled problem. In this case, setting R to 1 mm and L to 0.4 m gives a variation in x and y from 0 to 1.1 and 0 to 4 in the z direction. The mass balance in the cylindrical channels described by diffusion and convection is summarized by equations *(4)*:

$$\frac{\partial c}{\partial t} - \frac{D}{R^2}\frac{\partial^2 c}{\partial \tilde{x}^2} + \frac{1}{R}\frac{\partial c}{\partial x}u - \frac{D}{R^2}\frac{\partial^2 c}{\partial \tilde{y}^2} + \frac{1}{R}\frac{\partial c}{\partial \tilde{y}}v - \frac{D}{L^2}\frac{\partial^2 c}{\partial z^2} + \frac{1}{L}\frac{\partial c}{\partial \tilde{z}}w = 0 \quad in \quad \Omega_{channel} \qquad (4)$$

in the free streaming gas. The velocity vector is given analytically by

$$(u, v, w) = (0,\ 0,\ u_0(1 - \tilde{x}^2 - \tilde{y}^2)) \qquad (5)$$

In the porous structure, diffusion is the dominating transport mechanism while the catalytic reaction is described by a first order rate expression. This results in:

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D^{eff}\nabla c) = -kc \quad in\ \Omega_{catalyst} \qquad (6)$$

where k is the rate constant for the reaction, in s^{-1}, and D_{eff} is the effective diffusion coefficient in the porous catalyst in $m^2\ s^{-1}$. The specific surface area of the catalyst is included in the rate constant, k. The mass balance in the porous catalysts does not include a convective term and finally become:

$$\frac{\partial c}{\partial t} - \frac{D^{eff}}{R^2}\frac{\partial^2 c}{\partial \tilde{x}^2} - \frac{D^{eff}}{R^2}\frac{\partial^2 c}{\partial \tilde{y}^2} - \frac{D^{eff}}{R^2}\frac{\partial^2 c}{\partial z^2} + kc = 0 \quad in \quad \Omega_{catalyst} \qquad (7)$$

BOUNDARY AND INITIAL CONDITIONS

At the start of the simulation, the incoming air does not contain any toxic species but the content increases from 0 to c_0 in 10 seconds. This sudden increase is expressed by the boundary condition below:

$$c = c_o(1 - e^{(-0.5t)}) \quad at\ \partial\Omega_{inlet} \qquad (8)$$

The inlet concentration, c_0, is taken from Ramachandran *et al.* [4] study on the exhaust emission of natural gas engine which is equal to 0.0202 mol/m^3. The concentration of pollutants in the incoming gas stream increases according to the Figure 6. This expression gives a violent increase in concentration but the rate of increase is bounded, that is, the concentration has a continuous first derivative with respect to time. The boundary condition at the outlet is somewhat more difficult to obtain. But it is known that the convective flow is probably very large in the axial direction of the channel and that the transport by diffusion is probably negligible in the free streaming gas in this direction. It is therefore reasonable to assume that the transport by diffusion perpendicular to the outlet surface is negligible.

This results in the following boundary condition:

$$\tilde{N} \cdot n = cu \cdot n \quad at \quad \partial\Omega_{outlet} \qquad (9)$$

An insulating condition was assumed at all other boundaries and the flux vector defined as:

$$\tilde{N} \cdot n = 0 \quad at \quad \partial\Omega_{other} \qquad (10)$$

Furthermore, the concentration is 0 at $t = 0$, which gives the initial condition:

$$c = 0 \quad in \quad \Omega \quad at \quad t = 0 \qquad (11)$$

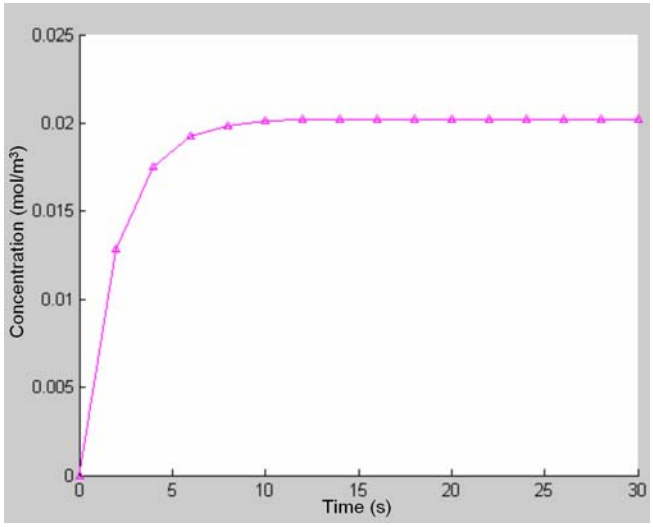


Fig. 6: Pollutants at monolith inlet

NUMERICAL IMPLEMENTATION

Simulation is done by defining the relevant physical quantities, and FEMLAB will internally compiles a set of PDEs representing the problem. Mesh was produced using FEMLAB itself and for the monolith channel the default mesh in FEMLAB with the mesh growth rate 1.4 and mesh curvature factor 0.4 is used (Fig. 7). The total of 6643 mesh elements with 1629 number of nodes and 2543 edges was used to yield a reasonable prediction. The modeling was carried out in the convection-diffusion time dependent navigator in chemical engineering module of FEMLAB. Time dependent iterative solver with "fldaspk" time stepping algorithm was used to solve this model.

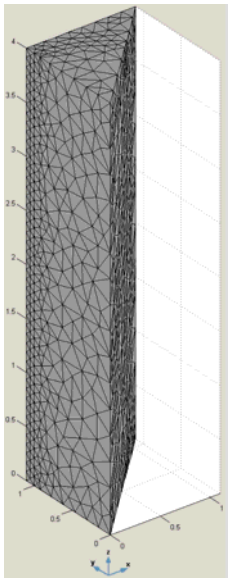


Fig. 7: 3D model meshing

The simulation setting and input parameter is shown in Table 6, and the system is assumed to work under isothermal condition. The monolithic reactor is assumed to work under transient isothermal condition at 750 K and the inlet NO_x concentration is 0.0202 mol/m^3. In this simulation the kinetic reaction study is considering only NO as the ratio of NO to other NO_x is 9:1[9], so other NO_x content in exhaust gas is negligible.

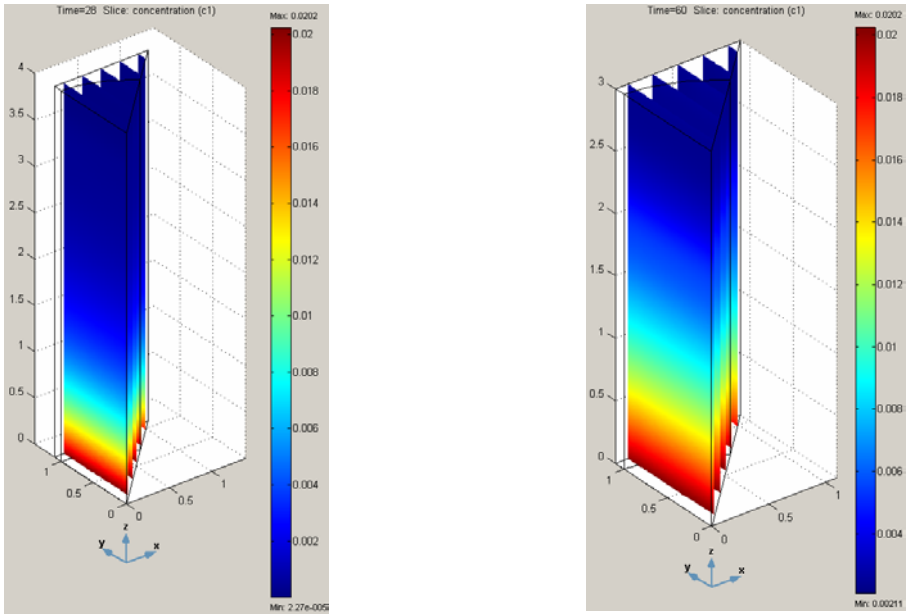
Table 6: Data for simulation

Name	Channel dimension		Unit
	R = 1mm, L = 0.4m	R = 1mm, L = 0.3m	
D	1e-5	1e-5	m^2/s
D^{eff}	8.9e-7	8.9e-7	m^2/s
R	1e-3	1e-3	m
L	4e-2	3e-2	m
t	0,2,4,6…60	0,2,4,6…30	s
w	uo*(1-x^2-y^2)	uo*(1-x^2-y^2)	m/s
v_o	0.5	0.5	m/s
c_o	0.02024458	0.02024458	mol/m^3
k_a	1.6	1.2	s^{-1}
k_d	0.6381	0.4785	s^{-1}
k_c	2.507	2.507	-
k_{diss}	8.85 e4	8.85 e4	s^{-1}
k_{n21}	1.53 e3	1.53 e3	$m^3/s{\cdot}mol$
k_{n22}	1.31 e2	1.31 e2	$m^3/s{\cdot}mol$

The effective diffusion coefficient, D^{eff}, accounts for porosity and tortuosity in the catalyst. The rate constant, k, accounts for specific surface area and reaction rate for the heterogeneous reaction on the surface of the catalyst. The flow velocities in the x- and y-direction, u and v, are assumed to be zero (no radial flow).

DISCUSSION

Features of this model are: reversible adsorption of NO, followed by instantaneous dissociation to form N* and O*, and N_2 formation via a bi-functional path (2N*) combination. The reaction rate of N_2 formation and NO* dissociation is independent of the catalyst surface area but the reversible NO adsorption is dependent on the catalyst surface area [8]. Figure 7 shows the simulation result of two different monolith channel dimension under steady state condition.



a) Channel dimension R = 1mm, L = 0.4m b) Channel dimension R = 1mm, L = 0.3m

Fig. 7: FEMLAB 3D model simulation result

Figure 8 shows that curve at 10s almost overlapping with results at 60s. Similar trends were observe after t = 10s until 60s indicate that the reaction has almost reach steady state condition at t = 10s under isothermal temperature of 750K. Based on the simulation of the TWCC reactor model with the monolith channel dimension of 0.4 m length and 1 mm radius for inlet NO_x concentration of 0.0202 mol/m^3 , it is found that the outlet

concentration of NO_x is around 22.7 μmol/m^3 (681 μg/m^3) at t = 10s. It indicates that up to 99% of NO_x reduction is achieved using this dimension of three-way catalytic converter. While, for the monolith channel dimension of L = 0.3 m and R = 1 mm, the NO_x outlet concentration is around 2.11 mmol/m^3 (63.3 mg/m^3) at t = 10s, that means up to 90% of NO_x reduction achieved.

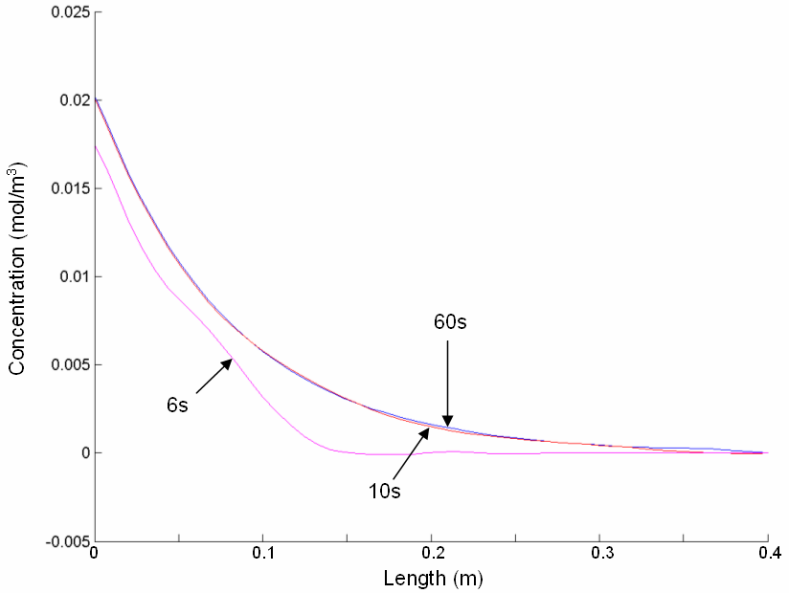
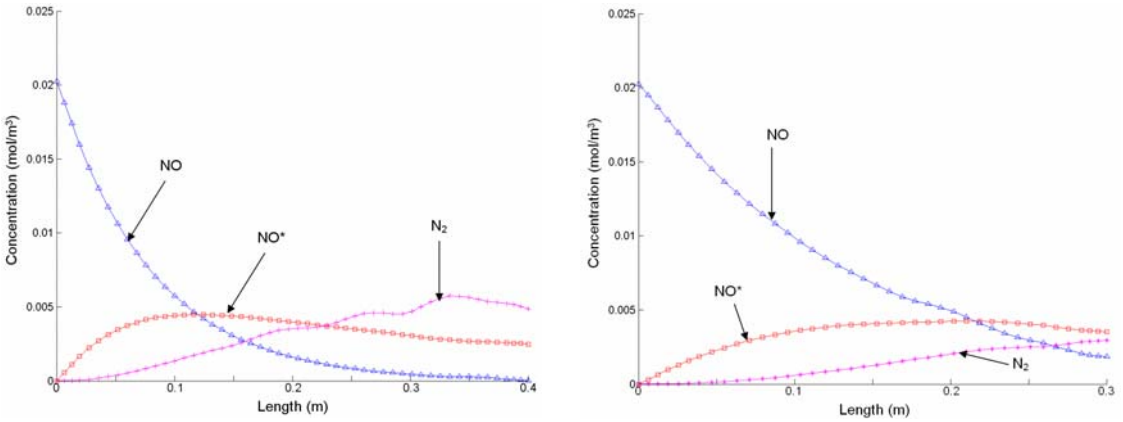


Fig. 8: NO concentration profile at t = 6, 10, and 30s

The gas concentration profile through the reactor is shown in Figure 9. The NO concentration reduced drastically before the reactor length of 0.2 m. The result is obvious since the other researchers [8, 10, 11] 8 use monolith lengths of between 0.15 to 0.2 m for their research and their findings show that a high portion of NO reduction is achieved.



a) Channel dimension *R* = 1mm, *L* = 0.4m b) Channel dimension *R* = 1mm, *L* = 0.3m

Fig. 9: Concentration profile of NO, N_2, and N along the reactor after t = 30s*

Wärnå, *et al.* [12] have run an experiment of NO_3^- reduction under isothermal condition in a monolith reactor under gas and liquid phases. For NO_3^- reduction, NO is the key intermediates in the catalyst surface which also the case with this simulation. Wärnå, *et al.* [12] only uses Palladium (Pd) catalyst in their experiment while in this study the three catalysts, Palladium-Platinum-Rhodium (Pd-Pt-Rh), are used. However the simulation results also show similar reduction profile that agrees with of Wärnå, *et al.* [12] findings. Figure 10 shows the NO_3^- reduction profile under isothermal condition by Wärnå, *et al.* [12].

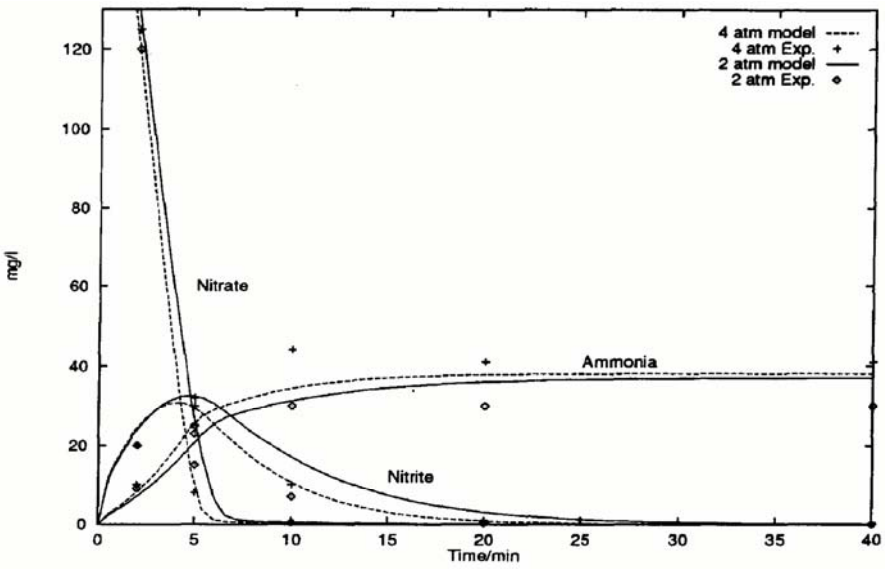


Fig. 10: Reduction of NO_3^- reduction under isothermal condition [12].

Wärnå, *et al.* [12] have run an experiment of NO_3^- reduction under isothermal condition in a monolith reactor under gas and liquid phases. For NO_3^- reduction, NO is the key intermediates in the catalyst surface which also the case with this simulation. Therefore, the simulation results also show similar reduction profile that agrees with of Warna *et al.*'s [12] findings. The computed outlet gas concentration also agree with other researcher [13, 14] finding that TWCC is capable of reducing up to 90% of the NO_x in the automobile exhaust gas.

CONCLUSION

Under the transient isothermal condition at 750 K, the monolithic reactor takes only about 10 second to achieve a steady state condition. That kind of operating condition normally occurs in the electric pre-heated monolithic reactor. TWCC is applicable for the NO_x abatement in CNG vehicle exhausts gas because from the simulation result TWCC is capable of reducing more than 90% of inlet NO_x concentration. Therefore, the installation of TWCC in the CNG vehicle will further reduce the exhaust emission from that car and comply with a stringent Euro IV regulation of automobile emission. The concentration profile obtained from the simulation is also in a very good agreement with a presented experimental data available in the literature. Thus, the modelling and simulation in this work can be use in the design and optimization of catalytic converter. Specifically, results obtained from the computer modelling exercise have demonstrated that finite element method is capable of modelling the NO_x abatement in TWCC.

ACKNOWLEDGEMENT

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NOTATIONS

R	=	Radius of monolithic reactor channel (m)
L	=	Length of monolithic reactor (m)
k_i	=	Reaction rate of species i (s^{-1} or $m^3s^{-1}mol^{-1}$)
D	=	Diffusivity coefficient (m^2/s)
D^{eff}	=	Effective Diffusivity coefficient (m^2/s)
t	=	Time (s)
u, v, w	=	Velocity vector in x, y, z direction
N_i	=	Flux condition, constant form
c, c_o	=	Concentration (mol/m^3)
k_a	=	Adsorption rate coefficient (s^{-1})
k_d	=	Desorption rate coefficient (s^{-1})
k_c	=	Equilibrium rate constant = k_a/k_d
k_{diss}	=	NO* dissociation rate coefficient (s^{-1})
k_{n21}	=	N_2 reaction rate ($m^3s^{-1}mol^{-1}$)
k_{n22}	=	N_2 reaction rate ($m^3s^{-1}mol^{-1}$)
x, y, z	=	3D Plane direction
L_t	=	Total surface site concentration $mol/m^2_{nobel\ metal}$)
θ_i	=	Fraction coverage of component, i,
M_i	=	Molecular weight of component, i, (kg/mol)
A_i or S_i^o	=	Preexponential factor (s^{-1} or -)
E_i^{act}	=	Activation energy (kJ/mol)