



## Fuels combustion effects on a passive mode silver/alumina HC-SCR catalyst activity in reducing NO<sub>x</sub>

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### ABSTRACT

The activity of a Ag/Al<sub>2</sub>O<sub>3</sub> catalyst in reducing NO<sub>x</sub> emissions in a passive mode hydrocarbon selective catalytic reduction (HC-SCR) was investigated using exhaust gas from the diesel engine operation on diesel, biodiesel (RME) and low temperature Fischer–Tropsch synthetic diesel (SD). The HC<sub>1</sub>:NO<sub>x</sub> ratio in the engine exhaust from the combustion of these fuels followed the order: diesel > SD > biodiesel and this order was mirrored in the catalyst activity in reducing NO<sub>x</sub> in presence of hydrogen (1000 ppm). Compared to diesel fuel, biodiesel combustion produces a higher amount of NO<sub>x</sub> with reduced concentrations of HCs, while both HC and NO<sub>x</sub> emissions were reduced in the engine exhaust from the combustion of SD fuel. Although, a higher NO<sub>x</sub> reduction in the SCR process was seen in the case of diesel fuelling, due to higher HC<sub>1</sub>:NO<sub>x</sub> ratio in the engine exhaust compared to biodiesel (RME) and SD, at low exhaust temperatures (190 °C) there was a gradual loss of the catalyst, NO<sub>x</sub> reduction activity. The incorporation of EGR within the engine operation, increased significantly HC<sub>1</sub>:NO<sub>x</sub> ratios in the exhaust, mainly by lowering the NO<sub>x</sub> concentration. Under these conditions, which can assumed to represent typical HC<sub>1</sub>:NO<sub>x</sub> ratios of a modern automotive diesel engine, higher NO<sub>x</sub> conversion was seen with SD, followed by diesel and biodiesel. For all the cases examined here the SD fuelling provides the lowest tailpipe NO<sub>x</sub> emissions. Hydrogen addition, i.e. at 500, 1000, 1500 and 3000 ppm in the passive mode Ag/Al<sub>2</sub>O<sub>3</sub> SCR catalyst needs to be optimized for the different HC<sub>1</sub>:NO<sub>x</sub> ratios and hydrocarbon species in the exhaust from the combustion of the three fuels.

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### 1. Introduction

To date, several methods have been proposed as a way to reduce NO<sub>x</sub> and PM emissions in diesel engines, and catalytic aftertreatment systems such as NO<sub>x</sub> traps, Selective Catalyst Reduction (SCR) using urea, Diesel Oxidation Catalysts (DOCs) and Diesel Particulate Filters (DPF) have proved to be the most effective [e.g. 1]. The selective catalytic reduction of NO<sub>x</sub> emissions in diesel engine exhaust gas with hydrocarbons (HC-SCR) has attracted considerable interest [e.g. 2]. Silver on alumina (Ag/Al<sub>2</sub>O<sub>3</sub>) catalysts are seen as the main candidates for this technology, and have been investigated in a laboratory and engine environment with model hydrocarbons and diesel fuel [e.g. 3–9]. However, there is only limited information on the activity of these catalysts under passive mode operation (no external hydrocarbon addition) and how the different species

in a diesel engine exhaust (i.e. C-containing) from the combustion of the different fuels can influence their activity performance in reducing NO<sub>x</sub> emissions.

The combustion of different diesel-type fuels (i.e. diesel, synthetic diesel (SD), biodiesel) produces exhaust with a range of HC:NO<sub>x</sub> ratios and hydrocarbon species that are mainly dependant on the physical and chemical properties of the fuels used for combustion. In Ag/Al<sub>2</sub>O<sub>3</sub> HC-SCR, hydrocarbon concentration and composition are very influential in the effectiveness of the catalyst in removing NO<sub>x</sub> emissions under lean conditions [4–6]. At low exhaust temperatures, increased carbon and nitrate species can deposit on the catalyst and reduce significantly the NO<sub>x</sub> removal efficiency [5,10–12]. Recently, we have reported that in order to avoid catalyst deactivation at low temperatures a balance between accumulation rate and oxidation rate of these species on the catalyst surface is required. This can possibly be achieved by controlling the concentration of hydrocarbon emissions reaching the SCR catalyst, i.e. engine out and quantity of the hydrocarbons injected (active control) [5,7]. In addition, hydrogen in small concentrations (less than 1500 ppm) apart from improving the catalyst activity in reducing NO<sub>x</sub> emission, can also keep the catalyst clean by enhancing NO to NO<sub>2</sub> oxidation over the catalyst that helps

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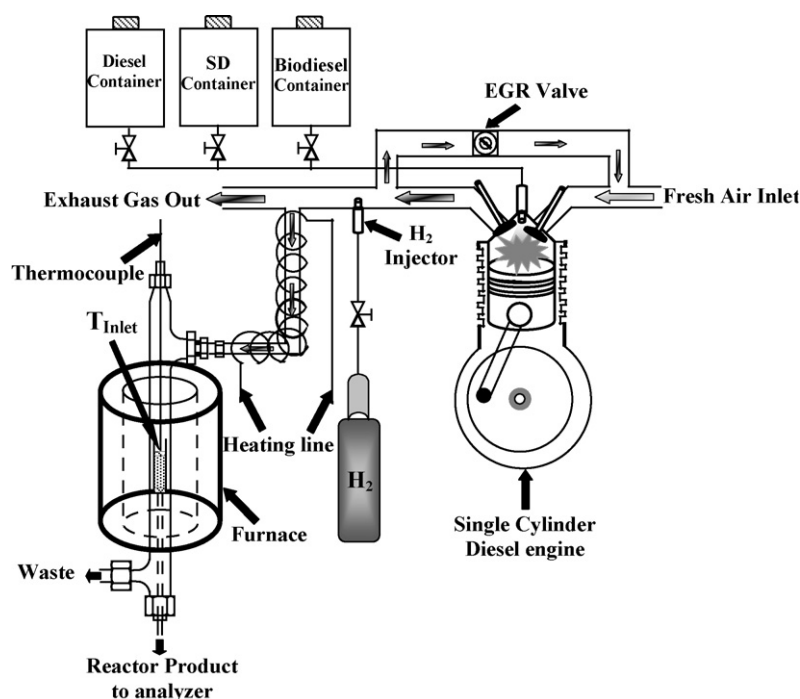


Fig. 1. Schematic diagram of diesel engine with SCR mini-reactor system.

in oxidizing the C-containing species (i.e. liquid fuel, soot) [5,6]. Hydrogen oxidation over the catalyst can also assist in maintaining the catalyst free of poisoning compounds through the increase of temperature and chemical interaction with the poisonous species [7,8].

In an earlier SCR study [13–20] using the same catalyst with simulated engine exhaust gas (e.g. CO, CO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>O, O<sub>2</sub> in N<sub>2</sub>), when diesel fuel was injected in the SCR system, the catalyst activity window was expanded to lower temperatures when compared to model hydrocarbons (e.g. octane, decane, dodecane). Catalyst deactivation was seen with both diesel fuels (synthetic and standard) but at low temperatures the maximum NO<sub>x</sub> conversion was enhanced and the rate of catalyst deactivation was weaker when the longer chain free of aromatic hydrocarbons synthetic diesel fuels was used and compared to diesel.

In this work the Ag/Al<sub>2</sub>O<sub>3</sub> HC-SCR catalyst activity in reducing NO<sub>x</sub> emissions was examined under passive mode operation (no external fuel injection) with actual exhaust gas from the diesel engine operating on diesel, biodiesel (RME) and synthetic diesel (SD) fuels. The effect of unburned hydrocarbons from these fuels with different H<sub>2</sub> additions under real diesel engine conditions as well as the effect of introducing EGR within the engine operation in order to vary the HC<sub>1</sub>:NO<sub>x</sub> ratio and hydrocarbons concentration were studied.

## 2. Experimental

The experimental apparatus was set up as detailed in Fig. 1. The Lister Petter TR1 diesel engine was used for this study as a source of exhaust gas in the SCR converter. The engine is a single cylinder, direct injection and the test rig has been described in more details in previous work [7,8,21]. 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 N m at 1800 rpm. This study was conducted at three engine loads of 2, 4 and 5 bar Indicated Mean Effective Pressure (IMEP) for engine fuelling on diesel (Ultra Low Sulphur Diesel), biodiesel (Rapeseed Methyl Ester) and synthetic diesel (SD). The fuels used were provided by Shell Global Solutions, UK and their properties are given in Table 1.

A part of the engine exhaust gas was cooled and recycled from the engine exhaust to the inlet (external EGR) and the volumetric flow rate of the EGR was calculated based on the reduction in the air volumetric flow rate. The effect of hydrogen concentration (500, 1000 and 3000 ppm) was investigated without the injection of any fuel into the HC-SCR mini-reactor system (passive mode).

The SCR mini reactor was located in a tubular furnace (Fig. 1). The H<sub>2</sub> was introduced and mixed with the engine exhaust gas before

Table 1  
Fuels properties.

| Fuel analysis                          | Method     | Diesel (ULSD) | Synthetic diesel (SD) | Biodiesel (RME) |
|--|------------|---------------|-----------------------|-----------------|
| Cetane number                          | ASTM D613  | 53.9          | 80                    | 54.7            |
| Density at 15 °C (kg m <sup>-3</sup> ) | ASTM D4052 | 827.1         | 784.6                 | 883.7           |
| Viscosity at 40 °C (cSt)               | ASTM D445  | 2.467         | 3.497                 | 4.478           |
| 50% distillation (°C)                  | ASTM D86   | 264           | 295.2                 | 335             |
| 90% distillation (°C)                  | ASTM D86   | 329           | 342.1                 | 342             |
| LCV (MJ kg <sup>-1</sup> )             |            | 42.7          | 43.9                  | 39              |
| Sulphur (mg kg <sup>-1</sup> )         | ASTM D2622 | 46            | 0.05                  | 5               |
| AROMATIC (wt%)                         |            | 24.4          | <0.3                  | –               |
| O <sub>2</sub> (wt%)                   |            | –             | –                     | 10.8            |

**Table 2**

Engine conditions and fuels tested (engine speed 1500 rpm), 0% EGR.

| Fuel      | IMEP (bar) | EGR (vol%) | $T_{inlet}$ (°C) | O <sub>2</sub> (vol%) | HC (ppm) | NO <sub>x</sub> (ppm) | HC:NO <sub>x</sub> | BSN |
|-----------|------------|------------|------------------|-----------------------|----------|-----------------------|--------------------|-----|
| Diesel    | 2          | 0          | 190              | 16.2                  | 413      | 359                   | 1.2                | 0.2 |
|           | 4          | 0          | 250              | 14.6                  | 418      | 622                   | 0.7                | 0.7 |
|           | 5          | 0          | 300              | 12.5                  | 428      | 948                   | 0.5                | 2   |
| SD        | 2          | 0          | 190              | 16.9                  | 182      | 208                   | 0.9                | 0.1 |
|           | 4          | 0          | 250              | 13.9                  | 280      | 494                   | 0.6                | 0.6 |
|           | 5          | 0          | 300              | 12.2                  | 385      | 697                   | 0.6                | 1.8 |
| Biodiesel | 2          | 0          | 190              | 16.6                  | 228      | 330                   | 0.7                | 0.1 |
|           | 4          | 0          | 250              | 13.6                  | 319      | 732                   | 0.5                | 0.5 |
|           | 5          | 0          | 300              | 12.2                  | 370      | 1025                  | 0.4                | 1.2 |

a fraction (3 l/min) of the whole exhaust gas is directed through the powdered catalyst packed bed. The exhaust gas temperature at the inlet of the catalyst was controlled by means of a temperature controller and kept equal to the actual exhaust gas temperature measured 30 cm downstream the engine exhaust valve.

A generic silver catalyst (2 wt%) was prepared by impregnating  $\gamma$ -alumina (surface area  $\sim 150 \text{ m}^2/\text{g}$ ) with aqueous  $\text{AgNO}_3$ , before drying and calcining (in air for 2 h at  $500^\circ\text{C}$ ). It was prepared as a powder, which was then granulated (for packed-bed testing). For each test 0.6 g (particle size  $250 < d < 355 \mu\text{m}$ ) of catalyst were used with a gas mixture flow rate of 3 l/min.

Gas analysis included measurement of carbon dioxide, carbon monoxide (NDIR–Non-Dispersive Infrared), hydrocarbons (FID–Flame Ionization Detector), oxygen (electrochemical method) and  $\text{NO}_x$ –NO (chemiluminescence) emissions.  $\text{H}_2$  and  $\text{N}_2\text{O}$  concentrations (the last is not shown as it was significantly lower) were measured by gas chromatography. For all the conditions, upstream and downstream the catalyst measurements of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), HC and  $\text{N}_2\text{O}$  were recorded. These measurements allowed us to distinguish between  $\text{NO}_x$  reduction and NO oxidation, and to determine the selectivity of  $\text{NO}_x$  reduction to  $\text{N}_2$ . Engine smoke was measured using a Bosch smoke meter and the readings are shown as Bosch Smoke Number (BSN).

### 3. Results and discussion

#### 3.1. Effect of exhaust gas temperature and composition

The combustion of oxygenated biodiesel (RME) increases  $\text{NO}_x$  emissions in the engine exhaust, a trend that is mainly dependant on both fuel type and engine design. Similarly high cetane number paraffinic synthetic diesel (SD) reduces  $\text{NO}_x$  emissions, while both type of fuels reduce HC emissions in the exhaust compared to diesel and hence affect the aftertreatment systems performance (Table 2).

The  $\text{NO}_x$  conversion over the silver SCR catalyst in the absence of hydrogen was similar for all the exhaust gas compositions and temperatures (Fig. 2). The actual exhaust temperature was varied by increasing the engine load from 2 to 4 bar and 5 bar IMEP and the temperatures were replicated at the inlet of the SCR catalyst by the mean of tubular furnace.

Hydrogen addition, i.e. 1000 ppm, magnified the influence of HC:NO<sub>x</sub> ratios and hydrocarbons quality from the combustion of the three fuels, on the passive mode catalyst activity (Figs. 2 and 3). The catalyst activity along the different engine conditions was in order of diesel > SD > biodiesel. The  $\text{NO}_x$  emission measurements were taken for 10 min (Fig. 3) after the inlet temperature was steady at each temperature point. In Fig. 2 only the final  $\text{NO}_x$  conversion recorded after 10 min is shown.

At low exhaust gas temperatures ( $\sim 190^\circ\text{C}$ , engine load 2 bar IMEP), with the presence of 1000 ppm  $\text{H}_2$ , the passive mode HC-SCR catalyst with diesel, shows significantly higher  $\text{NO}_x$  conversion (>90%, result is not directly shown) at the beginning of the tests,

compared to RME and SD (<50%), but the catalyst activity was rapidly declining down to approximately 60% after 10 min (e.g. Figs. 2 and 3). For diesel fuelling a higher amount of C-containing species, resulted in these being progressively adsorbed onto the surface of the catalyst, promoting catalyst deactivation [5,12]. For the engine fuelling with SD or biodiesel the loss in the SCR activity at isothermal conditions, was less notable than diesel, revealing that for diesel fuelling higher  $\text{H}_2$  additions are required (Fig. 3). According to Arve et al. [22] high molecule hydrocarbons (i.e. diesel fuel) are more effective in inhibit NO adsorption on the  $\text{Ag}/\text{Al}_2\text{O}_3$  catalyst active sites, resulting in reduced catalyst activity. It can be speculated that apart from the amount of hydrocarbons that influences the catalyst deactivation, the molecules of the diesel fuelling combustion by products (i.e. HC; Particulate Matter, PM) are having molecule sizes higher than the ones produced for the SD and RME fuelling. Un-combusted fuel especially for diesel and RME fuelling, may condensed more rigorously on the surface of the catalyst.

At higher engine loads (e.g. 4 bar IMEP) and exhaust gas temperatures (i.e.  $250^\circ\text{C}$ ) the HC:NO<sub>x</sub> ratios in the engine exhaust were reduced for all the fuels (Table 2). The HC:NO<sub>x</sub> reduction was more significant for diesel, resulting in a considerable drop in  $\text{NO}_x$  conversion over the SCR catalyst. The higher competition between C-species oxidation and  $\text{NO}_x$  reduction reaction, as hydrocarbons/soot oxidation with oxygen or  $\text{NO}_2$  [23] gradually becomes more dominant due to the increased temperature and  $\text{NO}_2$  concentration. Even for diesel exhaust, loss in the catalyst  $\text{NO}_x$  reduction activity was seen (Fig. 3).

Hydrogen effectiveness in helping oxidize the carbonaceous impurities was more obvious in biodiesel fuel combustion followed by SD (Fig. 3). Despite the low  $\text{NO}_x$  conversion rates, at higher temperatures the amount of  $\text{NO}_x$  converting to  $\text{N}_2$ , was significantly improved for all the fuels. Reduced diffusion limitations in the

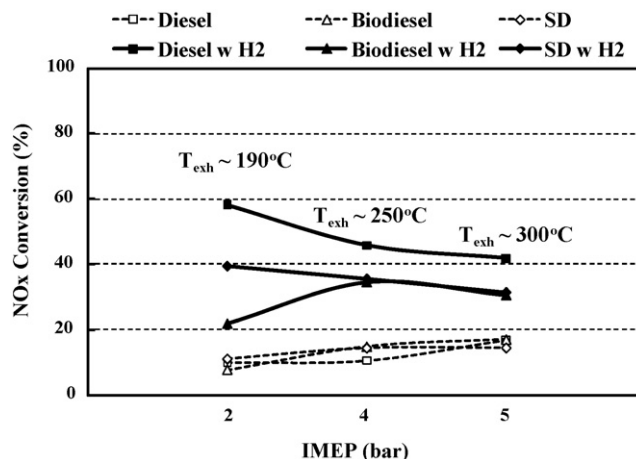


Fig. 2.  $\text{NO}_x$  conversion from the engine fuelling with diesel, biodiesel and SD at different engine loads at 1500 rpm speed. Hydrogen addition 0 and 1000 ppm.

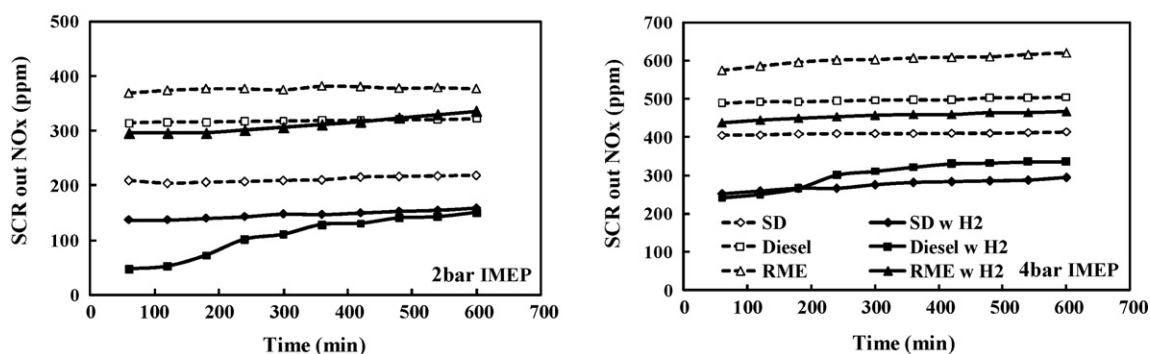


Fig. 3. NO<sub>x</sub> emissions measured after the SCR. Engine speed of 1500 rpm, 0% EGR, 0 and 1000 ppm H<sub>2</sub> for engine load of 2 bar ( $T = 190^{\circ}\text{C}$ ) and 4 bar ( $T = 250^{\circ}\text{C}$ ) IMEP.

Table 3

Engine conditions and fuels tested (engine speed 1500 rpm), 20% EGR.

| Fuel      | IMEP (bar) | EGR (vol%) | $T_{\text{inlet}}$ ( $^{\circ}\text{C}$ ) | O <sub>2</sub> (vol%) | HC (ppm) | NO <sub>x</sub> (ppm) | HC:NO <sub>x</sub> | BSN |
|-----------|------------|------------|---|-----------------------|----------|-----------------------|--------------------|-----|
| Diesel    | 2          | 20         | 200                                       | 15.62                 | 424      | 216                   | 2.0                | 0.5 |
|           | 4          | 20         | 260                                       | 13.3                  | 444      | 386                   | 1.2                | 1.3 |
|           | 5          | 20         | 310                                       | 9.6                   | 462      | 598                   | 0.8                | 3.6 |
| SD        | 2          | 20         | 200                                       | 15.99                 | 191      | 127                   | 1.5                | 0.4 |
|           | 4          | 20         | 260                                       | 12.29                 | 293      | 241                   | 1.2                | 1.1 |
|           | 5          | 20         | 310                                       | 9.87                  | 396      | 490                   | 0.8                | 3.0 |
| Biodiesel | 2          | 20         | 200                                       | 15.59                 | 233      | 239                   | 1.0                | 0.3 |
|           | 4          | 20         | 260                                       | 11.8                  | 327      | 418                   | 0.8                | 0.7 |
|           | 5          | 20         | 310                                       | 10.21                 | 381      | 525                   | 0.7                | 1.8 |

SCR (more available active sites due to clean catalyst surface) and increased probability of the reactants (HCs–NO<sub>x</sub>–H<sub>2</sub>) adsorption on the catalyst active sites, instead of passing through, are also made a contribution to hydrogen effectiveness.

### 3.2. The effect of EGR

The incorporation of exhaust gas recirculation (EGR) within the engine operation, increases the HC<sub>1</sub>:NO<sub>x</sub> ratio in the SCR system, primarily due to large NO<sub>x</sub> emissions reduction (Table 3). The engine NO<sub>x</sub> emissions reduction (ppm) was more significant for the biodiesel fuelling, a trend that we have previously explained [24]. In addition, there is also an increase in C-containing species such as HCs and smoke as illustrated in Table 3. At low temperatures ( $\sim 190^{\circ}\text{C}$ ), the SCR catalyst activity is higher for diesel ( $\sim 40\%$ ) followed by SD ( $\sim 35\%$ ) and biodiesel ( $\sim 20\%$ ). As the exhaust temperature increased (i.e. on changing the regime from 2 bar IMEP to 4 and 5 bar), NO<sub>x</sub> conversion in the SCR was significantly improved to approximately 50% for both, biodiesel and SD fuels.

Hydrogen addition (1000 ppm) with EGR enhanced NO<sub>x</sub> conversion to approximately 75 and 90%, respectively, for biodiesel and SD, however at  $190^{\circ}\text{C}$  exhaust temperature there is a gradual loss in the Ag/Al<sub>2</sub>O<sub>3</sub> SCR catalyst activity (e.g. Fig. 5 for 2 bar IMEP). Un-optimized HC<sub>1</sub>:H<sub>2</sub> ratios can accelerate C-containing species deposition onto the catalyst surface as we reported in our earlier work [25] and can be seen in Figs. 3 and 5. Although, Ag/Al<sub>2</sub>O<sub>3</sub> catalyst design can further be modified, to enhance HC oxidation, some loss in SCR process of NO<sub>x</sub> is expected.

At low exhaust temperatures, apart from the hydrocarbons, Particulate Matter (PM) and soot can also play an important role in catalyst activity and deactivation. In PM a large portion of the soluble organic fraction is adsorbed onto the soot layer leading to sticky particles which can cover the catalyst active sites without being able to be oxidized. As the temperature rises the catalyst can more effectively oxidize or even use in the SCR process the hydrocarbons adsorbed on the soot (part of the PM), strip off the soot/carbon that can blow out or possibly, but less likely, be oxidized on the catalyst

[23]. The combustion of fuels such as RME and SD are reported to reduce PM concentration in the exhaust gas but also to produce PM free of soot or with lighter SOF (soluble organic fraction) adsorbed on the soot that are more likely to be oxidized [26]. Base metal catalysts such as Ag/Al<sub>2</sub>O<sub>3</sub> catalyst used in this study are reported to be able to capture and also oxidize PM [27].

Modern diesel engines in order to control NO<sub>x</sub> emissions, are operated with large EGR percentages (up to 50 vol%), so if the proposed or improved version of the SCR catalyst find an application in a diesel engine, hydrogen addition among other technologies (e.g. engine recalibration), can be proposed as a solution to prevent catalyst deactivation under passive operation and improve low temperature activity (Figs. 4 and 5).

For the synthetic diesel and biodiesel combustion with EGR, NO<sub>x</sub> conversion over the SCR at temperature range of  $250\text{--}300^{\circ}\text{C}$  was improved by approximately 30% as the quantity of HC<sub>1</sub>:NO<sub>x</sub> was

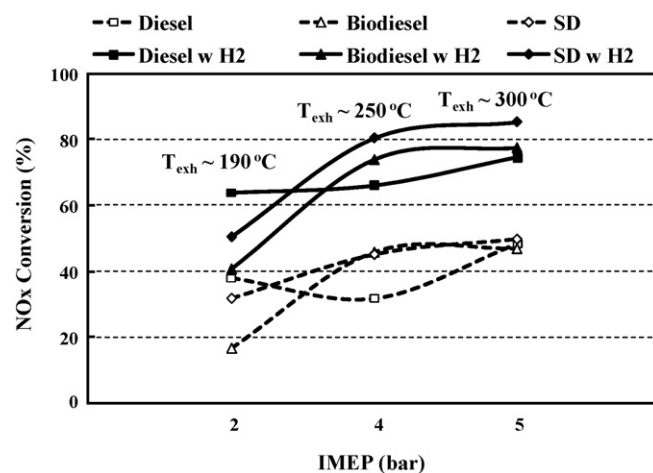


Fig. 4. HC-SCR activity in reducing NO<sub>x</sub> from the engine operation with 20% EGR for diesel, biodiesel and SD engine fuelling. H<sub>2</sub> = 1000 ppm.

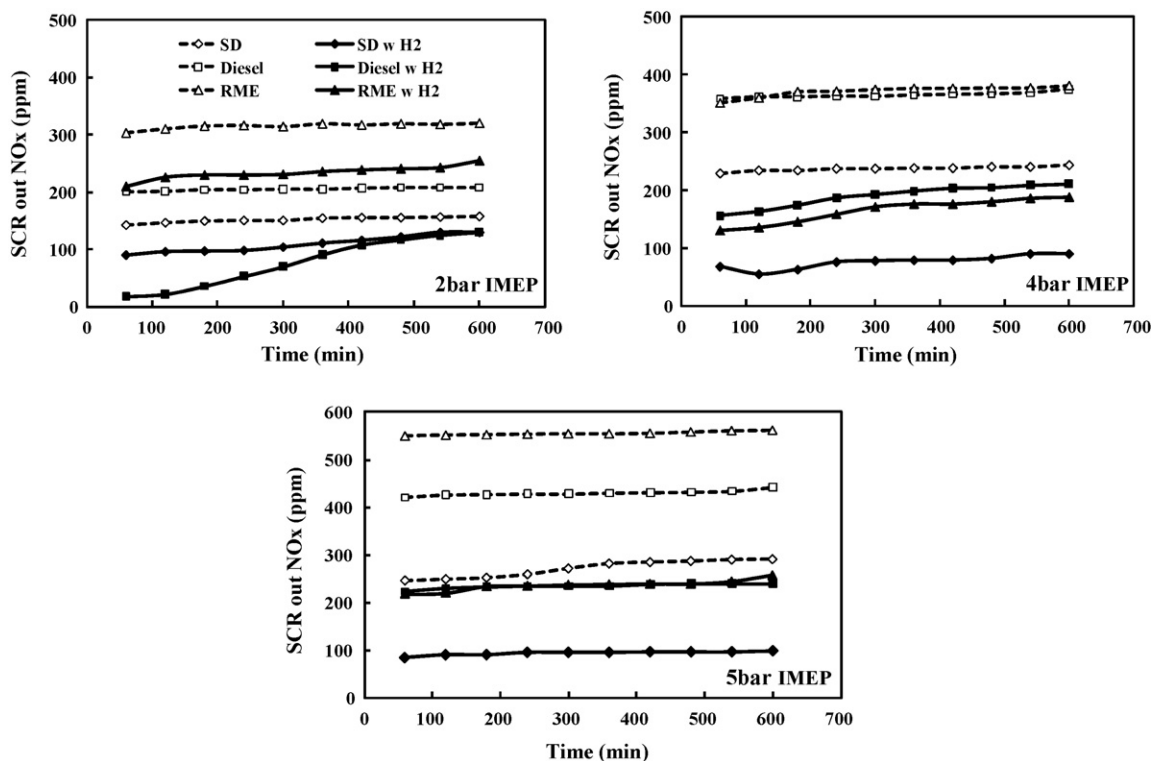


Fig. 5. NO<sub>x</sub> emissions measured after the SCR. Engine speed of 1500 rpm, 20% EGR, 0 and 1000 ppm H<sub>2</sub> for engine load of 2 bar ( $T=190^{\circ}\text{C}$ ), 4 bar ( $T=250^{\circ}\text{C}$ ), IMEP and 5 bar ( $T=300^{\circ}\text{C}$ ).

near optimum for the 1000 ppm H<sub>2</sub> addition. The NO<sub>x</sub> conversion trends (diesel > SD > biodiesel) seen over the SCR in the absence of H<sub>2</sub> at temperature of approximately  $190^{\circ}\text{C}$  for the three fuels were similar when 1000 ppm H<sub>2</sub> was introduced, but about 20–25% higher. These SCR activity/deactivation trends seen with the combustion of the three fuels cannot be fully explained with the analysis carried out. However, it is believed that it is related to a combination of (a) the HC:NO<sub>x</sub> ratios which was higher for diesel and (b) the range of hydrocarbons in the exhaust, that are expected to be more active from the simple component fuel (i.e. synthetic) compared to biodiesel and diesel [5,25]. The use of EGR significantly increases smoke and PM (soot and SOF) conditions that accelerate the loss in catalyst activity as can also be seen in Fig. 5. Engine fuelling with synthetic diesel such as gas-to-liquid (GTL) or biodiesel fuel is reported to be more tolerant to EGR percentages mainly due to cleaner combustion and reduced smoke/PM emissions, e.g. Table 3 and [24]. This can further enhance the Ag/Al<sub>2</sub>O<sub>3</sub> SCR catalyst in removing NO<sub>x</sub> emissions especially at high loads where the engine is less tolerant to EGR.

### 3.3. Effect of hydrogen concentration

Previous studies have shown that H<sub>2</sub> addition increases the performance of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts at low temperature operating conditions ( $<350^{\circ}\text{C}$ ) [19,28–31]. Satsuma et al. reported that hydrogen addition enhanced the rate of the SCR-NO<sub>x</sub> reaction by formation of small metallic charged Ag<sup>+</sup> clusters [15]. In this work the effect of hydrogen additions (i.e. approximately 500, 1000 and 3000 ppm) over a passive SCR system with engine exhaust gas from the combustion of the three fuels was investigated using exhaust and conditions from the low load engine operation (i.e. 2 bar IMEP). The NO<sub>x</sub> conversion activity for diesel, SD and biodiesel fuelling was significantly promoted by increasing the H<sub>2</sub> amounts (Fig. 6). Hydrogen addition enhances the SCR catalyst performance and its effectiveness is dependant on

the engine exhaust gas quality from the combustion of the three fuels.

In the combustion of diesel and synthetic diesel fuels, the exhaust gas contained enough unburnt hydrocarbon (HC<sub>1</sub>), that can be utilized in the presence of increased hydrogen addition to improve the catalyst activity in reducing NO<sub>x</sub> emissions. The maximum NO<sub>x</sub> reduction peaked at approximately 70% in the presence of 3000 ppm hydrogen and occurred in both diesel and synthetic diesel fuels. However, the diesel fuel combustion exhibited higher rates of deactivation meaning that greater amounts of H<sub>2</sub> are required to maintain constant NO<sub>x</sub> reduction. The silver catalyst exhibits strong selectivity for the removal of NO<sub>x</sub> in the synthetic fuel exhaust gas due to HC<sub>1</sub>:NO<sub>x</sub> ratios and operating temperature being near optimum. In addition the reduced NO<sub>x</sub> concentration from the combustion of SD fuel compared to diesel and biodiesel can reduce nitrate species formation and catalyst poisoning [11].

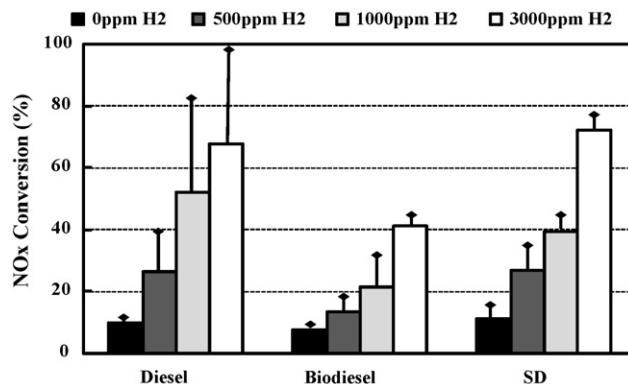


Fig. 6. The effect of H<sub>2</sub> additions. Engine speed of 1500 rpm, engine load of 2 bar IMEP ( $T=190^{\circ}\text{C}$ ).

In the biodiesel fuelling, increasing the amount of hydrogen led to the lowest observed activity, mainly due to lowest HC<sub>1</sub>:NO<sub>x</sub> ratios.

#### 4. Conclusions

The use of Ag/Al<sub>2</sub>O<sub>3</sub> catalysts in a passive mode HC-SCR system shows good NO<sub>x</sub> reduction under the different HC<sub>1</sub>:NO<sub>x</sub> ratios, followed the order diesel > SD > RME when the respective fuels are used for combustion. Additionally, introduction of optimized H<sub>2</sub> concentrations to reduce catalyst deactivation is required under high HC<sub>1</sub>:NO<sub>x</sub> ratios at low temperatures in order to achieve maximum NO<sub>x</sub> conversion efficiencies.

The combustion of biodiesel resulted in a lower rate of NO<sub>x</sub> reduction over the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, in the presence of hydrogen, compared to SD and diesel fuelled combustion due to the lower HC<sub>1</sub>:NO<sub>x</sub> ratios; high values of which are necessary for the NO<sub>x</sub> reduction reaction. At the low operating temperature conditions (~190 °C), diesel fuel led to more noticeable deactivation of the catalyst, but in contrast, biodiesel and SD fuelled combustion did not possess this dramatic deactivation characteristic. At the higher temperatures, it can be pointed out that the presence of hydrogen alone does not effectively reduce the NO<sub>x</sub> concentration, but hydrocarbon presence is also essential to achieve Ag/Al<sub>2</sub>O<sub>3</sub> catalyst activity for NO<sub>x</sub>, especially in terms of biodiesel fuelled combustions.

The use of EGR reduces the NO<sub>x</sub> emissions and at the same time enhances the HC:NO<sub>x</sub> ratios in the exhaust gas. EGR use with H<sub>2</sub> addition, in the case of biodiesel and SD fuels, dramatically improved the NO<sub>x</sub> conversion over the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst due to the comparatively cleaner combustions which produce less, hydrocarbons, smoke and PM (soot + VOF) as opposed to that of diesel fuel. However, in the case of diesel combustion, higher concentrations of H<sub>2</sub> are required to improve the catalyst activity. As a result, optimized HC<sub>1</sub>:H<sub>2</sub> ratios are very important for the improvement of the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst activity under different engine operating conditions.

From the work presented here and in accordance with the available literature it can be concluded that, engine fuel quality can influence significantly the performance of the aftertreatment systems in reducing emissions. Fuels such as synthetic diesel can also contribute in the improved engine-aftertreatment system efficiency and contribute in achieving future emissions regulations that include control of CO<sub>2</sub>.

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