Chapter 54 A Study of Three-Way Catalyst Deterioration Monitoring

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Abstract To meet the demand for Euro 6 regulations, a three-way catalyst (TWC) oxygen storage model and diagnosis algorithm are designed to detect the TWC deterioration. Oscillations are produced based on oxygen storage measurement, and then catalyst performance is evaluated based on catalyst oxygen storage states which are obtained by analyzing rear lambda signal. The algorithm is verified on the bench and the vehicle, and can meet the catalyst monitoring requirements of the EU 6 regulations.

Keywords Three-way catalyst (TWC) • Deterioration • Monitoring • Oxygen storage capability (OSC)

54.1 Introduction

As environment pollution has aggravated due to the development of industry, the emission standards are becoming stricter worldwidely. Table 54.1 shows a comparison of the emission limits for vehicles of categories M between the Euro emission standards and the EOBD regulations.

The most common aftertreatment device for gasoline engines nowadays is the three-way catalytic converter (TWC). It is able to reduce the HC, CO, and NO_x emissions significantly. However, the efficiency of these reactions significantly decreases with the ageing of the TWC. Under Euro V and Euro VI standards, a TWC fault must be reported when the emission limit of NO_x or HC is exceeded due to the deterioration of TWC.

There are many factors that influence the conversion efficiency of TWC, such as λ , catalyst temperature, and exhaust gas velocity [2]. Figure 54.1 shows the conversion efficiencies of NO_x, HC, and CO as a function of λ . As can be seen, only when λ within a very narrow range around the stoichiometric ratio, all the

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	CO (mg/km)	THC (mg/km)	NMHC (mg/km)	NO _x (mg/km)	PM (mg/km)	PN (Nb/km)
Euro 5b	1000	100	68	60	4.5	-
EU5 + EOBD	1900	-	250	300	50	-
Euro 6	1000	100	68	60	4.5	6.0 * E11
EU6 EOBD	1800	-	170	90	12	-

Table 54.1 Limits according to the European emission standards and EOBD regulations [1]

three components can be reduced by more than 90%. Figure 54.2 shows the effect of catalyst temperature on the conversion efficiencies. To keep high conversion efficiencies, the temperature of TWC should be located in the range between about 500 °C and thermal deterioration temperature. The exhaust gas velocity also affects the conversion efficiency of TWC, because the gas flow speed determines the duration of the gas stay in TWC. The lower exhaust gas velocity, the longer time exhaust gas stay in TWC, and the higher conversion efficiency of NO_x, HC, and CO.

The main causes of the conversion efficiency decrease are thermal deterioration, substrate meltdown, physical damage and poisoning. It is difficult to distinguish among all those failures causes. Fortunately, some researches have shown that the OSC (Oxygen Storage Capacity) of TWC has a close relationship with the emission conversion efficiency [3, 4]. Engineers usually use indirect method, such as a method based on catalyst temperature and a method based on catalyst OSC, to detect the failure of TWC [5, 6]. For cost reason, the second mentioned method is



Fig. 54.1 The relationship between catalyst conversion efficiency and oxygen storage capacity



used most commonly, which can be categorized into passive way and active way according to whether λ is interfered. The passive approach contains step counting method, amplitude ratio method and signal modeling method etc. The active approach contains sensor-/controller switch method and circuit-entering of rich-/ lean-steps method etc.

In this paper, an active method including four steps is developed. At first, the OSC of boardline catalyst is measured; Secondly, the amplitude of post- catalyst oxygen sensor signal is measured under certain oxygen load with boardline catalyst installed, which is regarded as a reference signal; In the third step, also the amplitude of rear oxygen signal is measured, but under certain oxygen load with an in-use catalyst installed which need to be monitored; Finally, those two amplitude values are compared each other to determine whether to report a final catalyst failure. This active method is different from other OSC based methods mentioned above.

54.2 **Project Target and Scheme**

In order to meet the OBD limitations of the Euro VI regulation, the eigenvalues of fault diagnosis, which is used to distinguish between aged catalysts and boardline catalysts, should meet the following requirements: $\phi_{\mu+6\sigma} < \theta_{\mu-6\sigma}$, where $\theta_{\mu-6\sigma}$ represents the lower bound of the boardline catalyst deterioration factor statistics, and $\phi_{\mu+6\sigma}$ represents the upper bound of the aged catalyst deterioration factor statistics, μ is the average of statistics, and σ is the standard deviation of statistics.

54.3 Oxygen Storage Model of TWC

54.3.1 Boundary Conditions

Since the limited effect on OSC measurement, the time that the exhaust gas spend to passes through TWC and the reaction time of the pre-catalyst and post- catalyst oxygen sensors are ignored.

54.3.2 Formula of TWC Oxygen Storage Capacity

The amount of oxygen that flow into TWC can be deduced according to the following steps:

$$\lambda_{\rm f} = \frac{\dot{m}_{\rm air}}{\dot{m}_{\rm airref}} = \frac{\dot{m}_{\rm air} \times 23\%}{\dot{m}_{\rm airref} \times 23\%} = \frac{\dot{m}_{\rm O_2}}{\dot{m}_{\rm O_2 ref}}$$
(54.1)

where λ_f is the air/fuel ratio from the oxygen sensor upstream of TWC; \dot{m}_{air} is the actual intake air mass flow; \dot{m}_{airref} is the intake air mass flow that is needed to get perfect combustion; \dot{m}_{O_2} is the actual intake oxygen mass flow; and \dot{m}_{O_2ref} is the oxygen mass flow desired.

Such that:

$$\dot{m}_{O_2 ref} = \frac{\dot{m}_{O_2}}{\lambda_f} \tag{54.2}$$

Then the difference between the actual oxygen mass flow and the desired oxygen mass flow can be denoted as:

$$\dot{m}_{O_2} - \dot{m}_{O_2 ref} = \left(1 - \frac{1}{\lambda_f}\right) \dot{m}_{O_2} = \left(1 - \frac{1}{\lambda_f}\right) \dot{m}_{air} \times 23\%$$
 (54.3)

The oxygen mass flow is a value not smaller than 0, so the formula (54.3) should be rewritten as:

$$\dot{m}_{O_2} - \dot{m}_{O_2 ref} = \left(1 - \frac{1}{fun(\lambda_f)}\right) \dot{m}_{air} \times 23\%$$
(54.4)

and fun(x) = $\left\{ \begin{array}{ll} 1 & x < 1 \\ x & x \geq 1 \end{array} \right.$

The oxygen mass that flow into TWC can be denoted as:

$$m_{O_2f} = 0.23 \int_0^t \left(1 - \frac{1}{fun(\lambda_f)}\right) \dot{m}_{air} dt$$
(54.5)

Similarly, the oxygen mass that flow out TWC can be denoted as:

$$m_{O_2 r} = 0.23 \int_0^t \left(1 - \frac{1}{fun(\lambda_r)}\right) \dot{m}_{air} dt$$
(54.6)

where λ_r is the air/fuel ratio from the oxygen sensor downstream of TWC.

The oxygen mass that is stored in TWC can be denoted as:

$$m_{O_{2}s} = m_{O_{2}f} - m_{O_{2}r} = 0.23 \int_{0}^{t} \left(\frac{1}{fun(\lambda_{r})} - \frac{1}{fun(\lambda_{f})}\right) \dot{m}_{air} dt$$
(54.7)

There are several restrictions for formula (54.7) to be applied, the reasons are:

- 1. The delay caused by gas flow is not considered.
- 2. The delay caused by oxygen sensor response is not considered.
- 3. Every signal from sensor contains signal error, and it causes accumulative error.
- 4. For physical reason, the upper limit of $m_{O_{2}s}$ is the OSC of the TWC, and the lower limit of $m_{O_{2}s}$ is zero.

In addition, linear oxygen sensor is located upstream of TWC, but usually two-point oxygen sensor is located downstream of TWC. Based on the two oxygen sensors, an OSC measurement process is designed as shown in Fig. 54.3, the steps are:



Fig. 54.3 Test process of OSC

- 1. Setting the lambda setpoint to rich side to clean the oxygen stored in the TWC.
- 2. The voltage from the downstream oxygen sensor go to high state at time t_0 means the oxygen in the TWC is cleared.
- 3. Setting the lambda setpoint to lean side at time t_0 to get oxygen to flow into the TWC.
- 4. The voltage from the downstream oxygen sensor converts to low state at time t₁ means the TWC is saturated and cannot store more oxygen.
- 5. According to formula (54.7), the OSC can be calculated with the following formula:

$$OSC = 0.23 \int_{t_0}^{t_1} \left(1 - \frac{1}{\lambda_f}\right) \dot{m}_{air} dt.$$

54.4 Verification and Improvement

The test has been performed on a three-cylinder gasoline engine. This engine is equipped with a linear oxygen sensor upstream of the TWC and a two-point oxygen sensor downstream of the TWC. The CANape and Matlab software tools are used to acquire and analyze the ECU data.

54.4.1 The OSC Measurement Result

OSC of substrate, boardline catalyst, aged catalyst and fresh catalyst are measured. The OSC distribution of each catalyst is shown in Fig. 54.4, and the x-axis is the internal temperature of catalyst during OSC measurement.

When catalyst temperature above 450 °C, the OSC of each catalyst meet the following inequality which indicates TWC deterioration level.

The lower catalyst temperature, the smaller the difference between boardline catalyst OSC and substrate OSC, when catalyst temperature blows 450 °C. It implies that the TWC light-off temperature is about 450 °C.

But the standard deviation of each catalyst OSC sampling data is too high to distinguish a failure catalyst from other catalysts with the " 6σ " confidence interval.



Fig. 54.4 Relationship between OSC and temperature

54.4.2 Diagnosis Algorithm Improvement

In order to distinguish between the boardline and aged catalyst more accurately, the nonlinearity, as shown in Fig. 54.5, between the amplitude of the downstream oxygen sensor voltage and the oxygen load, is taken into account in the proposed diagnosis algorithm. The oxygen load of a catalyst equals the oxygen mass flowing into the catalyst during an air/fuel ratio oscillation period in the engine working process.



When oxygen load is less than OSC, the oxygen that flows into catalyst can be stored completely. The amplitude of downstream oxygen sensor voltage grows slowly with the increase of oxygen load.

When oxygen load is larger than OSC, the oxygen that cannot be stored will flow out of catalyst. The amplitude of downstream oxygen sensor voltage grows quickly with the increase of the oxygen load.

Based on the OSC measurement and the nonlinearity mentioned above, a TWC can be monitored as following:

- 1. Install a boardline catalyst on a vehicle, and use the steps mentioned in Sect. 54.3.2 to measure the boardline catalyst OSC at several defined operation points.
- 2. Find the maximum value of the OSC sampling data measured in step 1, and label it as O₂ Load_{set}.
- 3. At the same defined operation points, set the oxygen load to O_2 Load_{set}, and save the amplitude of downstream oxygen sensor signal at each operation point as reference value map.
- 4. Install an in-use catalyst on a vehicle. Set the oxygen load to $O_2 \text{ Load}_{set}$ when monitoring, and get the amplitude of downstream oxygen sensor signal.
- 5. Divide the amplitude by reference value from the reference value map to get the deterioration factor sampling data of the in-use catalyst.

The reference value mentioned above is to reduce the effect of engine operation points on deterioration factor sampling data.

54.4.3 Diagnosis Algorithm Verification

On a vehicle equipped with a 1.0L turbo charged gasoline engine, set the oxygen load equal to 100 mg, and set the reference value equal to a constant of 0.0035, then the deterioration factor sampling data of an Euro VI standard boardline catalyst and an Euro VI standard aged catalyst at several engine operation points are obtained, which is shown in Fig. 54.6 and Table 54.2.

For the aged catalyst: $\phi_{\mu+6\sigma} = 1.3603 + 6 \times 0.6827 = 5.4565$;

For the boardline catalyst: $\theta_{\mu-6\sigma} = 13.6013 - 6 \times 0.6584 = 9.6509$;

 $\phi_{\mu+6\sigma} < \theta_{\mu-6\sigma}$ means that the new diagnostic strategy can distinguish fault catalyst from aged catalyst, and the gap between $\phi_{\mu+6\sigma}$ and $\theta_{\mu-6\sigma}$ provides the necessary security space for the practical application of the strategy.



Fig. 54.6 The catalyst deterioration factor statistics of boardline and aged catalytic

		Engine speed (RPM)											
		1200	1600	2000	2400	2800	3200	4000					
Aged catalyst: average $\mu = 1.3603$ variance $\sigma = 0.6827$													
Mass flow	100	2.44	0.21	0.17	0.7	2.06	1.88	1.6					
(mg/cyl)	150	0.78	0.85	0.3	0.25	1.19	1.4	0.79					
	200	0.41	0.96	0.64	1.26	1.74	1.83	1.01					
	250	0.82	1.75	0.94	1.55	2.01	1.85						
	300	0.74	2.13	1.28	2.33	2.06	1.77						
	350		2.64	2.15	1.92	1.82							
	400				1.46								
Boardline catalyst: average $\mu = 13.6013$ variance $\sigma = 0.6584$													
Mass flow	100	14.41	14.55	14.54	14.52	14.65	14.47	14.2					
(mg/cyl)	150	14.17	14.04	13.84	14.13	14.14	14.08	13.81					
	200	13.72	13.61	13.38	14.09	13.78	13.6	12.82					
	250	13.37	13.76	13.46	13.6	13.44	12.72						
	300	13.61	13.35	13.11	13.4	12.91	12.55						
	350		13.04	12.47	12.76	12.53							
	400				12.22								

Table 54.2 The statistics of the aged and boardline catalyst deterioration factors

54.5 Conclusion

1. Using the approach designed in this paper, the OSC values of several TWCs are measured. The OSC values of each TWC meet the following inequality:

OSC substrate < OSC boardline < OSC aged < OSC fresh

This means that the OSC value of a catalyst has relevance to its deterioration.

- 2. The 6σ probability distribution of boardline catalyst OSC and aged catalyst OSC are overlapped. This means that it is not precise to separate fault catalysts from good catalysts according to OSC value.
- 3. A new diagnostic strategy, determining a TWC fault according to the amplitude of downstream oxygen sensor signal when the TWC work under certain oxygen load, is proposed. The experiment result shows that the new diagnostic strategy can distinguish boardline catalysts from aged catalysts and can be taken into application to meet requirements of the EU 6 regulations.

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