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To cite this version:

Caroline Ngo, Damien Koenig, Olivier Sename, Hubert Béchart. A Reduced Model of Three Ways Catalyst Converter and Stored Oxygen Rate Estimation Using Switched Observer. ECC 2013 - 12th biannual European Control Conference, Jul 2013, Zurich, Switzerland. pp.n/c. hal-00937438

HAL Id: hal-00937438

https://hal.science/hal-00937438v1

Submitted on 28 Jan 2014

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A Reduced Model of Three Ways Catalyst Converter and Stored Oxygen Rate Estimation Using Switched Observer

Caroline Ngo, Damien Koenig, Olivier Sename and Hubert Béchart

***Abstract*— Pollutant emissions limitations ruled by the latest standards force car manufacturers to improve after treatment systems. This improvement is achieved by new systems on one hand, and by more efficient control strategies, on the other. This paper describes a 0-D model of Three Ways Catalyst converter (TWC) which is able to reproduce the transient dynamics of the converter although simple. A switched observer of stored oxygen rate is derived from this reduced model, and its convergence is proved. An estimation of the oxygen capacity of TWC provides precious information for on-board diagnosis or monitoring purpose.**

First, a description of the TWC dynamics and its reduced model will be described, then a discrete time switched observer of the stored oxygen rate and the free site capacity estimation by least squares method are presented.

I. Introduction

Incomplete fuel combustion in cylinder leads to pollutants emissions. Nowadays, severe norms impose car manufacturers strict pollutant emissions regulations. As a result, exhaust gas after treatment systems need to become more efficient. Manufacturers meet the constraints by developing new technologies, but also through more sophisticated engine control strategies. The present study deals with the major after treatment system of Spark Ignition (SI) engine : the Three Ways Catalyst (TWC) converter.

The distinctive feature of Three Ways Catalyst is its ability to convert the three major regulated pollutants (CO, HC and NO_x). Pollutants optimum conversion require the fuel air ratio to be at stoichiometry value. Above this value, mixture is defined as rich (excess of fuel in mixture) whereas below, the mixture is defined as lean (excess of oxygen). The fuel air ratio, through the injected fuel quantity in the engine, is controlled by Exhaust Gas Oxygen (EGO) sensor which indicates the presence of oxygen in exhaust pipe. However, catalyst system control strategy based on exhaust fuel air ratio measurements, without taking account of its internal dynamics, is not enough to meet futures restrictions. Over the years, researches focused on TWC converter mathematical models. However, modeling this system is a complex task due to the numerous chemical reactions involved, as presented in [15] [16].

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Many reduced models of TWC converter have been developed to satisfy new engine management strategy ([3][4][5][11][17]). Reduced model from [5] is focused on the oxygen storage and release rates, described by a static function. Transport time delay was assumed to be negligible. This model is very simple, however, dynamic response to TWC transients is not taken into account.
As in [5], authors in [11] described a simplified model dominated by the oxygen storage and release dynamics modeled by a polynomial function which parameters are identified from experimental data obtained at different engine conditions. The presented model include the effects of space velocity. These models are focused on the main dynamic of TWC : the oxygen storage dynamics. They are simple but have many parameters to adjust.

This paper aims to respond to model based needs to meet future standards and present an application of switched observer to chemical process.

A 0-D physical model based on simplified dynamics of TWC from [1] is presented, also focused on oxygen storage dynamics. This model has been validated on experimental results. A switched linear observer has been designed for oxygen storage rate monitoring, designed by solving multiple Linear Matrix Inequality (LMI) and the obtained gains guarantee the stability whatever switching sequence. Estimation of oxygen free sites density is done using least squares algorithm to take into account this parameter deviation in observer. An application will illustrate the presented method.

Notations : $(.)^T$ stands for transpose matrix and $(.) > 0$ denotes a positive definite matrix.

II. Main dynamics of Three Ways Catalyst converter

A. TWC dynamics focused on oxygen storage

Exhaust gas of a SI engine is mainly composed of unburnt hydrocarbons (HC), carbon monoxides (CO), nitrogen oxides (NO_x), which are the major regulated pollutants, and oxygen (O_2), essential to convert pollutants. The TWC is able to convert these three pollutants when gas flows through it. Indeed, thanks to its internal structure covered by precious metal (Palladium, Platinum, Rhodium), the TWC promote HC/CO oxidation and NO_x reduction reactions and convert them into water, carbon oxide and nitrogen.

NO_x reduction or HC/CO oxidation are realized according to the exhaust gas composition characterized by the Fuel Air Ratio, denoted R. When the gas is rich ($R > 1$), NO_x

are eliminated by HC and CO present in excess, whereas, during lean phase ($R < 1$), HC and CO are converted by NO_x present in excess this time. As illustrated by TWC efficiency curves (Fig. 1), best conversion rate for both reduction and oxidation reactions is located at stoichiometry value ($R = 1$).

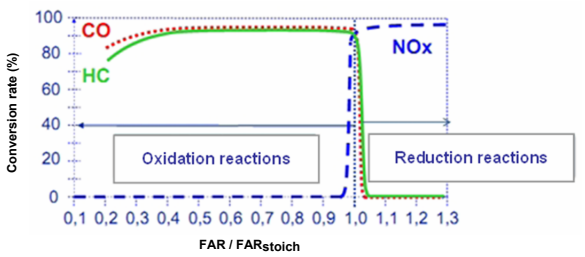

Fig. 1. Conversion efficiency

However, keeping R at stoichiometry value is impossible due to the high transients in driving conditions. To increase the efficiency of TWC conversions, Ceria oxides (Ce_2O_3) are added to fix oxygen. During lean phase, O_2 and NO_x excess facilitate Ceria oxidation, once stored, they can be released to convert pollutants when mixture is rich. By varying the fuel air ratio around stoichiometry, oxygen storage and release are stimulated and pollutants conversion is possible for any air-fuel mixture if storage management is optimum. Efficiency is then between 90% and 100%, and also depends on TWC temperature and gas flow rate. Indeed, heat activate the catalyst (chemical kinetics) and flow rate, if too high, prevent gas to stay long enough for being convert (mixture transport along converter).

TWC is affected by sulfur dioxides poisoning, but also by heat damages (overheat during misfires) which decrease the efficiency of conversions in time. As a result, the density of free sites for oxygen storage decrease, less oxygen is stored and pollutants at exhaust increase. Ageing of TWC represented by density of free sites has to be taken into account in the model and estimated.

B. Chemical reactions

As described in the previous section, five reactions mainly describe TWC dynamics. Exhaust gas elements react with each other according those main chemical reactions :

- NO_x reduction : $\frac{1}{x}NO_x + CO \rightarrow CO_2 + \frac{1}{2x}N_2$
- HC oxidation : $HC + \frac{1}{2}O_2 \rightarrow \frac{1}{2}H_2O + CO_2$
- CO oxidation : $CO + \frac{1}{2}O_2 \rightarrow CO_2$

The oxygen storage dynamics is modeled by the following reactions :

- Oxide adsorption when $R < 1$:
  $\frac{1}{2}O_2 + Ce_2O_3 \rightarrow 2CeO_2$
- Oxide desorption and CO conversion when $R \geq 1$:
  $CO + 2CeO_2 \rightarrow CO_2 + Ce_2O_3$

C. Reduced model of Three Ways Catalyst

Previous reactions can be grouped to reduce the model : one involve reducers and the other, involve oxides. $HC/CO/H_2$ can be represented by an equivalent reducer, denoted RED, and O_2/NO_x by equivalent oxide, denoted OX. Indeed, in first approximation, CO and H_2 have similar behavior and quantities of HC and NO_x are negligible compare to other components of exhaust gas. The previous chemical equations become :

- Oxygen adsorption : $OX + 2\Sigma \rightarrow 2\Sigma^*$
- Pollutants reduction : $\Sigma^* + RED \rightarrow \Sigma + CO_2/H_2O$

With :
Σ/Σ^* : Free/occupied oxygen storage site
OX : Equivalent oxide
RED : Equivalent reducer

The exhaust fuel air ratio is expressed with concentrations of equivalent reducer and oxide by :

$$R_{out} = 1 + K(\frac{1}{2}C_{RED}^{out} - C_{OX}^{out}) \tag{1}$$

All these simplifications lead to the following reaction rate equations :

- Oxygen rate dynamic :

$$\dot{\theta} = 2k_{ads}\, C_{OX}^{out}\, (1-\theta) - k_{red}\, C_{RED}^{out}\, \theta$$

- Exhaust fuel air ratio dynamic :

$$\dot{R}_{out} = vvh(R_{in} - R_{out}) + \frac{K\rho}{2}\left(2k_{ads}\, C_{OX}^{out}\, (1-\theta) - k_{red}\, C_{RED}^{out}\, \theta\right)$$

With :
θ : Oxygen ratio stored in TWC
$R_{in},\ R_{out}$: Inlet, resp. outlet fuel air ratio
vvh : Exhaust mass flow rate
T : Gas temperature in TWC
K : Concentration-FAR conversion coefficient
ρ : Density of free sites for oxygen storage
k_{ads} : Adsorption kinetic ($k_{ads} = k_{ads0}\, e^{\frac{-E_{ads}}{rT}}$)
k_{red} : Reduction kinetic ($k_{red} = k_{red0}\, e^{\frac{-E_{red}}{rT}}$)
r : Gas constant
$E_{ads},\ E_{red}$: Adsorption, resp. desorption activation energy
$C_{OX}^{out},\ C_{RED}^{out}$: Oxide, resp. reducer concentration

And parameters $k_{ads0},\ k_{red0},\ E_{ads},\ E_{red}$ are constant.

Other assumptions can be considered : when mixture is rich, it can be supposed that few oxides are present and adsorption is negligible, so $k_{ads} = 0$; on the contrary, when mixture is lean, $k_{red} = 0$ since reduction reactions are negligible.

Expressions of oxide and reducer concentration from (1) can be reduced again and approximated by :

$$C_{OX}^{out} = \frac{1-R_{out}}{K},\ if\ R_{out} < 1,\ 0\ otherwise$$
$$C_{RED}^{out} = \frac{2(R_{out}-1)}{K},\ if\ R_{out} \geq 1,\ 0\ otherwise$$

The model is composed of 3 inputs ($u = [R_{in}, vvh, T]$), 2 states ($x = [\theta, R_{out}]$) and measured output ($y = R_{out}$).

The non linear system is given by :

$$R_{out} < 1 \quad \begin{cases} \dot{x}_1 = \frac{2}{K}\, k_{ads}(u_3)\ (1-x_1)(1-x_2) \\ \dot{x}_2 = u_2(u_1 - x_2) \\ \quad +k_{ads}(u_3)\ \rho\ (1-x_1)(1-x_2) \end{cases}$$

$$R_{out} \geq 1 \quad \begin{cases} \dot{x_1} = \frac{2}{K}\, k_{red}(u_3)\ x_1(1-x_2) \\ \dot{x_2} = u_2(u_1 - x_2) \\ \quad +k_{red}(u_3)\ \rho\ x_1\ (1-x_2) \end{cases} \tag{2}$$

Simulation of the non linear model results against experimental data is presented in the following figures :

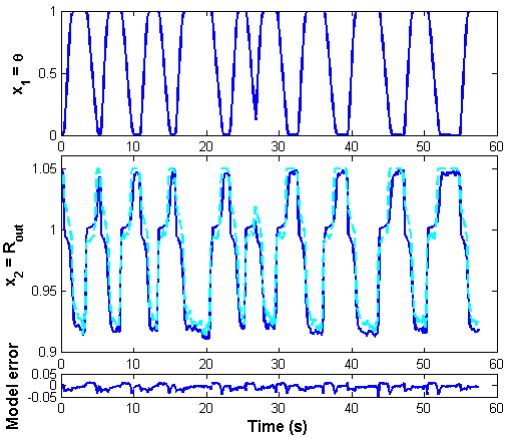

Fig. 2. Oxygen rate model and Fuel air ratio from experimental measurements (dashed) compared to the non linear model (solid)

Results of the non linear model simulation shows good fit of the model to data (Fig.2). The reduced model behave as expected : during rich phase, all stored oxygen have been released and $\theta = 0$, whereas during lean phase, $\theta = 1$ meaning that all free oxygen sites are occupied. The oxygen storage and release dynamics (TWC breathing) are also well modeled : during rich to lean and lean to rich transitions, $R_{out} = 1$. In the first case, TWC store all the oxygen present in gas and since mixture is lean, no oxide and reducer are present are TWC exhaust, so $R_{out} = 1$ during storage. In the second case, stored oxygen is released and react with reducer, as a result $R_{out} = 1$ during this process.

In order to apply a switched observer, this reduced model is linearized.

III. Switched linear model

The choice of switched system obtained by linearization over other form of representation is due to the nature of TWC's operating range (rich or lean ranges). In addition, the model is clearly non linear but dynamics are simple.

Let consider the following switched system :

$$\begin{cases} \dot{x}(t) = \sum_{i=1}^{n} \mu_i(x_2(t))(A_i x(t) + B_i u(t) + d_i) \\ y(t) = Cx(t) \end{cases} \tag{3}$$

With : $A_i = \frac{\partial f(x,u)}{\partial x}\Big|_{x_i,u_i}$, $B_i = \frac{\partial f(x,u)}{\partial u}\Big|_{x_i,u_i}$, $C_i = C = [0\ 1]$, $d_i = f(x_i, u_i) - A_i x_i - B_i u_i$
And : $\dot{x}(t) = f(x(t), u(t))$

The linearized system is given by the following matrices (A_i, B_i, d_i) :

– If $R_{out} < 1$:

$$A_i = \begin{pmatrix} \frac{2}{K} k_{adsi}(x_{2i}-1) & \frac{2}{K} k_{adsi}\ (x_{1i}-1) \\ \rho\ k_{adsi}(x_{2i}-1) & -u_{2i} + \rho\ k_{adsi}(x_{1i}-1) \end{pmatrix}$$

$$B_i = \begin{pmatrix} 0 & 0 & \frac{2}{K}\frac{E_{ads}}{r u_{3i}^2} k_{adsi}(x_{1i}-1)(x_{2i}-1) \\ u_{2i} & u_{1i} - x_{2i} & \frac{E_{ads}}{r u_{3i}^2}\ \rho\ k_{adsi}(x_{1i}-1)(x_{2i}-1) \end{pmatrix}$$

$$d_i = f(x_i, u_i) - A_i \begin{pmatrix} x_{1i} \\ x_{2i} \end{pmatrix} - B_i \begin{pmatrix} u_{1i} \\ u_{2i} \\ u_{3i} \end{pmatrix}$$

– If $R_{out} \geq 1$:

$$A_i = \begin{pmatrix} \frac{2}{K} k_{redi}(1-x_{2i}) & -\frac{2}{K} k_{redi} x_{1i} \\ \rho\ k_{redi}(1-x_{2i}) & -u_{2i} - \rho\ k_{redi} x_{1i} \end{pmatrix}$$

$$B_i = \begin{pmatrix} 0 & 0 & \frac{2}{K}\frac{E_{red}}{r\ u_{3i}^2} k_{redi} x_{1i}(1-x_{2i}) \\ u_{2i} & u_{1i} - x_{2i} & \frac{E_{red}}{r\ u_{3i}^2}\ \rho\ k_{redi} x_{1i}(1-x_{2i}) \end{pmatrix}$$

$$d_i = f(x_i, u_i) - A_i \begin{pmatrix} x_{1i} \\ x_{2i} \end{pmatrix} - B_i \begin{pmatrix} u_{1i} \\ u_{2i} \\ u_{3i} \end{pmatrix}$$

Each model i represents an operating point and to switch between the n models, measured $x_2 = y = R_{out}$ is chosen as switching variable. μ_i is the switching signal and satisfies the following convex properties :

$$\begin{cases} \sum_{i=1}^{n} \mu_i(x(t)) = 1 \\ 0 \leq \mu_i(x(t)) \leq 1 \end{cases}$$

Here, μ_i is constant and equals to 0 or 1 according to switching variable value so, if $\mu_i(x_2(t)) = 1$, (A_i, B_i, d_i) are activated.

Four set of points are chosen to model the dynamics (n=4), they represent lean and rich steady state phases and fuel air ratio transitions. Operating points are obtained by mathematical identification based on non linear model data.

The chosen points are given in the following table :

		x_{1i}	x_{2i}	u_{1i}	u_{2i}	u_{3i}
Rout < 1	**i = 1**	0.973	0.956	0.952	12.51	473
	i = 2	0.989	0.998	0.999	11.61	400
Rout ≥ 1	**i = 3**	0.447	1.004	1.003	14.12	596
	i = 4	0.024	1.038	1.041	11.05	569

TABLE I
Sets of operating points for the four sub models

In the case where switching variable is not measurable, this switched linear model can be extended to estimate the switching variable. This approach is presented in [10],[9].

Validation is done from non linear model data obtained by simulation with experimental data in input. Inlet FAR is a step signal between the values of $R_{in} = 0.92$ and $R_{in} = 1.05$ with non constant sample time, temperature and mass flow rate are constant. Model identification results are shown in the following figures :

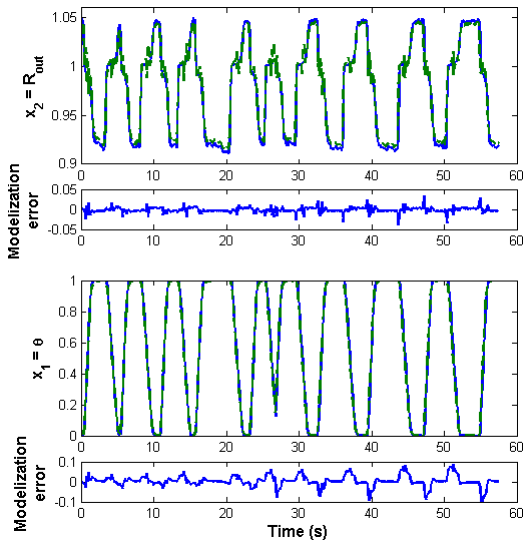

Fig. 3. Fuel air ratio and Oxygen fraction rate from non linear model (solid) compared to the switched model (dashed)

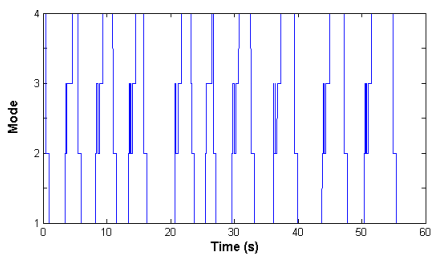

Fig. 4. Switching sequence

Good results are obtained by this switched model although simple : modelization error of FAR remains small in spite of noise from switches. Whereas, model of oxygen rate from switched model is equivalent to the one from non linear model, and is not affected by switching sequence. Noise from switches of FAR is not a problem since this value is measurable. This model has been applied on data different from the one used in identification process which justify the validity of this switched model.

In the following sections, a discrete time switched observer and a parameter estimation are presented for $x_1 = \theta$ and ρ monitoring. Parameter estimation is used as an input for the observer in order to take into account the TWC ageing.

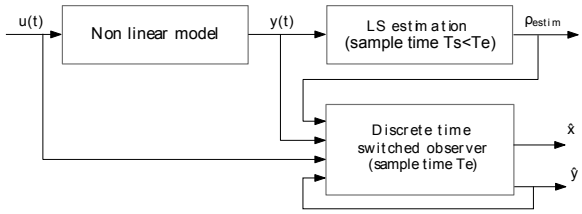

Fig. 5. Observation and estimation process scheme

IV. Discrete time switched observer : application to oxygen storage rate θ

Optimization of the oxygen storage management can be achieved by monitoring the stored oxygen fraction θ. Since this value is not measurable, an observer has to be designed. This section presents a discrete time switched observer with multiple Lyapunov functions designed by solving LMIs ([2][12]).

A. Switched observer synthesis

The expression of the discrete time switched observer is of the following form :

$$\begin{cases} \hat{x}_{k+1} = \sum_{i=1}^{n=4} \mu_i(x_{2k})(A_{di}\hat{x}_k + B_{di}u_k + d_{di} + L_i(y_k - \hat{y}_k)) \\ \hat{y}_k = C_d\hat{x}_k \end{cases} \tag{4}$$

Where L_i is the observer gain of the current model i and A_{di}, B_{di}, d_{di} and C_d are the discrete matrix of A_i, B_i, d_i and C, respectively (with a sample time of 10 *ms*).

These matrices depend on the known parameter ρ estimated by least squares algorithm described in Section V.

From (3) and (4), the state estimation error dynamic is given by :

$$e_{k+1} = \sum_{i=1}^{n=4} \mu_i(x_{2k})(A_i - L_iC)e_k \tag{5}$$

$$e_k = x_k - \hat{x}_k$$

Problem : Considering the switched model (3) and the switched observer (4), find the gains L_i such that the estimation error dynamics (5) is globally asymptotically stable.

Theorem 1 : Observer gain For $i, j \in 1, 2, ..., n$, where i represent k and j, k+1, if the pair (A_{di}, C) is detectable for all i, if there exist matrices $P_i \in \mathbb{R}^{m\times m}$, positive definite and symmetric and, $U_i \in \mathbb{R}^{m\times p}$ such that the following LMI is verified for all (i, j) :

$$\begin{bmatrix} -P_i & A_{di}^T P_i^T - C_d^T U_i^T \\ P_i A_{di} - U_i C_d & P_j - 2P_i \end{bmatrix} < 0$$

then, the discrete time switched observer (4) of system (3) exist and the gains are given by $L_i = U_i P_i^{-1}$.

Sketch of proof : (steps similar to [7], [12])

To guarantee convergence toward 0 of the estimation error (5), the following inequality should be satisfied :

$$V(k+1, e_{k+1}) - V(k, e_k) < 0$$

for all k, where $V(k, e_k) = e_k^T P_k e_k > 0$ is a candidate Lyapunov function, with $P_k = P_k^T$ and $P_k > 0$.

Let $P_i = P_k$ and $P_j = P_{k+1}$, the difference $V(k+1, e_{k+1}) - V(k, e_k)$ along the solution of (5) becomes :

$$-P_i + (A_{di}^T P_i^T - C_d^T L_i^T P_i^T) P_i^{-1} P_j P_i^{-1} (P_i A_{di} - P_i L_i C_d) < 0$$

By Schur's complement, this inequality is equivalent to :

$$\begin{bmatrix} -P_i & (A_{di} - L_i C_d)^T P_i^T \\ P_i(A_{di} - L_i C_d) & -P_i P_j^{-1} P_i \end{bmatrix} < 0$$

With $U_i = P_i L_i$, and by noticing that $P_i^T P_j^{-1} P_i \geq 2P_i - P_j$, the LMI to solve becomes :

$$\begin{bmatrix} -P_i & A_{di}^T P_i^T - C_d^T U_i^T \\ P_i A_{di} - U_i C_d & P_j - 2P_i \end{bmatrix} < 0$$

B. Switched observer synthesis with pole assignment

A solution to improve the performances of the observer is to add constraints on matrices A_{di} and C_d in the previous LMI to force poles assignment in sub-region ([12],[14]).

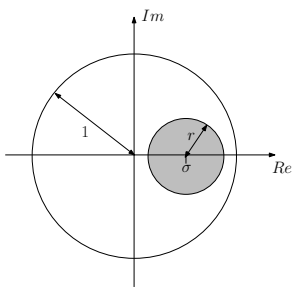

Fig. 6. Sub-region for pole location

Theorem 2 : Pole placement To place the poles of the observer into a circle smaller than the unit circle, a simple change of matrix in the previous LMI is used : A_{di} is replaced by $\frac{A_{di} - \sigma I}{r}$ and C_d is replaced by $\frac{C_d}{r}$, where σ is the small circle center coordinates and r is the small circle radius.

The LMI to solve becomes :

$$\begin{bmatrix} -P_i & (\frac{A_{di} - \sigma I}{r})^T P_i^T - (\frac{C_d}{r})^T U_i^T \\ P_i(\frac{A_{id} - \sigma I}{r}) - U_i(\frac{C_d}{r}) & P_j - 2P_i \end{bmatrix} < 0$$

C. Observer results

The switched observer has been validated against the same data used previously in switched model validation paragraph. Initial states values are different from data to see observer performances. Pole placement application will not be illustrated.

Figures show that observer converge and is not affected by switches. Maximum value of error estimation for $\hat{x}_1$ and $\hat{x}_2$ is 30%. Although this value is quite high, error converge quickly to 0 such as the results are satisfactory.

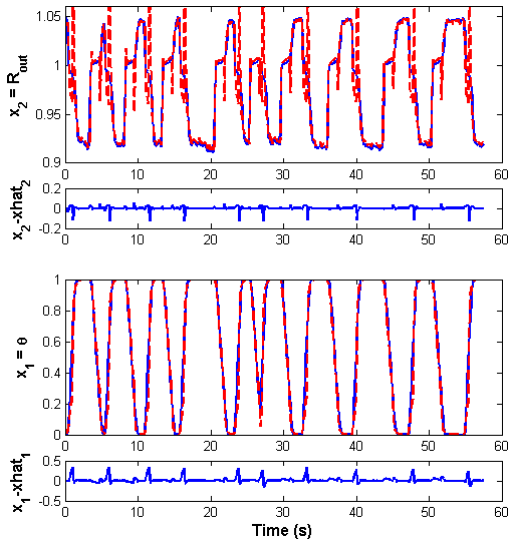

Fig. 7. Fuel air ratio and Oxygen fraction rate from non linear model (solid) compared to observer result (dashed)

The presented results prove that observer is efficient for oxygen storage rate monitoring (Fig.7) which can be employed in advance control strategies including oxygen storage management.

V. Free sites density ρ estimation by least squares algorithm

Future standards will impose On Board Diagnosis (OBD) of TWC. Catalytic converters are mostly affected by sulfur poisoning or overheat which reduce the surface available to convert pollutants. As a result, density of free oxygen site ρ decrease, leading to efficiency loss of TWC. By monitoring the parameter ρ, the TWC ageing can be taken into account by the observer to adapt oxygen storage management, and is a precious information for OBD.

To monitoring ρ, an estimation by least squares method is chosen (see [13]). One can remark that an adaptive observer, PI observer or addition of the parameter in the state vector could have been used to estimate both states and parameter as in [8] or [6].

However, two reasons explain this choice :

- The parameter ρ varies slowly (years), so online estimation is not useful for observer.
- System with addition of ρ as a state and $\rho(k+1) = \rho(k)$, is not observable when $x_{1i} = \theta_i = (0, 1)$ or $x_{2i} = 1$ (eq.(2)).

As a result, decoupling the problem of observation and estimation was preferable.

The recursive least squares estimation is done with the values from the non linear model. The non linear model presented in section II is of the form :

$$h(x) = \rho f(x, u) + g(x, u)$$

With :

$$h(x) = \dot{x}_2$$
$$g(x,u) = u_2(u_1 - x_2)$$
$$\begin{cases} f(x,u) = k_{ads}(u_3)(1-x_1)(1-x_2) & (if\ x_2 < 1) \\ f(x,u) = k_{red}(u_3)x_1(1-x_2) & (if\ x_2 \geq 1) \end{cases}$$

Since $\dot{x}_2$ is used to estimate the parameter, the least square algorithm is more advantageous : data from non linear model are stored to run the algorithm afterward. Moreover, the parameter ρ varies slowly, the sample time of estimation process can be smaller than the observer one (see Fig. 5) to provide known parameter to observer as online estimator.

The objective is to estimate the parameter ρ using least squares criteria :

$$J_\Theta(N) = \sum_{i=0}^{N} (y(i) - \Theta^T \Phi(i-1))^2$$

With :
y : Measured output
Φ : Vector composed of measured output and input
Θ : Vector of parameter to be estimated

Recursive least squares algorithm can be applied by writing :

$$y(x,u) = h(x) - g(x,u)$$
$$\Phi(x,u) = f(x,u)$$
$$\Theta = \rho$$

The following result is obtained by running estimation algorithm with a sample time of Ts = 1e-4 s with an observer running with a sample time of Te = 0.06 s.

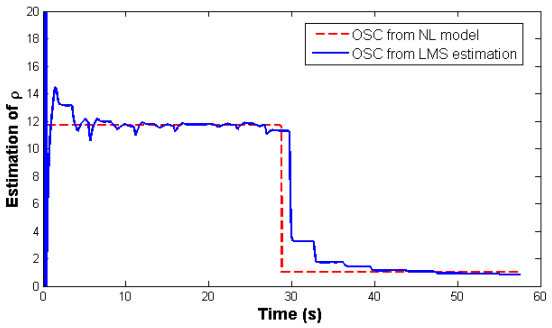

Fig. 8. Free site density estimation (solid) - Parameter value (dashed)

The estimation converge to the parameter value even when parameter real value changes, showing that this algorithm used in a recursive way is fast and suitable for monitoring application, especially the ageing of TWC.

VI. Conclusion

In this paper, a reduced model well suited for control thanks to its simplicity in the form of ordinary differential equations of small order, is developed based on oxygen dynamics of the TWC.

A multiple model linearization representation permits to design a discrete switched observer by solving multiple LMIs, considering all the possible cases. Structural constraints can be added in observer synthesis to force its poles to be in a specified circle. A parameter estimation based on recursive least squares algorithm is provided, treated separately from the observer problem.

Successful application of the oxygen fraction rate θ observation and estimation of the free site density ρ will improve the oxygen storage management, needed for future standards.

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