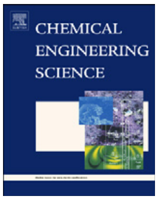
Chemical Engineering Science 73 (2012) 373–387

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces



A low-dimensional model for describing the oxygen storage capacity and transient behavior of a three-way catalytic converter

Pankaj Kumar [a], Imad Makki [c], James Kerns [c], Karolos Grigoriadis [b], Matthew Franchek [b], Vemuri Balakotaiah [a,*]

[a] *Department of Chemical and Biomolecular Engineering, University of Houston, TX 77204, United States*
[b] *Department of Mechanical Engineering, University of Houston, TX 77204, United States*
[c] *Ford Motor Company, Dearborn, MI 48125, United States*

ARTICLE INFO

Article history:
Received 24 October 2011
Accepted 5 December 2011
Available online 18 January 2012

Keywords:
Chemical reactor
Model reduction
Catalyst deactivation
Catalysis
Three-way converter
Real-time simulation

ABSTRACT

We propose a low-dimensional model of the three-way catalytic converter (TWC) that would be appropriate for real-time fueling control and TWC diagnostics in automotive applications. The model reduction is achieved by approximating the transverse gradients using multiple concentration modes and the concepts of internal and external mass transfer coefficients, spatial averaging over the axial length and simplified chemistry by lumping the oxidants and the reductants. The reduced order model consists of seven ordinary differential equations and captures the essential features of a TWC providing estimates of the oxidant and reductant emissions, fractional oxidation state (FOS) and total oxygen storage capacity (TOSC). The model performance is tested and validated using data on actual vehicle emissions resulting in good agreement for both green and aged catalysts including cold-start performance. We also propose a simple catalyst aging model that can be used to update the oxygen storage capacity in real time so as to capture the change in the kinetic parameters with aging. Catalyst aging is accounted via the update of a single scalar parameter in the model. The computational efficiency and the ability of the model to predict FOS and TOSC make it a novel tool for real-time fueling control to minimize emissions and diagnostics of catalyst aging.

1. Introduction

Automobile emissions such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x) are regulated through the Clean Air Act. Shown in Table 1 is the LEV II emissions standards as followed by California Air Regulation Board (CARB). LEV III, to be phased-in over 2014–2022, introduces even stricter emissions standards. Apart from emissions, the 1990 amendment to the Clean Air Act, also requires the vehicle to have a built-in On-Board Diagnostics (OBD) system. The OBD is a computer based system designed to monitor the major engine equipment used to measure and control the emissions. Having an optimal fueling controller for the three-way catalytic converter (TWC) utilizing a transient physics based model for the TWC will play a major role in satisfying future low emission and OBD guidelines.

The TWC is a reactor used to simultaneously oxidize CO and HC to CO_2 and H_2O while reducing NO_x to N_2. The air–fuel mixture entering the TWC is often quantified using the normalized air to fuel ratio (A/F), defined as

$$\lambda = \frac{(A/F)_{actual}}{(A/F)_{stoichiometry}}.$$

Thus, $\lambda > 1$ corresponds to a (fuel) lean operation while $\lambda < 1$ corresponds to a rich operation. It is well known that there exists a narrow zone around stoichiometry ($\lambda = 1$) where the TWC efficiency is simultaneously maximum for all the major pollutants (Heywood, 1988; Heck et al., 2009). Thus, gasoline engines are normally controlled to operate around stoichiometry. However, in real world operating conditions, slight excursions from the stoichiometric condition are often observed. Thus, ceria stabilized with zirconia is added in the TWC to act as a buffer for oxygen storage, among other reasons (Kaspar et al., 1999), and to help curb the breakthrough of emissions.

Traditionally, the TWC is controlled based on catalyst monitor sensors (CMS) set points (Fiengo et al., 2002; Makki et al., 2005), specifically universal exhaust gas oxygen sensor (UEGO) and heated exhaust gas oxygen sensor (HEGO) set points. An overview of oxygen sensor working principles can be found in Brailsford et al. (1997), Riegel et al. (2002), and Baker and Verbrugge (2004). Both UEGO and HEGO sensors measure the air-to-fuel ratio (A/F). However, while HEGO is a switch type oxygen sensor with sharp

---

* Corresponding author.
E-mail address: bala@uh.edu (V. Balakotaiah).

0009-2509/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2011.12.001

Table 1
LEV II emission standards for passenger cars and light duty vehicles under 8500 lbs, g/mile (CEPA (California Environmental Protection Agency), 2011).

Category	50,000 miles/5 years					120,000 miles/11 years				
	NMOG	CO	NO*x*	PM	HCHO	NMOG	CO	NO*x*	PM	HCHO
LEV	0.075	3.4	0.05	–	0.015	0.09	4.2	0.07	0.01	0.018
ULEV	0.040	1.7	0.05	–	0.118	0.055	2.1	0.07	0.01	0.011
SULEV	–	–	–	–	–	0.01	1.0	0.02	0.01	0.004

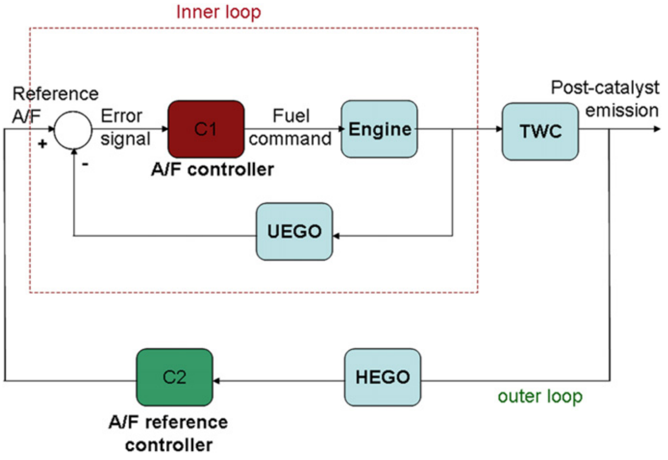


Fig. 1. Schematic diagram of inner and outer loop control strategy.

Table 2
Numerical constants and parameters used in TWC simulation.

Constants	Value
a	10×10^{-9} m
R_Ω	181×10^{-6} m
δ_c	30×10^{-6}m
$2\delta_s$	63.5×10^{-6} m
k_f	0.0386 W m^{-1} K^{-1}
Cp_f	1068 J kg^{-1} K
Cp_w	1000 J kg^{-1} K
ρ_w	2000 kg m^{-3}
ϵ_w	0.41
τ	8
Sh_∞	3.2
Nu_∞	3.2
$Sh_{i,\infty}$	2.65
Λ	0.58

transition around stoichiometry, UEGO can be used to measure A/F over a wider range. Shown in Fig. 1 is a block diagram representation of a typical inner and outer loop TWC control strategy (Makki et al., 2005). A TWC unit, usually consists of two bricks separated by a small space. In partial volume catalyst, the HEGO sensor is located in between the two bricks, while in a full volume catalyst the HEGO is placed after the second brick i.e., at the exit of the TWC. The advantage of using a partial volume system is that it provides fueling control in a delayed system, i.e., even if there is breakthrough detected after brick one, the second brick will still reduce emissions. With OBD requirement to monitor the entire catalyst performance, a full volume catalyst has to be used. Typically, UEGO is placed after the engine for more accurate A/F measurement while HEGO is preferred to measure A/F after the TWC because of its lower cost and faster response time. The inner loop controls the A/F to a set value while the outer loop modifies the A/F reference to the inner loop to maintain the desired HEGO set voltage (around 0.6–0.7 V, depending on design and calibration) to achieve the desired catalyst efficiency. With this arrangement we rely on emissions breakthrough at the HEGO sensor to determine if the catalyst is saturated (lean) or depleted (rich) of oxygen storage and as such it imposes a limitation on the controller design.

If the true oxidation state of the catalyst can be measured or modeled, then a model based approach to tighter control on breakthrough emissions would be feasible. Emission control then would be less dependent on sensor location and thus applicable for both partial and full volume catalyst systems. This can be achieved using a physics based model for the TWC. In the literature, most of the models for TWCs are represented by a set of partial differential equations (PDEs) in time and space (Oh and Cavendish, 1982; Siemund et al., 1996; Auckenthaler et al., 2004; Pontikakis et al., 2004; Joshi et al., 2009a) and as such their discretization results in several hundreds of ordinary differential equations (ODEs) depending upon the number of grid points used for describing spatial variations and species considered. Although such models provide a good description of the actual system, they are computationally expensive for on-board implementation. On the other hand, the over-simplified control based oxygen storage models (Muske and Jones, 2004; Brandt et al., 1997) treat the TWC as a limited integrator and are usually empirically designed. Such models may not be accurate over a wide range of operating conditions encountered in a real system and are inadequate for tight emissions control.

In this work, we present a low-dimensional TWC model that would be appropriate for real-time on-board fueling control and TWC diagnostics. The reduced order model thus obtained retains the essential features and gives high fidelity with respect to oxygen storage and is yet computationally efficient enough for implementation in the control algorithm. The model predicts the fractional oxygen storage (FOS) level (or “bucket level”) and the total oxygen storage capacity (TOSC) (or “bucket size”) of the TWC. These quantities directly impact the ability to regulate the state of the catalyst and the prediction of aging resulting in accurate fueling control and TWC diagnostics, respectively. The model performance is tested using actual vehicle emissions resulting in good agreement. The model development and its validation are discussed in the following sections. The parameters used for TWC simulation are listed in Table 2.

2. Model development

The TWC is a monolith that composed of multiple parallel channels (400–900 cpsi) with catalyst loaded around the wall surface called washcoat. Shown in Fig. 2 is a schematic representation of a close-coupled three-way catalytic converter and the physical phenomena occurring over a single channel. The TWC can be modeled as a three-dimensional system involving convection–diffusion and reaction with variations in radial and axial directions. Assuming azimuthal symmetry, reduces the system to a two-dimensional model. Using a low-dimensional method and utilizing the effective mass transfer coefficient concepts, the two-dimensional model can be further reduced to a one-dimensional model with variation along the axial direction alone (Joshi et al., 2009a). However, the above models are still represented by PDEs along the length and time, and as such are difficult for real-time implementation. In this work, we further simplify the one-dimensional model by axially averaging to obtain a zero-dimensional model, represented by a set of ODEs. The axially averaged model, referred in the literature as the ‘Short Monolith Model’ is known to have the same qualitative features of the full PDE model (Gupta and Balakotaiah, 2001).