

# A Study of Hydrogen Addition on Diesel Oxidation Catalyst Activities under the Real Diesel Engine

Kampanart Theinnoi<sup>1,\*</sup>, Athanasios Tsolakis<sup>2</sup>, Boonlue Sawatmongkhon<sup>1</sup> and Sathaporn Chuepeng<sup>3</sup>

<sup>1</sup>Combustion Technology and Alternative Energy Research Centre (CTAE),  
College of Industrial Technology, King Mongkut's University of Technology North Bangkok, Bangkok, 10800,  
THAILAND

<sup>2</sup>School of Mechanical Engineering, University of Birmingham, Birmingham B15 2TT, UK

<sup>3</sup>Department of Mechanical Engineering, Faculty of Engineering at Si Racha, Kasetsart University, Chonburi, 20230,  
THAILAND

## Abstract

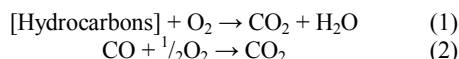
The impact of small hydrogen concentration (approximately 1000 ppm H<sub>2</sub>) on the performance of a commercial Diesel Oxidation Catalyst (DOC) in reducing carbonaceous components and oxidising NO into NO<sub>2</sub> under actual diesel engine exhaust gas conditions has been investigated. The experimental work was carried out at steady-state engine conditions for the short time periods; hence the catalyst tolerance to sulphur was not investigated. Hydrogen addition enhances hydrocarbon (HC) and carbon monoxide (CO) oxidation at lower temperatures and promotes nitrogen oxide (NO) to nitrogen dioxide (NO<sub>2</sub>) oxidation in the diesel exhaust gas. Trends that are expected to enhance Diesel Particulate Filter (DPF) regeneration at low temperatures and improve the activity of other aftertreatment systems such as Lean NO<sub>x</sub> catalysts. The hydrogen benefit was found to be dependent on the engine operation (i.e. use of exhaust gas recirculation-EGR), space velocity, exhaust gas condition and composition.

**Keywords:** Diesel oxidation catalyst, NO/NO<sub>2</sub> ratios, Hydrogen

## 1. Introduction

Nowadays, the aftertreatment technologies such as diesel oxidation catalyst, selective catalytic reduction (SCR), NO<sub>x</sub> traps and diesel particulate filter have been introduced for diesel engine due to the stringent emission regulations. However, the most important is the high performance (e.g. activity or regenerative) aftertreatment system to reduce toxic gas (i.e. carbon monoxide, hydrocarbon, nitrogen oxide, soot) are required. Hydrogen addition is dominant to enhance the aftertreatment reduction activity including the regeneration process [1-2]. For example, the small amount of hydrogen enhanced the higher NO<sub>x</sub> reduction of SCR under low and moderate exhaust gas temperatures [3]. In additions, enhancing the regeneration of a DPF by shortening the regeneration process and enhancing durability by avoiding high temperature uncontrolled regeneration lead to improved system fuel economy [4-6].

One of modern commercial diesel catalysts is the diesel oxidation catalyst which has been introduced as standard equipment for diesel vehicle. The benefits of the DOC include oxidation of several exhaust gas components by oxygen, which is mainly presented in lean burn combustion exhaust gas. The diesel pollutants such as non-regulated, carbon monoxide, hydrocarbons, organic fraction of diesel particulates (SOF) are also reduced or eliminated over DOC. The processes can be described via following reactions.



Furthermore, the oxidation of NO to NO<sub>2</sub> is another reaction which may be considered undesirable in some applications:



Concerns have been raised that the DOC poisoned reduces the oxidation activities for long term operation. Hence, hydrogen (H<sub>2</sub>) addition can improve oxidation

reaction with hydrocarbon, carbon monoxide and hydrogen (H<sub>2</sub>) over DOC. It can be used to further enhance the transformation of NO to NO<sub>2</sub> oxidation. The amount of NO to NO<sub>2</sub> conversion is dependent on the hydrocarbon that is the main fuel composition and engine exhaust gas temperature. However, as NO<sub>2</sub> is more toxic than nitric oxide (NO), concern for emitted NO<sub>2</sub> emission will hold further difficulty [7]. In addition, DOC also provides supplementary heat for the soot oxidation due to the oxidation reaction of CO, HC and H<sub>2</sub> [8].

This preliminary study to examine the benefits of small quantities of H<sub>2</sub> additions on NO to NO<sub>2</sub> conversion over the DOC was carried out using actual engine exhaust gas. The effects of exhaust gas composition with different operating temperatures and space velocities as well as EGR were investigated.

## 2. Experimental

### 2.1 Engine test rig

The experimental studies were carried out on a Lister Petter model TR1 diesel engine. The engine is a single cylinder, direct injection diesel engine, equipped with an externally cooled EGR system. The standard injection timing was set at 22 Crank Angle Degree (CAD) Before Top Dead Centre (BTDC) by the manufacturer. The main engine specifications are as follows: bore 98.4 mm, stroke 101.6 mm, conrod length 165.0 mm, displacement volume 773 cm<sup>3</sup>, compression ratio 15.5, maximum power 8.6 kW at 2500 rpm and maximum torque 39.2 Nm at 1800 rpm.

### 2.2. Diesel oxidation catalyst

The DOC used for the aftertreatment system was prepared by impregnating low loading supported platinum (Pt) based catalyst coated onto honeycomb monolith substrate (diameter of 115 mm and length 75 mm) with a high cell density (600 cpsi). The space velocity (SV) of 28,000, 38,000 and 48,000 h<sup>-1</sup> (28k, 38k and 48k h<sup>-1</sup>) based on the DOC volume and volumetric flow rate of the exhaust gas remained constant throughout the series of tests.

\*Corresponding Author: E-mail: ktn@kmutnb.ac.th

H<sub>2</sub> (99.95% purity supplied from a gas cylinder) was introduced and homogeneously mixed with the engine exhaust gas before directed through to the DOC. The 1000 ppm H<sub>2</sub> concentration was investigated.

### 2.3. Emission analysis

Horiba Mexa 7100DEGR gas analyser was used for measurement of carbon dioxide, carbon monoxide by Non-Dispersive Infrared (NDIR), oxygen by electrochemical method, nitrogen oxide (NO<sub>x</sub>) and nitrogen monoxide (NO) by Chemiluminescence detection (CLD), and hydrocarbons by flame ionization detector (FID). H<sub>2</sub> concentrations were measured by gas chromatography (GC) equipped with a Thermal Conductivity Detector (TCD). For all the conditions, upstream and downstream of the DOC, NO<sub>x</sub> (NO+NO<sub>2</sub>) and HC were monitored.

### 2.4 Fuel

The fuels used were Ultra Low Sulphur Diesel (ULSD). The fuel properties have been collated and illustrated in Table 1.

Table1. Fuel Properties

Fuel Analysis	Method	Diesel (ULSD)
Cetane Number	ASTM D613	53.9
Density at 15 °C (kg m <sup>-3</sup> )	ASTM D4052	827.1
Viscosity at 40 °C (cSt)	ASTM D445	2.467
50% Distillation (°C)	ASTM D86	264
90% Distillation (°C)	ASTM D86	329
LCV (MJ kg <sup>-1</sup> )		43.3
Sulphur (mg kg <sup>-1</sup> )	ASTM D2622	46
Aromatics (% wt)		24.4
O <sub>2</sub> (%wt)		-

### 2.5 Experimental procedure

The experimental apparatus is detailed and illustrated in Figure 1.

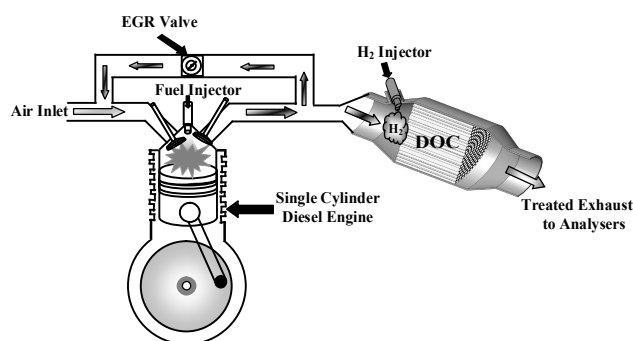


Fig.1 Schematic diagram of DOC reactor

In this work, all tests were carried on the effects of small H<sub>2</sub> additions on the DOC performance and on the NO to NO<sub>2</sub> oxidation over the DOC under range of actual diesel exhaust gas. The effects of exhaust gas composition with different operating temperatures, space velocities and exhaust gas recirculation with hydrogen addition are also investigated. The experiment examined under an engine speed of 1200, 1500 and 1800 rpm in order to investigate the effects of space velocity on the NO to NO<sub>2</sub> oxidation

over the DOC. The engine load of 2, 4, 5 bar Indicated Mean Effective Pressure (IMEP) for engine fuelling on diesel, approximately 25%, 50%, 75%, of maximum load, respectively to investigate the effect of temperature on DOC. The effect of cooled EGR 20% by volume was investigated. A proportion of exhaust gas was directed from the engine exhaust to the inlet (external EGR) and the volumetric flow rate of the EGR was calculated according to the reduction in the air volumetric flow rate.

## 3. Results and discussion

### 3.1 Effect of exhaust gas temperature and composition

The effect of exhaust gas temperature and addition of hydrogen on the DOC performance to eliminate CO and HC is presented in Figure 2. Temperatures were set up by running the engine at constant engine speed, 1500 rpm, and 2, 3, 4 and 5 bar IMEP. Regardless of hydrogen addition, DOC shows the significant decrease of CO, especially at relatively high temperatures. In contrast, HC concentration slightly increases as exhaust temperature increases. Hydrogen show marginal effect on conversion of CO and HC. This reveals that over DOC, hydrogen itself is not reacting directly with both CO and HC.

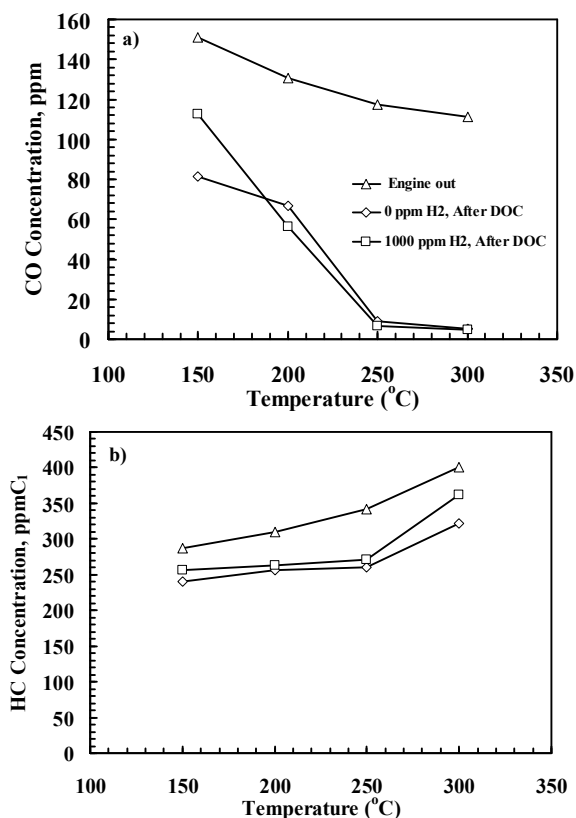


Fig.2 The effect of exhaust gas temperature and composition on DOC for a) CO concentration b) HC concentration 'with' and 'without' hydrogen additions

The concentration of NO<sub>x</sub> as a function of exhaust gas temperature is shown in Figure 3a. When engine is operated at higher loads, high exhaust temperatures, NO<sub>x</sub> concentration is intensified. This increased NO<sub>x</sub> forms from the thermal NO<sub>x</sub> mechanism - the reaction at high temperatures of nitrogen found in combustion air and oxygen during combustion processes. Obviously, hydrogen did not affect significantly the quantity of NO<sub>x</sub>. Interestingly, as shown in Figure 3b, the formation of NO<sub>2</sub>

in DOC at relatively high temperatures can be clearly observed.  $\text{NO}_2$  plays an important role in the elimination of soot formed from the engine. In general, most soot requires the high operating temperature above  $400\text{--}500^\circ\text{C}$  to achieve burn-off or oxidation with  $\text{O}_2$ . However, the high reactivity of  $\text{NO}_2$  for PM oxidation reaction will occur at a low temperature  $200\text{--}300^\circ\text{C}$  [9]. Therefore, the advantages associated with  $\text{NO}_2$  have been implemented to DPF in order to enhanced soot oxidation and improvement in filtration efficiencies at low exhaust temperature.

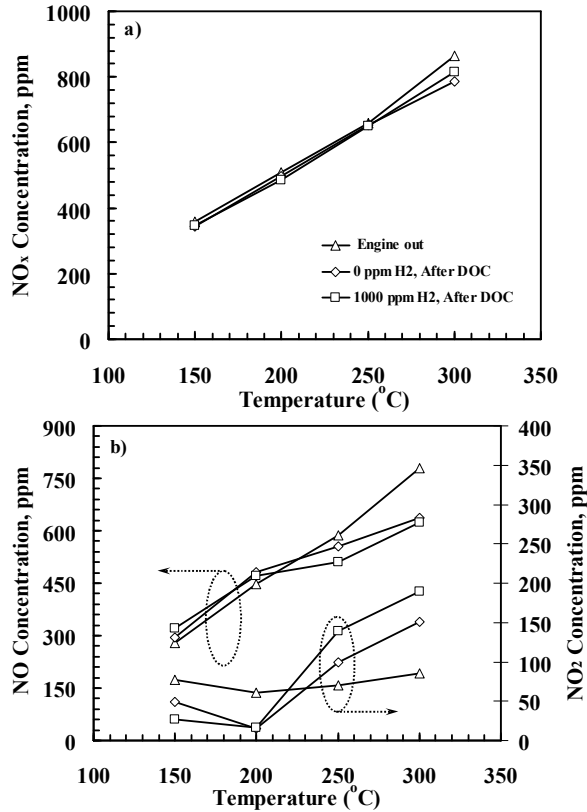


Fig.3 The effect of exhaust gas temperature and composition on DOC for a)  $\text{NO}\text{--}\text{NO}_2$  concentrations b)  $\text{NO}_2/\text{NO}$  ratios 'with' and 'without' hydrogen additions

### 3.2 The effect of EGR

The effect of EGR on the oxidation of CO and HC is illustrated in Figure 4 and 5. The engine load was fixed at 4 bar IMEP with engine speed 1500 rpm. The operating temperature is approximately  $250^\circ\text{C}$ .

The EGR technique reduces  $\text{NO}_x$  by lowering combustion temperature through reduced oxygen concentration in the combustion chamber, as well as through heat absorption [10]. The EGR also retards the start of the combustion and associated with incomplete combustion. This leads to the increased level of HC and CO in engine exhaust gas [11, 12]. The introduce EGR slightly improves the reduction of CO. Without EGR, DOC, normally, shows very high performance of the removal of CO by more than 90% conversion. In additions, DOC with EGR addition has no significant effect on CO conversion, as can be seen in Fig. 4. However, EGR show strongly affect on the elimination of HC over DOC. The performance is enhanced from less than 20% of HC reduction to more than 40% of that.

Figure 5 demonstrates the effect of EGR on the ratio of  $\text{NO}_2$  to  $\text{NO}$ . EGR shows the improvement of the

ratio in conditions that hydrogen are absent in the exhaust. When small quantity of hydrogen is added to the system, the  $\text{NO}$  generating to  $\text{NO}_2$  over the DOC is obviously decreased due to the higher concentration of C-containing species in the exhaust and reduced oxygen availability with EGR addition. In contrast with the result presented in Figure 3b, hydrogen can be used to boost the quantity of  $\text{NO}_2$  and to reduce simultaneously the amount of  $\text{NO}$ . These suggest that the benefit of hydrogen on the formation of  $\text{NO}_2$  over DOC is circumscribed by the amount of EGR.

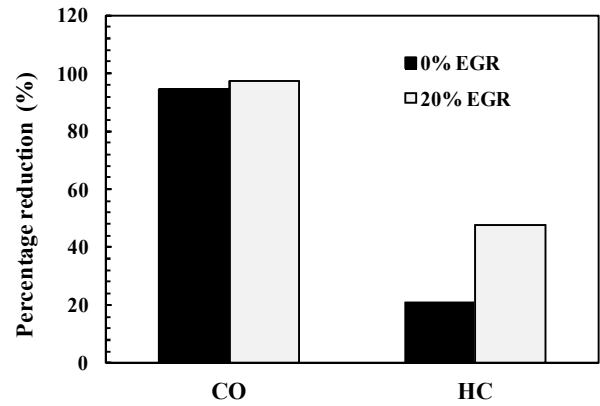


Fig.4 The effect of exhaust gas recirculation on DOC for CO and HC reduction 'with' and 'without' EGR

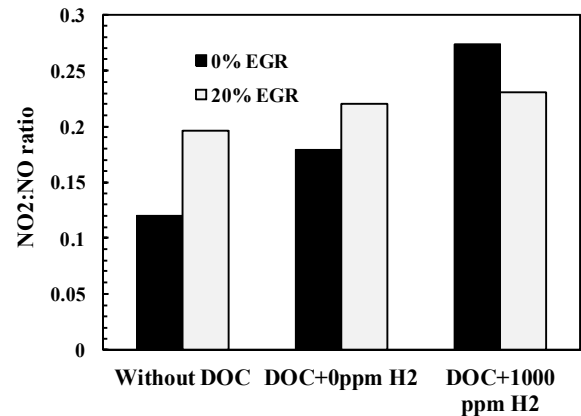


Fig.5 The effect of exhaust gas recirculation on DOC for  $\text{NO}_2/\text{NO}$  ratios 'with' and 'without' EGR

### 3.3 Effect of space velocity

To study the effect of space velocity on the removal of CO and HC, and on the ratio of  $\text{NO}_2$  to  $\text{NO}$ , three engine speeds of 1200, 1500 and 1800 rpm at a constant engine load of 4 bar IMEP were employed representing SVs of 30k, 40k and  $50\text{ k h}^{-1}$ , respectively. The SV ( $\text{h}^{-1}$ ) is defined as following equation;

$$\text{SV}(\text{h}^{-1}) = \frac{Q_v}{V_{\text{rec}}} \quad (4)$$

Where  $Q_v$  ( $\text{m}^3/\text{h}$ ) is the exhaust gas volumetric flow rate and  $V_{\text{rec}}$  ( $\text{m}^3$ ) is the reactor volume.

Figure 6 shows that the variations of space velocity make slightly change in the oxidation of CO. On the other hand, the increases of space velocity reduce visibly the DOC efficiency for eliminating HC contained in exhaust gas. These indicate that HC need longer contact time (smaller space velocity) to transform HC into  $\text{CO}_2$  and water (eq. 1) than CO need to convert itself to  $\text{CO}_2$  (eq. 2).

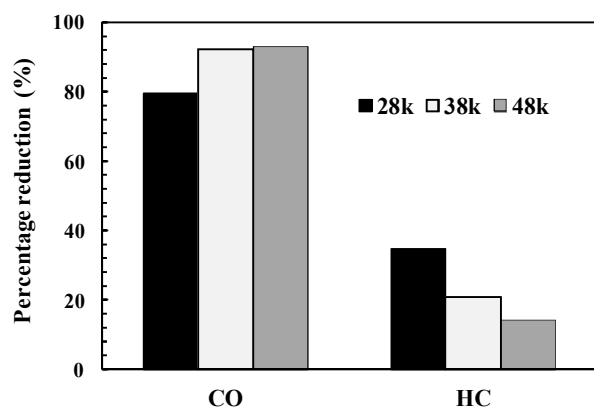


Fig.6 The effect of exhaust gas recirculation on DOC for CO and HC reduction with various space velocities.

The amount of  $\text{NO}_x$  in the exhaust gas was similar over the different engine speed conditions and remained approximately the same after the DOC as shown in Fig 3a. As mentioned early, hydrogen promotes remarkably the formation of  $\text{NO}_2$  over DOC. Interestingly, with the addition of hydrogen the  $\text{NO}_2$  to NO ratio is declined when the space velocity is increased, as displayed in Figure 7. This may lead to the supposition that the formation of  $\text{NO}_2$  from NO over the DOC is a slow chemical reaction. Smaller space velocity (by decreasing speed engine or increasing catalyst size) is more influential in oxidising NO to  $\text{NO}_2$ . However, the optimisation of space velocity to get the full benefit from hydrogen to improve the  $\text{NO}_2/\text{NO}$  ratio is also required.

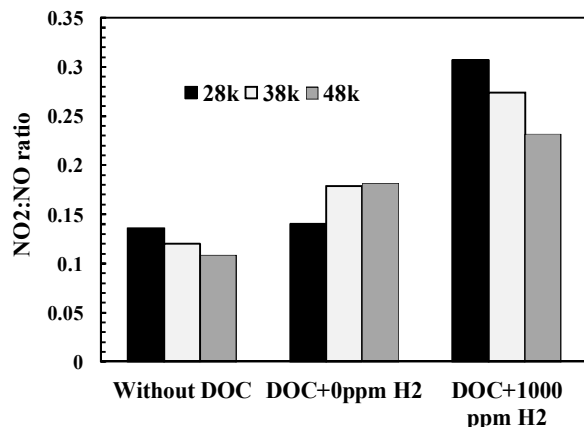


Fig.7 The effect of space velocity on DOC for  $\text{NO}_2/\text{NO}$  ratios with various space velocities

#### 4. Conclusion

The performance of DOC in terms of not only the removal of CO and HC from exhaust gas but also the production of  $\text{NO}_2$  used in the regeneration process by DPF was studied. Sensitivity of DOC to exhaust gas composition (i.e. CO, HC and  $\text{H}_2$ ) and operating condition (i.e. temperature and space velocity) was investigated. The elimination of CO by DOC is crucially depended on exhaust gas temperature but is hardly functioned with EGR and space velocity. In terms of HC reduction, EGR shows significant improvement effect. However, the conversion of HC over DOC is slightly affected by exhaust gas temperature. Unfortunately, the efficiency of DOC to reduce HC is deteriorated by space velocity. Interestingly,

the production of  $\text{NO}_2$  is apparently observed through the ratio of  $\text{NO}_2$  to NO when hydrogen is adopted in DOC system. Nevertheless, this positive effect of hydrogen is declined by raising space velocity.

#### 5. Acknowledgement

Support for this work by the Engineering and Physical Science Research Council–EPSRC (EP/F025483/1) and for supporting the postdoctoral research of Dr. Theinnoi at the University of Birmingham.

#### 6. References

- [1] Theinnoi K., Tsolakis A., Sitshebo S., Houel V., and Rajaram R.R. (2008). Hydrogen Promotion of Low-Temperature Passive Hydrocarbon-SCR Over a Silver Catalyst, *Energy & Fuels*, 22 (6), pp.4109–4114.
- [2] Satokawa S., Shibata J., Shimizu K., Satsuma A., and Hattori T. (2003). Promotion Effect of  $\text{H}_2$  on the Low Temperature Activity of the Selective Reduction of NO by Light HCs over  $\text{Ag}/\text{Al}_2\text{O}_3$ , *Applied Catalysis B: Environmental*, 43, pp.179–186.
- [3] Theinnoi K., Gill S.S., Tsolakis A., York A.P.E., Megaritis A., and Harrison R. (2012) Diesel Particulate Filter Regeneration Strategies: Study of Hydrogen Addition on Biodiesel Fuelled Engines, *Energy & Fuels*, 26 (2).
- [4] Lee J.H., Paratore M., and Brown D. (2008) Evaluation of Cu-Based SCR/DPF Technology for Diesel Exhaust Emission Control, SAE Paper No. 2008-01-0072.
- [5] Giovanni G., Jen H., Warner J.R., Girard J.W., Kim J.Y., and Lambert C.K. (2008) Enhanced Durability of a Ce/Zeolite Based SCR Catalyst, SAE Paper No. 2008-01-1025.
- [6] Allansson, R., Blakeman, P. G., Cooper, B. J., Phillips, P.R., Thoss, J.E., Walker, A.P. (2002). The Use of the Continuously Regenerating Trap (CRTTM) to Control Particulate Emissions: Minimising the Impact of Sulfur Poisoning, SAE Paper No. 2002-01-1271.
- [7] Hori, M., Koshiishi, Y., Matsunaga, N., Glaude, P., and Marinov, N. (2002). Temperature dependence of NO to  $\text{NO}_2$  conversion by n-butane and n-pentane oxidation, *Proc Combust Inst*, 29(2), pp. 2219–2226.
- [8] Katare S.R., Patterson J.E., and Laing P.M. (2007) Aged DOC is a Net Consumer of  $\text{NO}_2$ : Analyses of Vehicle Engine-dynamometer and Reactor Data, SAE Paper NO 2007-01-3984.
- [9] York, A.P.E., Ahmadinejad, M., Watling, T. C., Walker, A.P., Cox, J.P., Gast, J., Blakeman, P.G., Allansson, R. (2007) Modeling of the Catalyzed Continuously Regenerating Diesel Particulate Filter (CCR-DPF) System: Model Development and Passive Regeneration Studies, SAE Paper No. 2007-01-0043.
- [10] Ladommatis N., Abdelhalim S. M, Zhao H., and Hu, Z. (1998) The effects of carbon dioxide in exhaust gas recirculation on diesel engine emissions, *Proceedings of the IMechE Part D Journal of Automobile Engineering*, Vol. 212, pp.25–42.
- [11] Tsolakis A. (2006) Effects on Particle Size Distribution from the Diesel Engine Operating on RME-Biodiesel with EGR, *Energy&Fuels*, Vol.20, pp1418–1424.
- [12] Tsolakis, A., Megaritis, A., Wyszynski, M.L., and Theinnoi, K. (2007) Engine Performance and Emissions of a Diesel Engine Operating on Diesel-RME (Rapeseed Methyl Ester) Blends with EGR (Exhaust Gas Recirculation), *Energy*, Vol. 32, pp.2072–2080.