

Rapidly Pulsed Reductants in Diesel NO_x Reduction by Lean NO_x Traps: Effects of Mixing Uniformity and Reductant Type

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ABSTRACT

Lean NO_x Traps (LNTs) are one type of lean NO_x reduction technology typically used in smaller diesel passenger cars where urea-based Selective Catalytic Reduction (SCR) systems may be difficult to package. However, the performance of lean NO_x traps (LNT) at temperatures above 400 °C needs to be improved. The use of Rapidly Pulsed Reductants (RPR) is a process in which hydrocarbons are injected in rapid pulses ahead of a LNT in order to expand its operating window to higher temperatures and space velocities. This approach has also been called Di-Air (diesel NO_x aftertreatment by adsorbed intermediate reductants) by Toyota. There is a vast parameter space which could be explored to maximize RPR performance and reduce the fuel penalty associated with injecting hydrocarbons. In this study, the mixing uniformity of the injected pulses, the type of reductant, and the concentration of pulsed reductant in the main flow were investigated. We found that all of these parameters are important for the RPR system performance.

To obtain a uniformity of flow with the injected species to approach that of a plug flow, we developed a design using specific mixers to maximize the performance of RPR. The initial hypothesis for the required mixing process was to uniformly mix the injected reductants with the main flow in the radial direction, while keeping the axial mixing as low as possible. This goal was achieved by incorporating different mass transport processes, i.e. advection in the radial direction, and diffusion in the axial direction. Numerical investigation of the mixing of high frequency pulsed gaseous hydrocarbons into the main exhaust flow was performed to design an effective mixer to satisfy the desired mixing conditions. This mixing process and a fast injection system (down to 1 ms pulse duration) was shown to have uniform radial mixing and axially separated pulses of reductants that gave the optimal mixing condition and achieved the highest RPR NO_x conversion performance.

Employing the designed mixer, a range of reductants (H₂, CO, C₂H₄, C₃H₆, and C₃H₈) were tested under similar operating conditions over a Pt/Rh LNT. The effectiveness of different reductants for NO_x conversion in different temperature regimes was found to be as follows: T < 270 °C: H₂ > CO > C₃H₆ > C₂H₄; 270 °C < T < 500 °C: C₃H₆ > H₂ > CO > C₂H₄; T > 500 °C: C₃H₆ > C₂H₄ > H₂ ~ CO. In terms of the selectivity of converted NO_x, H₂ resulted in significant ammonia formation at low temperatures, but overall, the N₂ selectivity was as follows: CO ~ C₃H₆ > C₂H₄ >> H₂. Generally, it was concluded that hydrocarbon reductants provided higher NO_x conversion in the mid-range and especially higher temperature ranges with relatively high nitrogen selectivity. However, it was observed that the reactivity of hydrocarbons and the availability of oxygen had a significant influence on their performance, especially as the pulsing frequency was increased and reduction reaction time became more limited.

In this study we have shown that the use of rapidly pulsed reductants (RPR) can be studied in the laboratory with the equipment and methods presented here. In studies with a LNT catalyst, the variations in NO_x performance with several reductants at reasonably high frequencies were shown. This suggests that this system should be able to provide useful information for optimizing the performance of LNT catalysts at high temperatures.

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INTRODUCTION

New standards on fuel economy of vehicles and stringent regulations on greenhouse gases encourage the use of lean burn GDI and diesel engines for their inherently higher fuel conversion efficiency [1, 2].

Although lean combustion achieves higher thermal efficiency, lean NO_x emissions control is challenging especially with more stringent regulations such as the U.S. light duty Tier 3 and Europe's New Driving Emission (RDE) regulations. Two current diesel NO_x

aftertreatment approaches, Selective Catalytic Reduction (SCR) with aqueous urea and Lean NO_x Traps (LNTs), would require modifications to satisfy the upcoming regulations. For instance, vehicles equipped with SCR are expected to have a 50% increase in urea consumption from current Euro 6 levels to meet future RDE requirements [3].

LNTs, which use a NO_x storage and reduction (NSR) process, are employed mostly on diesel passenger cars and have been studied extensively to determine the effect of hydrocarbon type, pulsing parameters, reactions pathways etc. Li et al. have found that the overall NO_x conversion under cyclic lean/rich conditions is dependent on the balance of lean/rich timing. The NO_x conversion at moderate temperatures, 250 - 400°C, was found to be a direct function of reaction stoichiometry. That is, the quantity of trapped NO_x under lean conditions must be balanced by the quantity of reductants during the rich step. On the other hand, reaction kinetics dominate the performance at lower temperatures, while decreases in the NO_x storage capacity limit the performance at higher temperatures [4].

Hydrocarbon reductants have been shown to be more effective for NO_x conversion at higher temperatures as compared with CO, possibly due to the higher desorption temperature of HC components. Hydrogen was observed to be a better reductant at lower temperatures, however as the temperature increases the performance drops due to non-selective consumption of H₂ in the system [5, 6]. As far as reaction products are concerned, ammonia is formed during regeneration due to H₂ rich condition. In addition, using in situ FTIR, Ba and Al isocyanates have been observed on the Pt-Rh/Ba/Al₂O₃ catalyst (spillover from the precious metal sites) during regeneration with CO; subsequent isocyanate hydrolysis has been proposed as the pathway to NH₃ formation when CO is the reductant. Also, at 250 C, the usual inhibiting effect of CO was observed using Operando IR spectroscopy [8, 9].

Overall, one issue with conventional LNT technology is the limited operating temperature window and space velocity, typically 250 to 450°C, to achieve high NO_x conversion. At high engine loads the post-turbo exhaust temperature can exceed 600°C, and space velocity can reach 150,000/h. At these conditions, the NO_x conversion of conventional LNT drops significantly. Therefore, in high load driving cycles the use of urea SCR is preferred and can obtain up to 30% lower emissions versus a LNT [9].

The Di-Air system proposed by Toyota researchers has the capability to expand the viable operating temperature range of LNT catalysts to 600°C and above, as illustrated in Fig.1 [10]. Also, the system allows for higher NO_x conversion at increased space velocities. The system utilizes fast and short cycle pulses of hydrocarbons injected ahead of a conventional LNT catalyst.

Previous studies have been done to find the underlying mechanism of Di-Air, which lead to the conclusion that adsorbed NO_x intermediates generated on the base catalyst and partially oxidized hydrocarbons caused by rapidly pulsed reductants are responsible for the high NO_x conversion of Di-Air. It is not clear whether all of these intermediates contribute to NO_x conversion in Di-Air. Also, it was observed that

intermediates generated from HCs, such as R-NCO and R-CN, are more strongly adsorbed to the surface than the intermediates generated from CO or bulk nitrates, and can adsorb on the catalyst surface for a number of seconds even at temperatures as high as 600°C [11, 12].

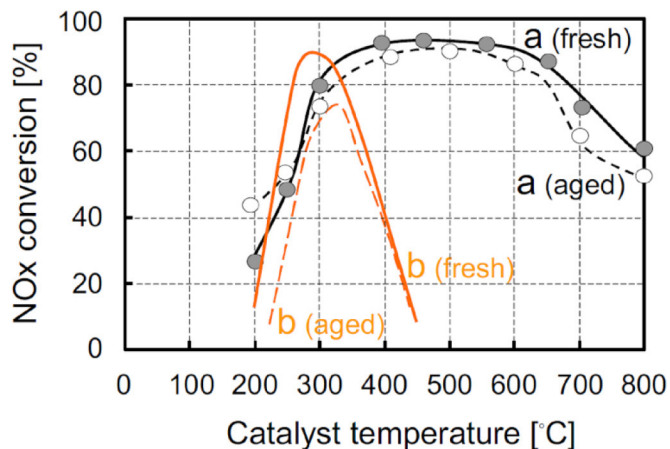


Figure 1. Comparison of conversional LNT (curve b) and Di-Air (curve a), from reference [10].

More recent studies have shown that the decomposition of Ba(NO₃)₂ or the reduction of NO_x storage capacity above 400°C is not the limiting factor in the reaction; instead, the stability of HC intermediates on the surface limits the reaction at temperatures near 600°C. Also, the inhibitory effect of CO₂, or surface carbonates on the NSR reaction is reduced as the pulsing frequency increases, which emphasizes the reduced importance of the storage mechanism [13]. In addition to improved NO_x conversion at high temperatures and space velocities, improved low temperature NO_x conversion is observed over LNT catalysts and more improvement is observed for dual layer LNT+SCR catalyst. However, when using a dual layer LNT+SCR catalyst, the high temperature NO_x conversion drops due to increased mass transfer resistance through the layers [14].

Mixing quality is considered important in many diesel aftertreatment systems [14,15,16,17], such as injected urea in SCR systems and fuel injection for soot filter regenerations, in which a small, secondary flow is injected into a much higher exhaust flow. In these systems, the uniformity of the mixture on the front face of a catalyst, i.e., radial uniformity, is of significant importance. A number of numerical and experimental studies have been performed to analyze and improve mixing of an injected flow into a main exhaust flow in these systems [19,20,21,22]. In all of the previous studies, the performance of RPR was found to be greatly affected by the mixing of injected reductants. Thus, in this study, the separate effects of axial and radial mixing uniformity were investigated. Reductants were injected into the main flow of simulated exhaust gas in a flow reactor, upstream of a mixer and a conventional LNT catalyst. A pneumatic injection system was designed to inject high frequency pulses as low as 1ms in duration.

A numerical and experimental study of the mixing of pulsed propane into a main reactor flow has been performed; an approach has been postulated to obtain near ideal plug flow pulses which are well mixed laterally and well-separated axially. This mixing pattern was initially hypothesized to be suitable for RPR operation. Later this hypothesis

was validated by evaluating the effect of axial and radial mixing on RPR performance. In the first step, using analytic fluid mechanical approaches a general design was proposed. The selected design was fabricated, and an effective method has been employed to empirically evaluate the mixing quality and the effect of some mixer arrangements and flow parameters on mixing, using a diesel oxidation catalyst (DOC) and fast flame ionization detector (FFID). The results were analyzed and an optimum mixing condition is selected to be used in the rest of the study.

Finally, the effect of reductant type and reactivity on RPR performance using a research Pt/Rh LNT sample is investigated by injecting hydrogen and carbon monoxide, as well as three different gaseous hydrocarbons, propane, propylene and ethylene as reductants. The results were analyzed to specify the performance of each reductant, and obtain insight into the underlying mechanism of the RPR process.

DESIGN AND DEMONSTRATION OF QUASI-PLUG FLOW RAPID REDUCTANT INJECTION SYSTEM

Mixer Geometry Design and Numerical Simulation

The design objective is to provide a mixing condition in which the injected reductant (propane here) is completely mixed in the radial direction of the test tube, but pulses are well separated in the axial direction. In other words, a condition in which the radial mass transfer rate is higher than the axial mass transfer rate is most desirable. One approach is to enhance mixing using advection mass transfer in the radial direction, and turbulent diffusion in the axial direction; this can be achieved by injecting HC as a jet in the radial direction. In this case we can relate mass transfer rate into directions by defining the relative turbulent Peclet number as:

$$Pe = \frac{LV_r}{D_t} \quad (1.1)$$

where V_r is the relative jet velocity magnitude with respect to the main flow, L is the advection length scale, which here is equal to tube radius (i.e., $L = R$), and D_t is the turbulent mass diffusivity or eddy diffusivity. D_t is the coefficient of proportionality between the eddy flux ($u'c'$) and the mean concentration gradient ($\nabla \bar{c}$):

$$\overline{u'c'} = -D_t \nabla \bar{c} \quad (1.2)$$

Writing the Peclet number as $Pe = Re_t Sc_t$ would be very helpful since there exist several previous research studies, which have investigated the influence of the turbulent Schmidt number, Sc_t , on the predicted concentration of species, and optimum values of Sc_t for various engineering flow and concentration fields. Although the values 0.7 or 0.9 have been used for most of the CFD studies for turbulent mass diffusion and have been set as the default in most commercial codes, in the case of turbulent jet-in-cross flows values of the turbulent

Schmidt number ranging from 0.2 to 0.8 have been recommended. The effect of Sc_t and its optimum value is currently being investigated and will be discussed in the future.

Evaluation of Different Geometric Designs

Considering the general geometries, we have decided to generate a radial jet by impinging a concentric axial jet to a circular disc located in the center of test tube. After impacting the plate the axial jet deviates to the radial direction and generates the desired flow field. A number of different geometries were investigated to select the most effective one. Thereafter, other flow and arrangement parameters were investigated experimentally on the selected geometry in order to tune the mixer. Depicted in Fig. 2 are the candidate geometries defined to investigate the effect of different shapes on mixing quality. In Cases 1 and 2, a plug nozzle was added to the circular plate which was designed for linear variation of axial velocity in the x-direction, in order to prevent flow separation and reduce the mixer pressure drop. In Cases 3 and 4 a circular outer ring was added to the mixer to generate counter rotating vortex pairs to the flow that were found to be of crucial importance to the mixing process.

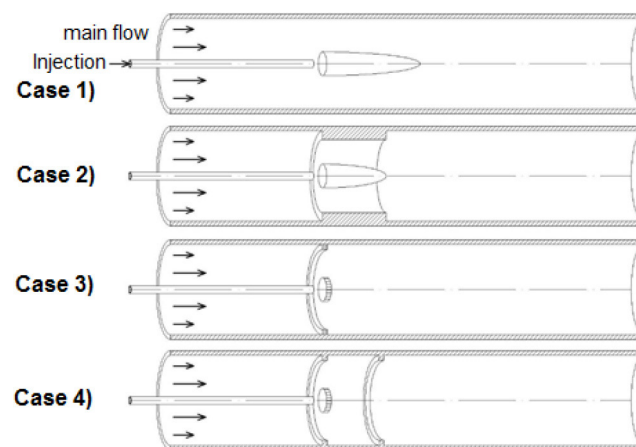


Figure 2. Candidate mixer geometries.

3D unsteady two phase homogenous simulation of mixing was performed using Ansys CFX. A multi zone structured grid with a maximum y^+ value of $y^+=8.6$ was generated. The computational domain was divided by two, and a symmetry boundary condition was used to decrease the computational effort. As a convergence criterion, the computations were continued until the global residuals decreased to less than 10^{-6} for discretized equations for both the steady and unsteady solutions.

A steady state numerical solution of the main flow was used as the initial condition for the unsteady CFD calculations. The inlet boundary condition was set to 4000 sccm of a mixture of 10% oxygen and 90% nitrogen with 5% turbulent intensity, and the outlet was set to uniform zero pressure. An expression was used to define the variable injection mass flow rate with time to inject a mixture of 5% propane and 95% nitrogen as a pulse of 100ms duration.

Turbulence Model

Since the current mixing problem is mostly associated with turbulent diffusion, the choice of turbulence model is critical to obtain acceptable results. Since there was no empirical data available in the beginning of the design procedure, we selected the turbulence model based on the literature. In order to achieve more accurate and robust results, the RNG k- ϵ turbulence model, which is based on a renormalization analysis of Navier-Stokes equations, was employed. The rapidly straining flow and high streamline curvatures, which are present in this case study, make the RNG k- ϵ turbulence model a proper choice with acceptable accuracy and relatively low computational cost [23].

Numerical Simulation Results

Fig.3 depicts contours of main flow concentration in three different time steps (5, 100, and 200ms after the start of injection) for geometries of Fig. 2.

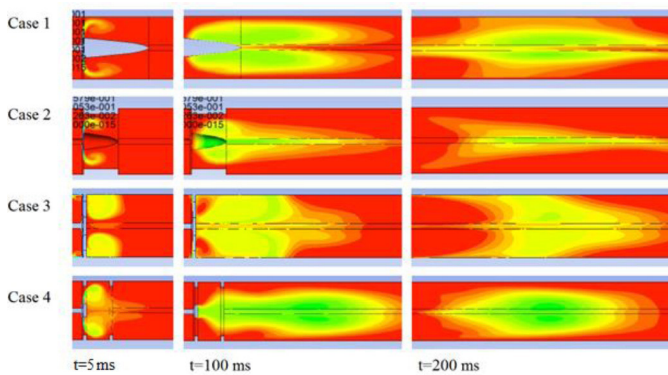


Figure 3. Contours of main flow concentration in three different time steps for cases 1 to 4 (Red shows the regions of main flow, green shows the regions of high reductant concentration).

As shown in Fig. 3, mixers with a plug nozzle (case 1 and 2) did not provide sufficient lateral mixing and tended to bring the injected flow to the center of the tube. This was the result of shear imposed by the relatively high surface area of the plug nozzle. Mixer plates without a plug nozzle (Case 3 and 4) provided better mixing, although they caused a higher pressure drop relative to mixers with a plug nozzle. Cases 3 and 4 utilized thin outer rings located on the surface of the tube. These rings were important, for they generated small counter rotating vortices (COV) near the surface of the tube which COV tended to bring the injected flow towards the surface and changed the parabolic shape of an injected HC front to a near flat distribution, similar to plug flow (see the front surface of injected HC in case 3 at $t=100$ ms). In case 4 another ring was added downstream of the mixer plate to further improve mixing, but the results were unsatisfactory, so case 3 was selected as the general design for the rest of the study. The selected mixer geometry (Case 3) and other structural parts were fabricated from 316 stainless steel using water jet cutting machine to validate the mixing process experimentally and tune the mixer.

Experimental Validation and Mixer Tuning

The mixing measurement procedure incorporates a Combustion fast-FID to measure the HC concentration upstream and downstream of a DOC (Fig. 4) with a very high time resolution. The catalyst used for mixing measurements was a commercial Pt/Pd DOC on a 400 cpsi cordierite monolith with a 4.5 mil wall thickness, 1" in length and 3/4" in diameter. The substrate was bored through in order to fit the FFID upstream probe with 1/8" diameter. The FFID is capable of sampling up to 1400 Hz (every 0.7ms). However, as the sampling rate is increased, noise may appear on the output ports of the unit. Hence, a 200Hz sampling rate was used for the measurements here which provided sufficient time resolution to clearly determine the shape of pulses. Catalyst temperature was measured using a thermocouple located in the core of the DOC monolith.

Measure of Mixing Quality

In order to quantify the mixing quality based on our measurements, an index was chosen that allowed the different systems to be compared. Of the number of methods available in the literature, the most relevant one is Uniformity Index (UI) which is usually defined over the inlet face of the catalyst as:

$$UI(\phi) = 1 - \frac{\sum |\phi_f - \bar{\phi}| A_f}{2\bar{\phi} \sum A_f} \quad (2.1)$$

where $\phi = \phi$ is the fuel to air equivalence ratio. This method is very helpful for our application, since it accounts for the uniformity of air to fuel ratio on the surface of the catalyst. However, it overlooks the axial distribution of ϕ which is considered important for RPR application. Therefore, we have modified this index and defined it as:

$$UI(\phi) = 1 - \frac{\int |\phi - \bar{\phi}| dv}{2\bar{\phi} V} \quad (2.2)$$

which is expressed over the volume of flow (V) and is capable of accounting for the radial uniformity of the HC pulses as well as their axial separation. Consider a single channel of the DOC monolith. One can assume negligible mixing inside the channel due to very small Re number and residence time. Thus, each channel will maintain a sample of $\frac{D\phi}{Dt}$ at the surface of the catalyst. Since we maintain average of $\bar{\phi} = 1$ during our pulses, any local rich regions of the mixture would indicate imperfect mixing. If we use a DOC without any oxygen storage capacity (OSC), the rich regions of the mixture, the red area in Fig.5, will not be completely oxidized and can be detected by measuring the HC breakthrough downstream of DOC, as shown in Fig. 9.

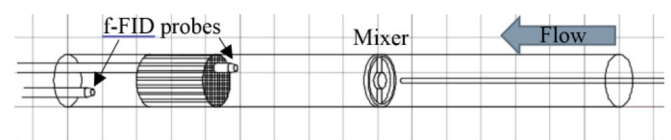


Figure 4. Arrangement of test tube for measurement of mixing uniformity.