

## Global oxidation kinetics for platinum diesel oxidation catalysts

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### Introduction

Diesel engines are gaining increasing popularity based on their increased fuel economy and better performance characteristics among other propulsion systems. Its widespread use is often limited by the perennial soot-NO<sub>x</sub> trade-off which needs to be addressed to meet the emission regulations. The presence of diesel oxidation catalyst (DOC) is vital in reducing the hydrocarbon and CO emissions which result due to complex combustion strategies. Efficient aftertreatment models are essential to the performance of DOC when used with other aftertreatment components. While the existing models adequately capture the heat and mass transfer effects in a monolith, the biggest bottle-neck for a converter model is the reaction kinetics.

Voltz *et al.* [1] defined oxidation rates for C<sub>3</sub>H<sub>6</sub> and CO for stoichiometric exhaust for temperatures between 200°C and 370°C. Diesel exhaust is typically lean and hence its oxidation kinetics can be sufficiently different from those reported by Voltz *et al.* The work we report consists of properly dividing the concentration and temperature domain into discrete bins, generating low and medium conversions for all species based on the inlet concentration and temperature combinations using a high space velocity capability reactor (upto 2 million hr<sup>-1</sup>) and, finally using a simplified 1D reactor code coupled with an optimization routine to infer oxidation rates. An objective function which critically evaluates data at all conversions is defined. An optimization methodology to generate proper initial guesses and to successively simplify the overall reaction rate is also detailed.

### Test Matrix and Experiments

Reasonable upper bounds which correspond to both conventional and PCI (pre-mixed compression ignition) were chosen for the different species typically present in diesel exhaust. C<sub>3</sub>H<sub>6</sub> was used as a representative hydrocarbon. The concentrations for the test matrix ranged between the typical inlets as seen by the front face of the DOC and very small concentrations (10's of ppm) expected downstream of the reactor. Four discrete temperatures which are equally spaced in 1/T between 200°C and 415°C were chosen to span the practical regime.

Lightly loaded thin washcoat monolith samples were used to perform all the experiments. Typical inlet consisted of C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub> and NO as trace species and, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O in excess. All samples were hydro-thermally aged at 650°C for 16 hours before testing. Experiments were carried on in a vertical stainless steel tubular reactor which could hold varying sample sizes. Volumetric space velocities between 50,000 hr<sup>-1</sup> and 2,000,000 hr<sup>-1</sup> were achieved by varying reactor flow rates and catalyst size. Heating of the sample was achieved by flowing air, N<sub>2</sub>, CO<sub>2</sub> and vaporized water through two inline heaters. Species except H<sub>2</sub>

were analyzed using FTIR at inlet and outlet. H<sub>2</sub> was measured independently using an H-sense. All measurements were done at 1.6 atm to ensure proper flow through the FTIR.

### Modeling

A 1D reactor code which could calculate the exit concentrations was coupled to Matlab's 'fmincon' to minimize the difference between model predictions and experimentally measured exits/conversions. An objective function which is critically sensitive to differences between model predictions and experimental measurements at all conversions and which makes balanced and effective use of all the data was defined. A method to develop proper initial guesses that effectively exploit local optimization methods was devised to determine the rate constants. The optimization parameters (rate constants) were properly scaled for the optimization. Equations (1) (2) and (3) detail the scaling of the activation energies, pre-exponentials and adsorption constants before optimizing for the same.

$\hat{E} = \frac{E}{RT_r}$	(1)
$\hat{A} = \frac{Va_i}{w_r} A e^{-\hat{E}} x_{g,i} x_{O_2} c_r^2$	(2)
$\hat{A}a_i = Aa_i e^{-\hat{E}a_i} c_r x_{r,i}$	(3)

### Results and Discussions

Starting with a modified form of the rate form given in [1], we used the objective function to infer the rates for all the species and in the process evaluate the inhibition/enhancement due to various species on the rates. The final rate forms for C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub> and NO (NO<sub>2</sub>) oxidation rates are given in equations (4) and (5).

$r_i = \frac{k_i c_i c_{O_2}}{G}$ Where $i = C_3H_6, CO$ or $H_2$ and $k_i$ and $K_i$ are Arrhenius constants	(4)
$r_{NO} = \frac{k_{NO} c_{NO} \sqrt{c_{O_2}}}{G} \left[ 1 - \frac{c_{NO_2}}{K_{eq} c_{NO}} \sqrt{\frac{c_{ref}}{c_{O_2}}} \right]$	(5)
$G = (1 + K_{CO} c_{CO})^2 (1 + K_{NO} c_{NO})$	(6)

### Significance

Global oxidation kinetics for C<sub>3</sub>H<sub>6</sub>, CO, H<sub>2</sub> and NO (NO<sub>2</sub>) for a platinum DOC which are valid over a wide concentration and temperature domain are reported in this work.

### References

1. Sterling E. Voltz, Charles R. Morgan, David Liederman and Solomon M. Jacob, Ind. Eng. Chem. Prod. Res. Develop, vol. 12, No. 4, p-294, 1973