Rapidly Pulsed Reductants for Diesel NOx Reduction with Lean NOx Traps:
Global Kinetic Modeling of Operating Regimes

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**Highlights**
- Rich HC pulses are required for high NOx conversion (in lean cycle-averaged flow)
- An optimal pulsing frequency ($f_{\text{m}}$) for RPR is always found that maximizes NOx conversion
- The global kinetic model includes the axial mixing of pulses seen at high frequencies
- Model: $f_{\text{m}}$ results from balance between improved NOx storage & inefficient NOx reduction

1. Introduction
Lean NOx Traps (LNTs) are often used to reduce NOx on smaller diesel passenger cars where urea-based Selective Catalytic Reduction (SCR) systems may be difficult to package. However, the performance of LNTs at temperatures above 400°C needs to be improved. Rapidly Pulsed Reductants (RPR, also known as Di-Air \cite{1}) is a process in which hydrocarbons (HC) are injected in rapid pulses ahead of the LNT in order to improve its performance at higher temperatures and space velocities. A further goal of RPR is to reduce the fuel penalty associated with the fuel injections to regenerate the LNT.

2. Methods
The rapidly pulsed reductants approach was used with a research Pt/Rh LNT formulation 90 gpcf of precious metal (Pt/Pd/Rh = 8/0/1) with no ceria and was studied experimentally using a synthetic flow reactor and a high frequency injection system \cite{2}. The effects of the pulsing frequency, amplitude, duty cycle, temperature, space velocity, and NOx concentration on the NOx conversion and the reaction products were investigated. Fig. 1(a) and 1(b) demonstrate NOx/ethylene conversion and several product distributions as a function of pulsing frequency at constant fuel penalty for a 600°C inlet temperature.

**Figure 1.** RPR frequency sweep at $T_{\text{inlet}} = 600^\circ$C (a) NOx/ethylene conversion and catalyst temperature (b) product selectivity

A global reaction kinetic model including NOx and oxygen storage, steam reforming, water gas shift, and ammonia formation was used. In this model, either a power law or a Langmuir–Hinshelwood structured rate expression is employed. The kinetic parameters were only tuned to fit the low frequency response of the LNT. For this purpose, a wide range (88) of low frequency (60s rich/ 180s lean) switching tests were performed on a differential reactor with varying inlet compositions and temperatures.

3. Results and discussion
We find that at any given temperature, fuel penalty, and space velocity there exists an optimal pulsing frequency ($f_{\text{m}}$) which maximizes the NOx conversion for a range of reductants: hydrocarbons (ethylene,
propylene, propane, dodecane), H₂, and CO and is usually found between 0.5-2 Hz [3]. For the temperature range of 450-600°C, the overall frequency response of the RPR process can be divided into two regimes: low frequencies (i.e., frequencies lower than the optimal frequency) and high frequencies (i.e., frequencies higher than the optimal frequency). The existence of an optimal frequency can be explained as a trade-off between NOx storage efficiency and NOx reduction effectiveness in the low and high frequency regimes as follows: (1) By decreasing the frequency relative to the optimal frequency, the NOx reduction and purging of the LNT becomes very efficient; however, as the lean periods become longer this results in lower NOx storage efficiency and lower overall cycle-averaged NOx conversion. (2) By increasing the frequency relative to the optimal frequency, the storage becomes more efficient due to shorter lean periods, but the effectiveness of the rich pulses for converting the stored NOx and purging the LNT decreases. This is mainly due to axial mixing of the rich pulse which reduces the capability of the pulse to effectively react with the stored NOx.

Figure 2. Cycle-averaged NOx conversion from bench reactor and the model. The kinetic model captures the low frequency regime while the pulse mixing has been included to also capture the high frequency regime.

As indicated in Fig. 2, showing cycle-averaged NOx conversion in the pulsing frequency domain, the global kinetic model is able to predict well the improvement in cycle-averaged NOx conversion as the pulsing frequency is increased, due to shorter NOx storage periods and the improvement in its storage efficiency. However, the kinetics used does not indicate any reduction in NOx conversion as the frequency is increased further. The mixing and attenuation of reductant pulses that has been included in the model predicts well the optimal pulsing frequency and the reduction in NOx conversion at high frequencies.

4. Conclusions
(a) For a wide range of reductants including HCs, CO, and H₂ an optimal pulsing frequency was observed that maximizes NOx conversion at constant fuel penalty associated with reductant pulses. (b) A global kinetic model based on conventional LNT reactions predicts the overall features of RPR reaction in the frequency domain, (c) Model and experiments suggest improved NOx storage and inefficient NOx reduction due to reductant mixing as factors responsible for improvement and drop of NOx in frequency domain.

References

Keywords
Lean NOx Traps; Rapid Hydrocarbon Pulsing; Global Kinetic Modeling; High Temperature NOx Reduction