

# Comparative evaluation of ammonium carbamate and UWS based SCR system for diesel engine NO<sub>x</sub> reduction under WHTC

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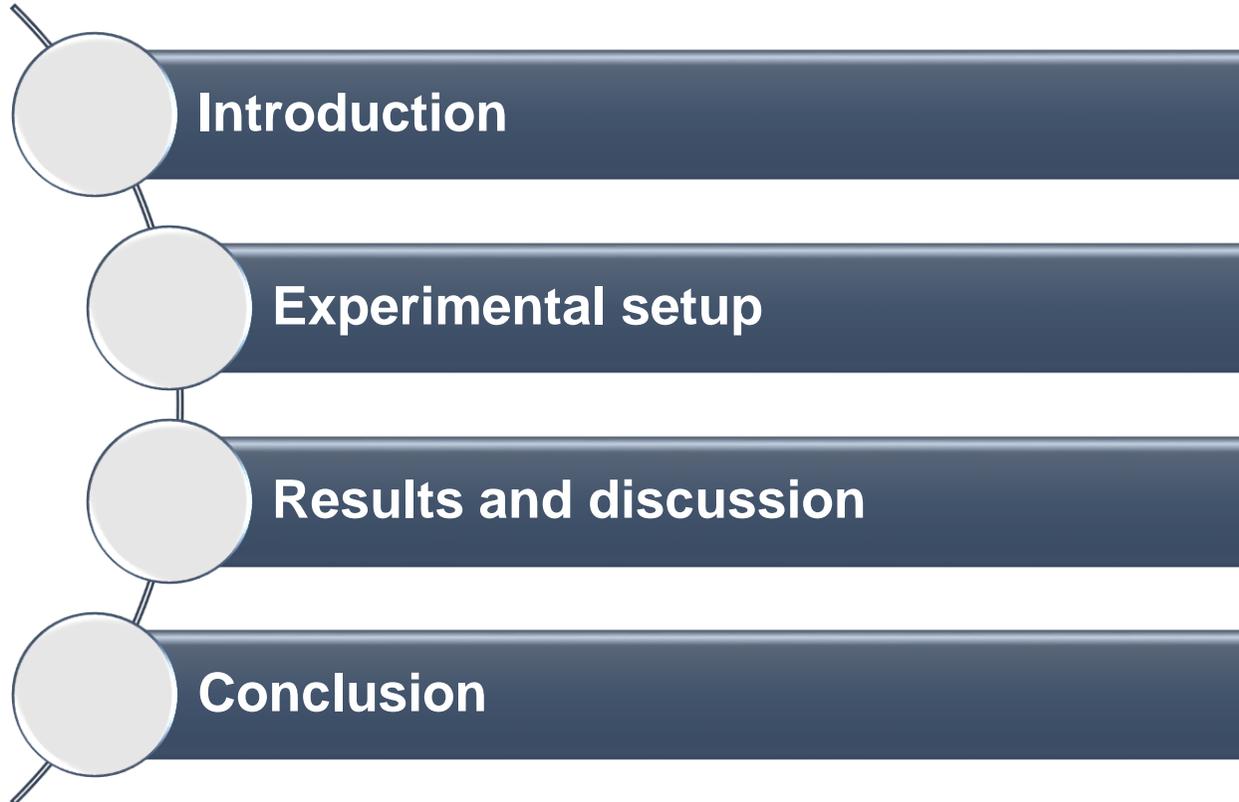
(2) Korea Institute of Machinery and Materials (KIMM)

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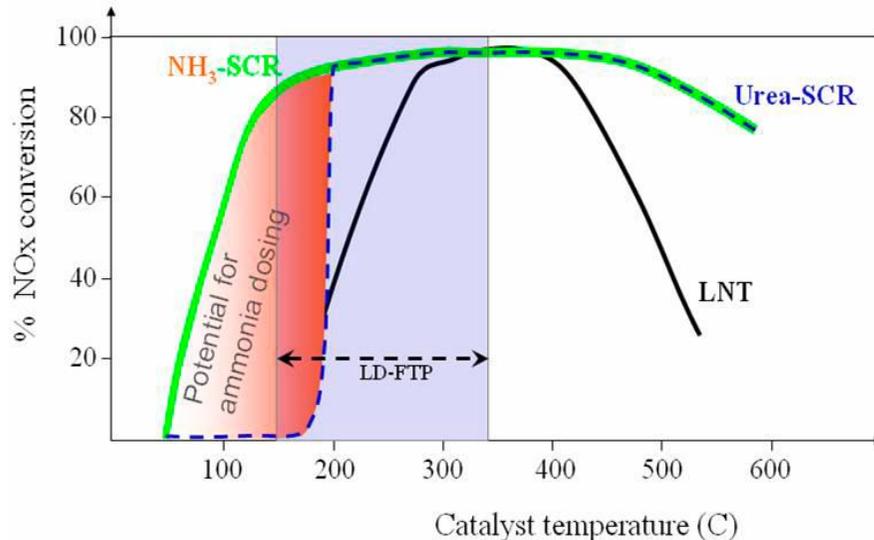
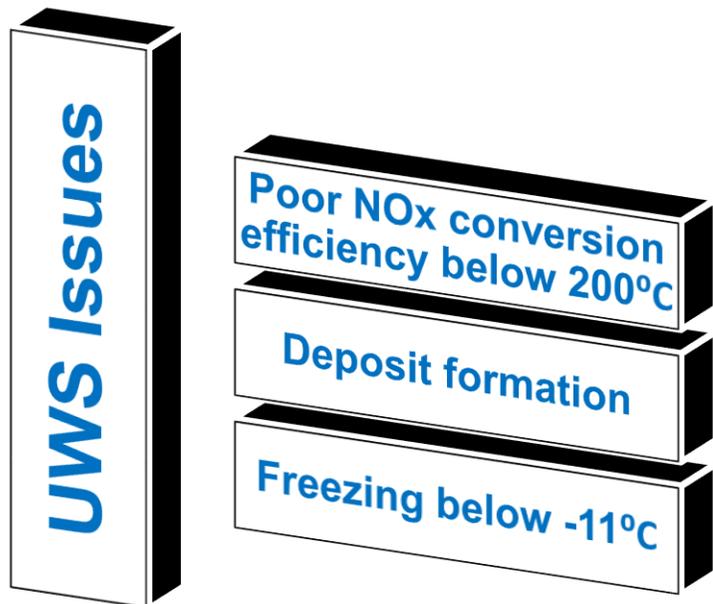
2021 CLEERS virtual workshop

# Outline

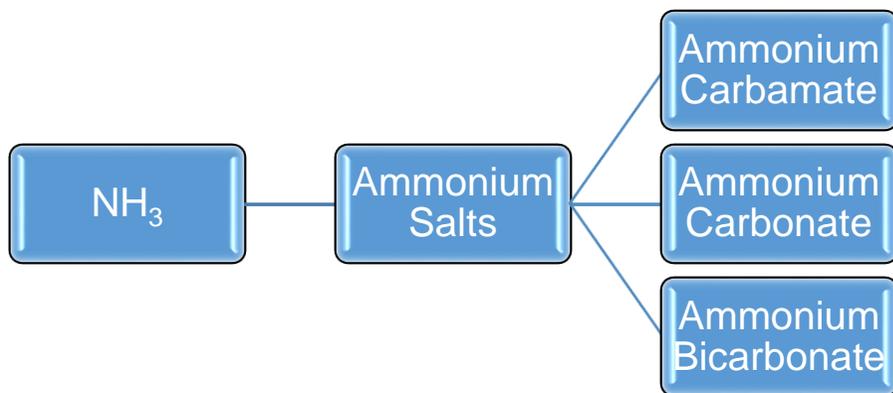
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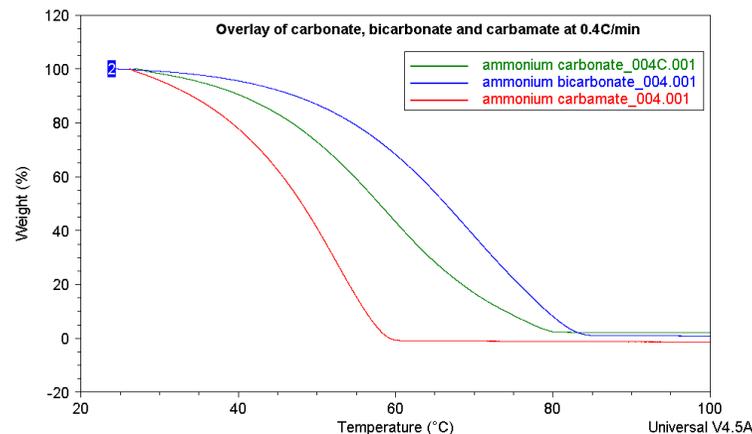
# 1. Introduction



Effectiveness of NO<sub>x</sub> conversion vs exhaust temperature [1]



Ammonia transport materials [2]



TGA analysis of ammonium salt decomposition [2]

[1] T. Johannessen, H. Schmidt, J. Svagin, J. Johansen, J. Oechsle, R. Bradley, Ammonia storage and delivery systems for automotive NO<sub>x</sub> aftertreatment, SAE Tech. Pap. 2008 (2008). doi:10.4271/2008-01-1027

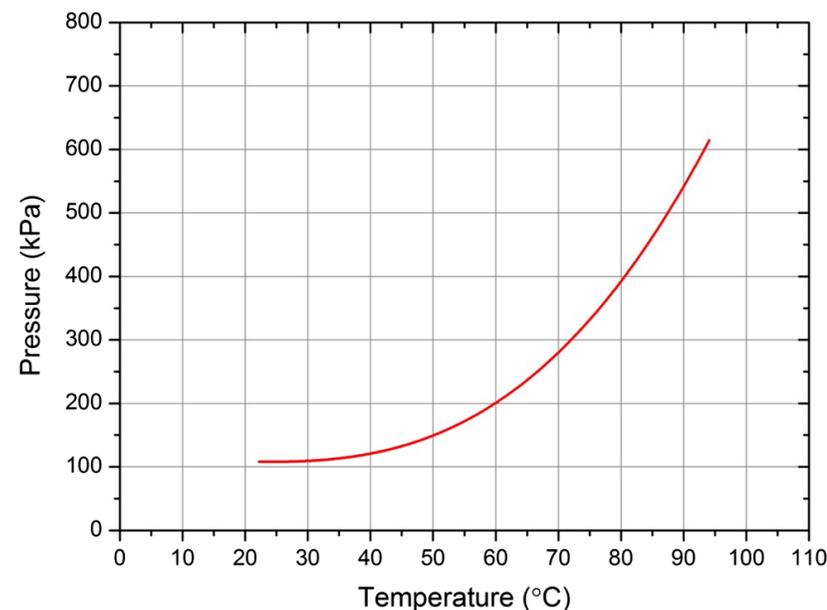
[2] G. Fulks, G.B. Fisher, K. Rahmoeller, M.C. Wu, E. D'Herde, J. Tan, A review of solid materials as alternative ammonia sources for lean NO<sub>x</sub> reduction with SCR, SAE Tech. Pap. (2009). doi:10.4271/2009-01-0907

# 1. Introduction

- Advantages of Ammonium carbamate based SCR system
  - ✓ Greater ammonia density than UWS
  - ✓ Opportunity to inject gaseous ammonia at low exhaust gas temperature
  - ✓ Increases NO<sub>x</sub> reduction performance at low exhaust gas temperature
  - ✓ Eliminates deposition problem
  - ✓ Low decomposition temperature compared with other ammonium salts
  - ✓ The system size is more compact

Property	UWS	Ammonium Carbamate
Chemical Formula	$(\text{NH}_2)_2\text{CO} + \text{H}_2\text{O}$	$\text{NH}_2\text{COONH}_4$
Molar weight (g/mol)	N/A	78.07
Density (g/cm <sup>3</sup> )	1.086	1.6
Moles of NH <sub>3</sub> per mole	2	2
Moles of NH <sub>3</sub> per kg	10.8	25.6
Decomposition Temp (°C)	--	60
Volume Factor (Norm to AdBlue)	1	0.29

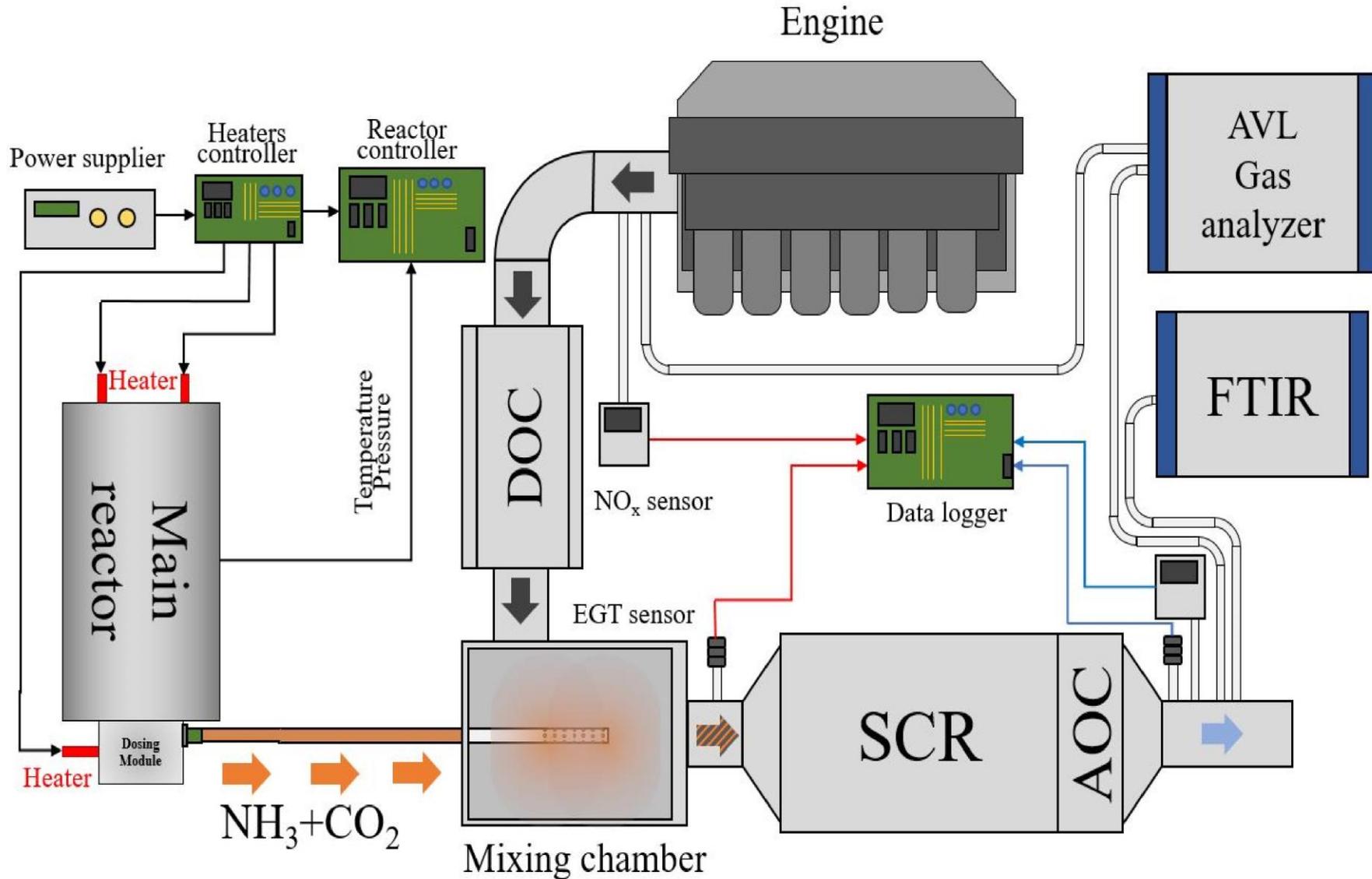
Comparison of UWS and ammonium carbamate properties



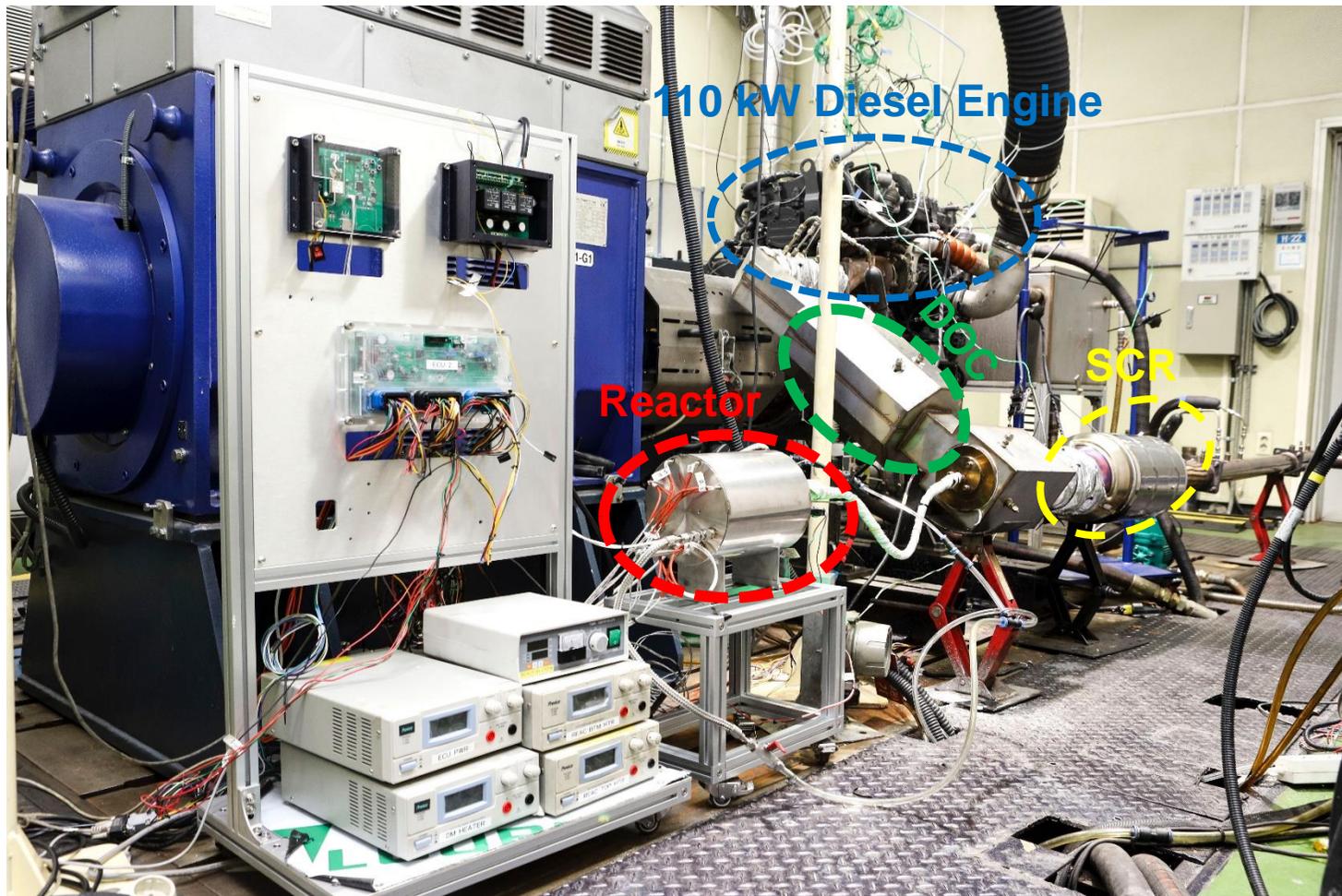
Equilibrium pressure of AC with respect to temperature measured in a closed chamber [3]

[3]Kim Y, Raza H, Lee S, Kim H. Study on the thermal decomposition rate of ammonium carbamate for a diesel NO<sub>x</sub> reducing agent-generating system. Fuel 2020;267. <https://doi.org/10.1016/j.fuel.2020.117306>

## 2. Experimental setup



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### Engine specification

Engine Displacement(L)	3.9
Compression ratio	17
Max. power(kW/rpm)	110/2500
Emissions standard	EURO-4

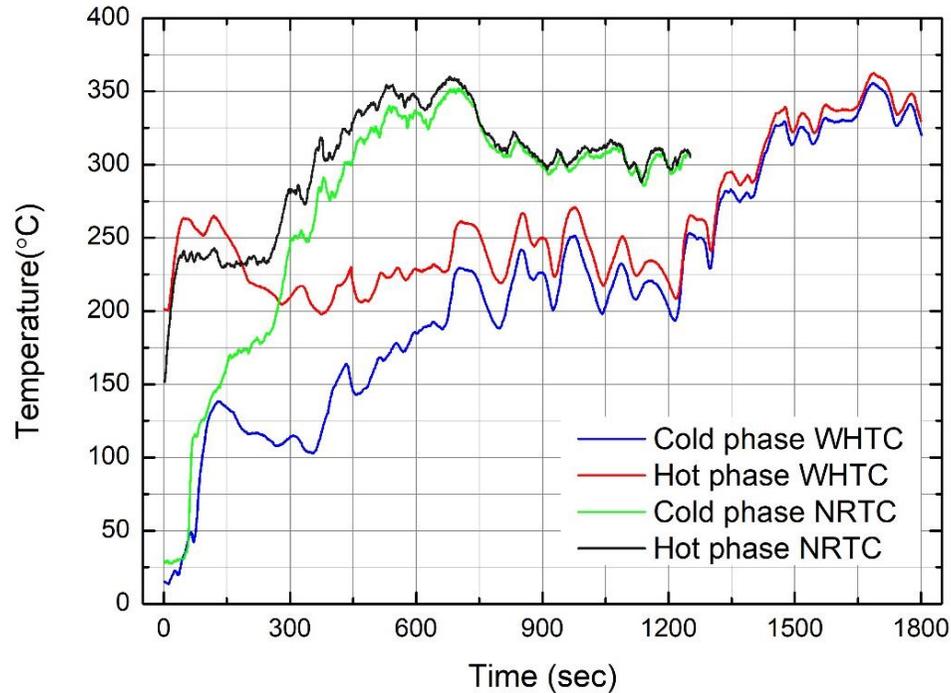
### Catalyst specification

DOC (Diesel Oxidation Catalyst)	Pt/Pd (D191mm, L152mm, Vol. 4.3L)
SCR (Selective Catalytic Reaction)	Cu-Zeolite (D203mm, L356mm, Vol. 11.5L)
AOC	Pt (D203mm, L5.1mm, Vol. 1.6L)

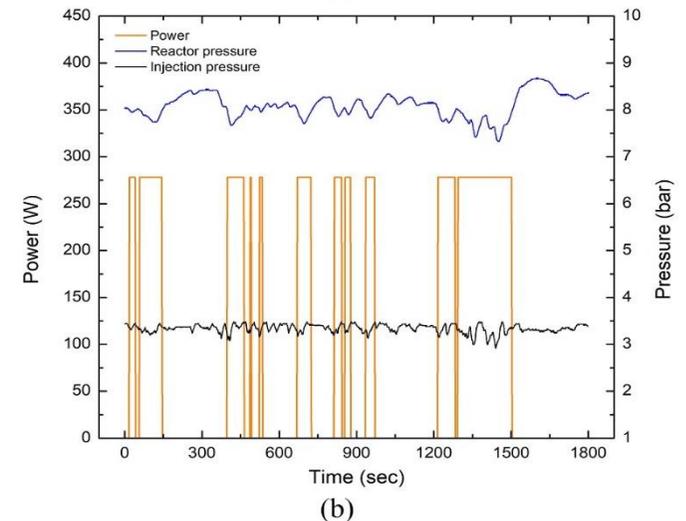
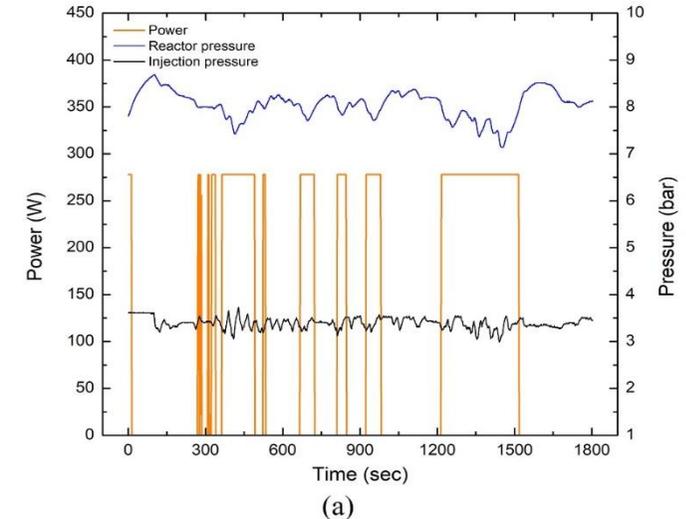


# 3. Results and discussion

## Comparison of UWS and AC based system under WHTC and NRTC



- Ammonia gas and UWS injection commenced after 92 seconds and 678 seconds during the cold phase of WHTC, respectively
- For NRTC test, ammonia gas and UWS injection commenced after 80 seconds and 290 seconds during the cold phase, respectively
- The reactor and injection pressure was well maintained at about 8 bar and 3 bar respectively during the WHTC test

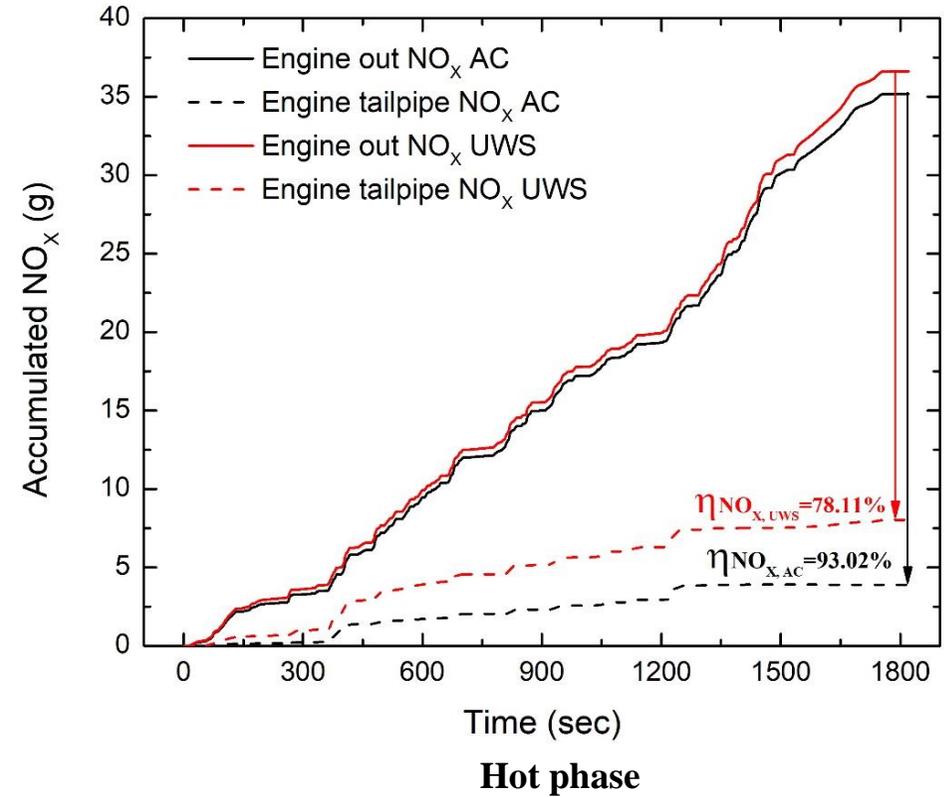
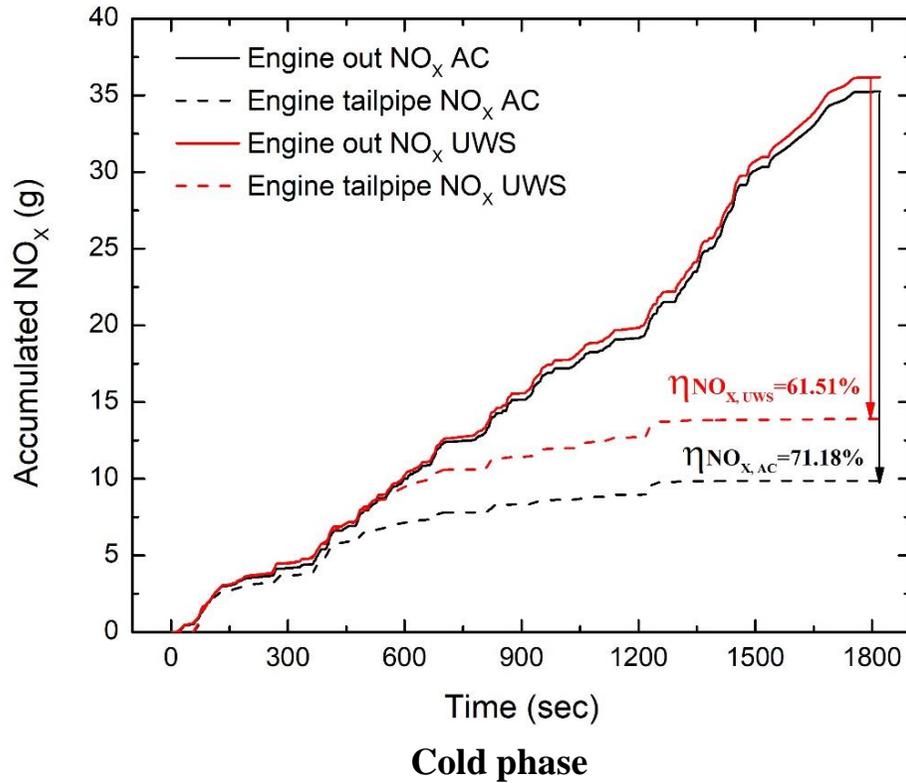


(a) Cold phase and (b) hot phase of WHTC

# DeNO<sub>x</sub> performance comparison of AC and UWS under WHTC

**Test Conditions:** Cold phase time = 30 min, Soaking time = 10 min, Hot phase = 30 min, NH<sub>3</sub>/NO<sub>x</sub> = 1.0

UWS injection threshold temperature = 200°C, Ammonia gas injection threshold temperature = 100 °C

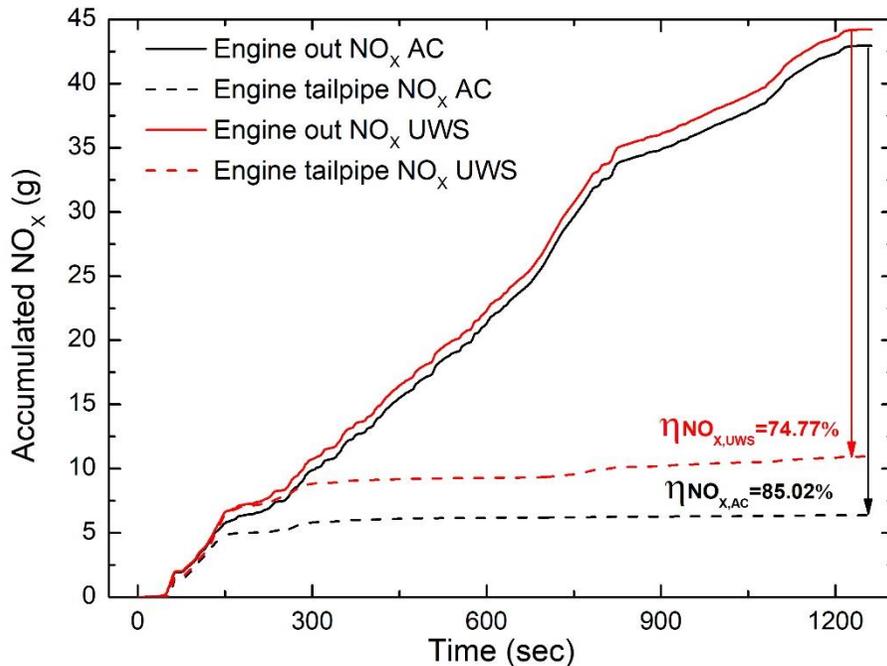


- Ammonia gas injection showed better deNO<sub>x</sub> efficiency than UWS
- Early injection and superior adsorption of gaseous ammonia leads to an increase the NO<sub>x</sub> conversion efficiency compared with UWS

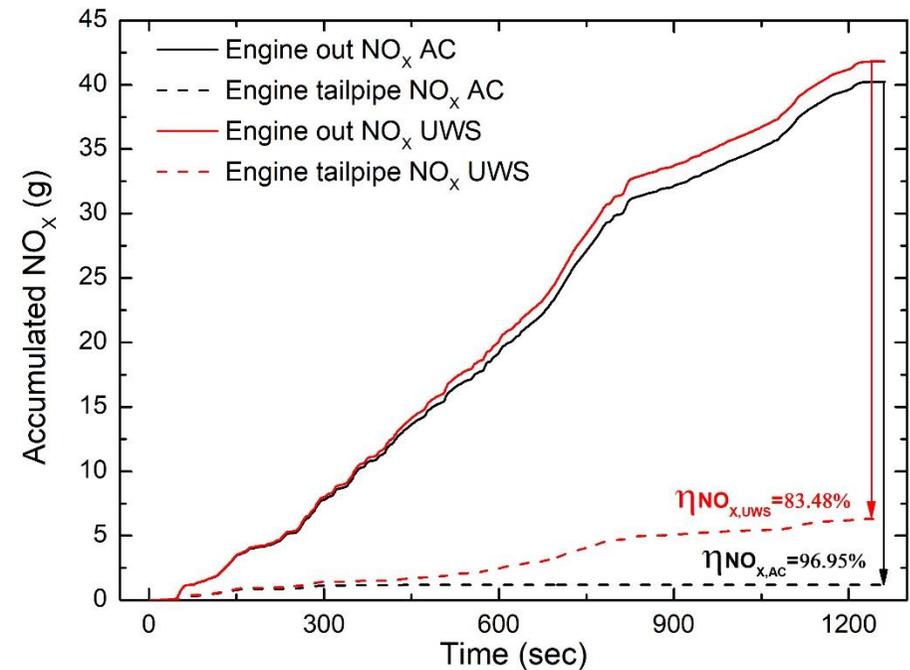
# DeNO<sub>x</sub> performance comparison of AC and UWS under NRTC

**Test Conditions:** Cold phase time = 20min 38sec, Soaking time = 20 min, Hot phase = 20min 38sec, NH<sub>3</sub>/NO<sub>x</sub> = 1.0

UWS injection threshold temperature = 200°C, Ammonia gas injection threshold temperature = 100 °C



**Cold phase**

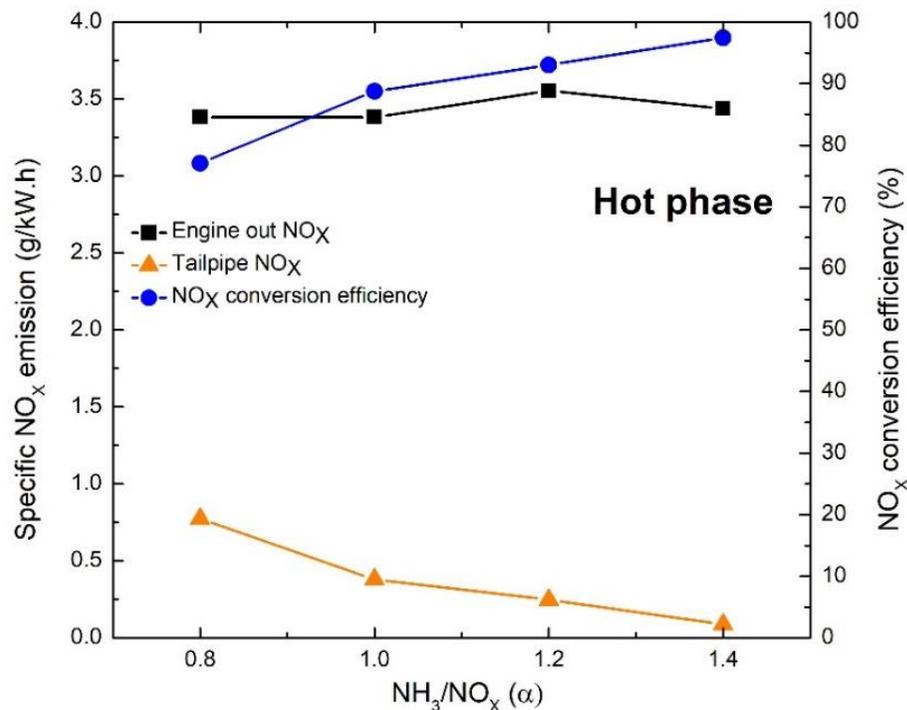
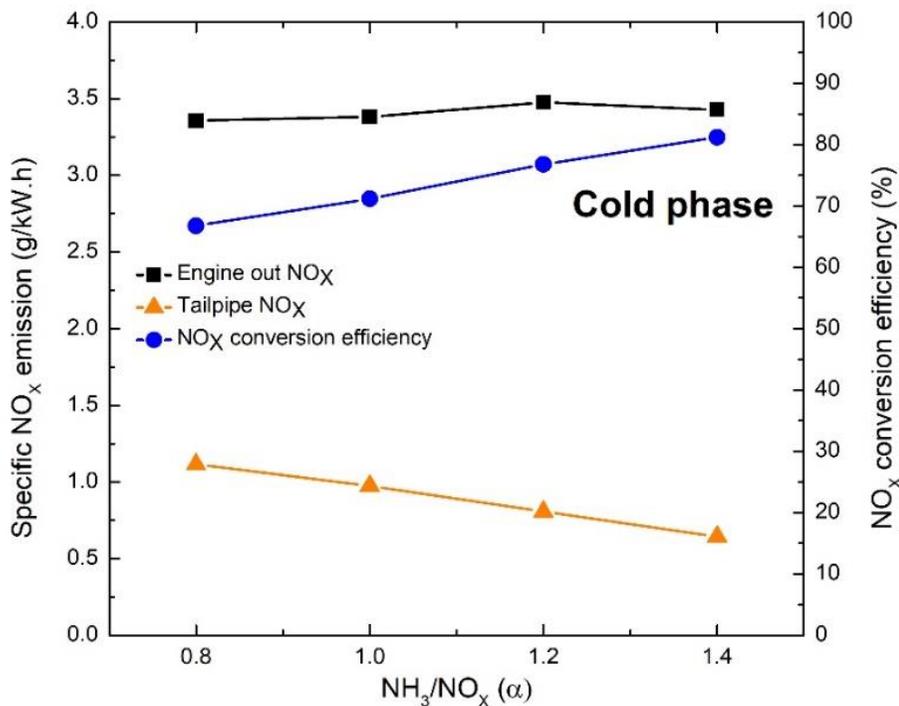


**Hot phase**

- The deNO<sub>x</sub> efficiencies of AC improve 8.71% and 11.93% than UWS during the cold and hot phase, respectively
- Compared with WHTC, the deNO<sub>x</sub> efficiency under NRTC tests was higher under both phases for each reducing agent, owing to the rapid heat-up of SCR, higher exhaust gas temperature, and early injection

# The effect of $\text{NH}_3/\text{NO}_x(\alpha)$ ratio on the de $\text{NO}_x$ performance

**Test Conditions:** Cold phase time = 30 min, Soaking time = 10 min, Hot phase = 30 min, Ammonia gas injection threshold temperature = 100 °C



- The de $\text{NO}_x$  performance of AC based system increases as the  $\text{NH}_3/\text{NO}_x (\alpha)$  ratio increases
- At  $\text{NH}_3/\text{NO}_x=1.4$ , maximum of 81% and 97%  $\text{NO}_x$  conversion efficiency was observed during the cold and hot phase, respectively

The NH<sub>3</sub> adsorption and desorption rate expressions are given by equations (1) & (2) [4]

$$r_{ads} = A_{ads}c_{NH_3}(1 - \theta) \quad (1)$$

$$r_{des} = A_{des}e^{-\frac{E_{des}(1-\gamma\theta)}{RT}}\theta \quad (2)$$

Where  $\theta$  is fractional NH<sub>3</sub> storage in the catalyst, which can be represented by the following equation (3)

$$\theta = \frac{\Omega}{\Omega^*} \quad (3)$$

The NH<sub>3</sub> adsorption and desorption rates from equation (1) & (2) are used to calculate the instantaneous fractional NH<sub>3</sub> storage with time by the following equation (4)

$$\frac{d\theta}{dt} = r_{ads} - r_{des} \quad (4)$$

The rate of adsorption and desorption were then used to calculate the NH<sub>3</sub> release amount by the following equation (5)

$$NH_{3,release} = \Omega^*(r_{des} - r_{ads}) \quad (5)$$

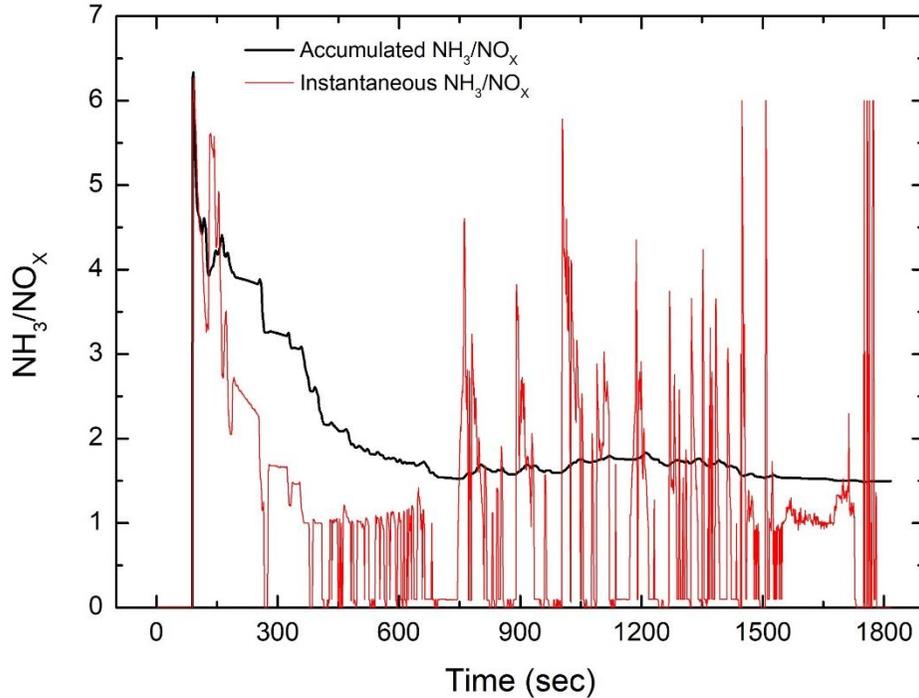
Parameter	Unit	Value
$A_{ads}$	m <sup>3</sup> /mol/s	1
$A_{des}$	1/s	1.0E07
$E_{des}$	kJ/mol	107
$\Omega^*$	mol/m <sup>3</sup>	20
R	J/mol-K	8.314

NH<sub>3</sub> storage parameters used in the storage model

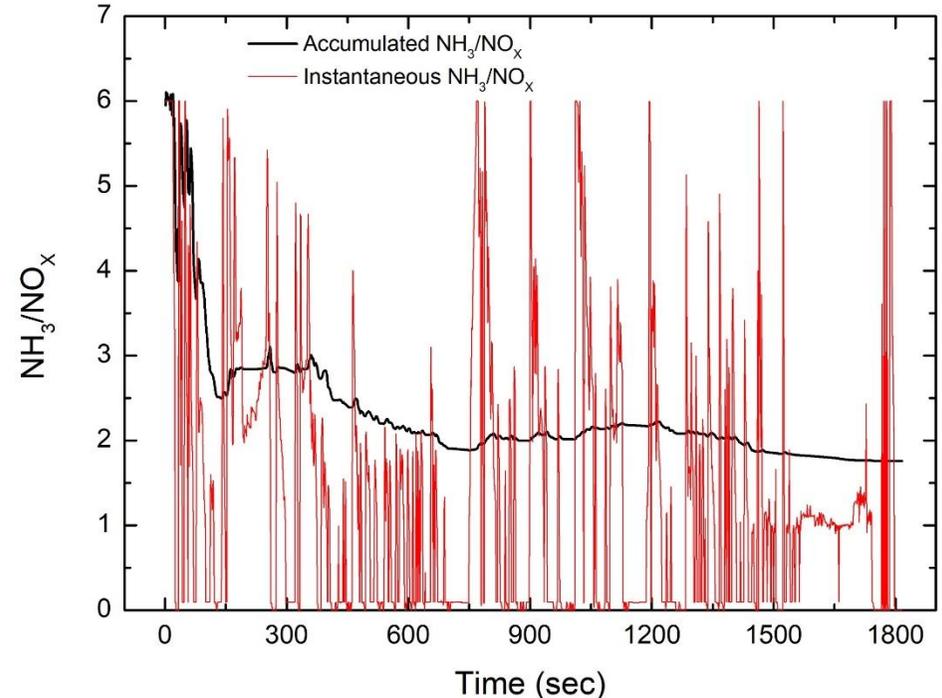
[4] Devarakonda M, Lee J, Muntean G, Pihl J, Daw S. 1D model of a copper exchanged small pore zeolite catalyst based on transient SCR protocol. SAE Tech Pap 2013;2. <https://doi.org/10.4271/2013-01-1578>

# Ammonia adsorption-desorption model based injection

**Test Conditions:** WHTC cold phase time = 30 min, Soaking time = 10 min, Hot phase = 30 min, Ammonia gas injection threshold temperature = 100 °C



**Cold phase**

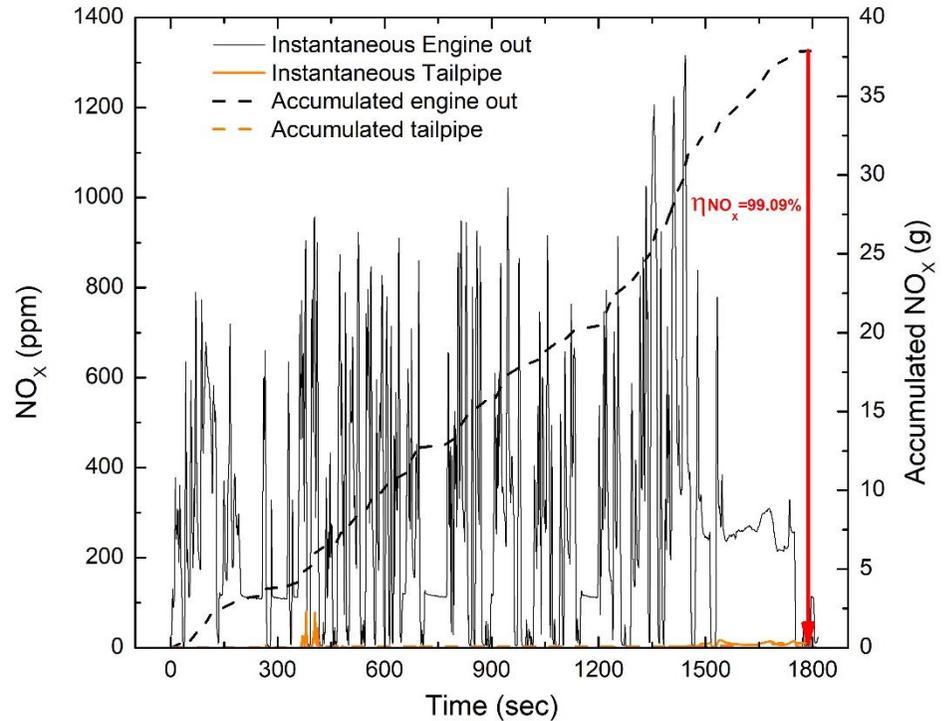
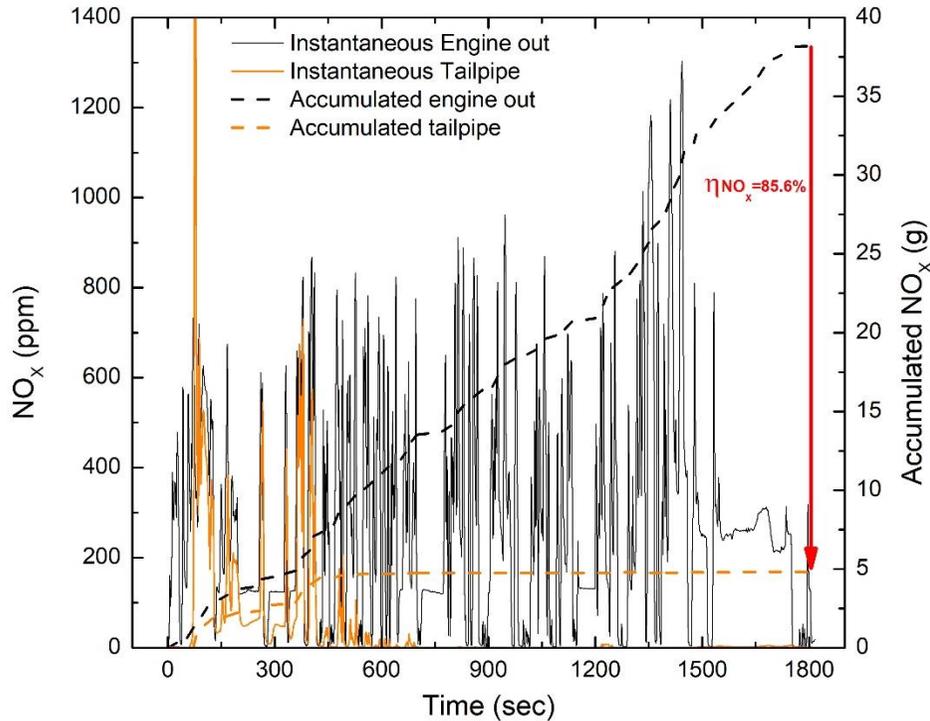


**Hot phase**

- $\text{NH}_3/\text{NO}_x$  ( $\alpha$ ) ratio fluctuated according to the injected  $\text{NH}_3$  demand depending upon adsorption-desorption rates
- Overall accumulated injected amount during the cold and hot phase of WHTC was equivalent to  $\text{NH}_3/\text{NO}_x$  ratio of 1.5 and 1.7, respectively

# Effect of model based injection on the deNO<sub>x</sub> performance

**Test Conditions:** WHTC cold phase time = 30 min, Soaking time = 10 min, Hot phase = 30 min, Ammonia gas injection threshold temperature = 100 °C

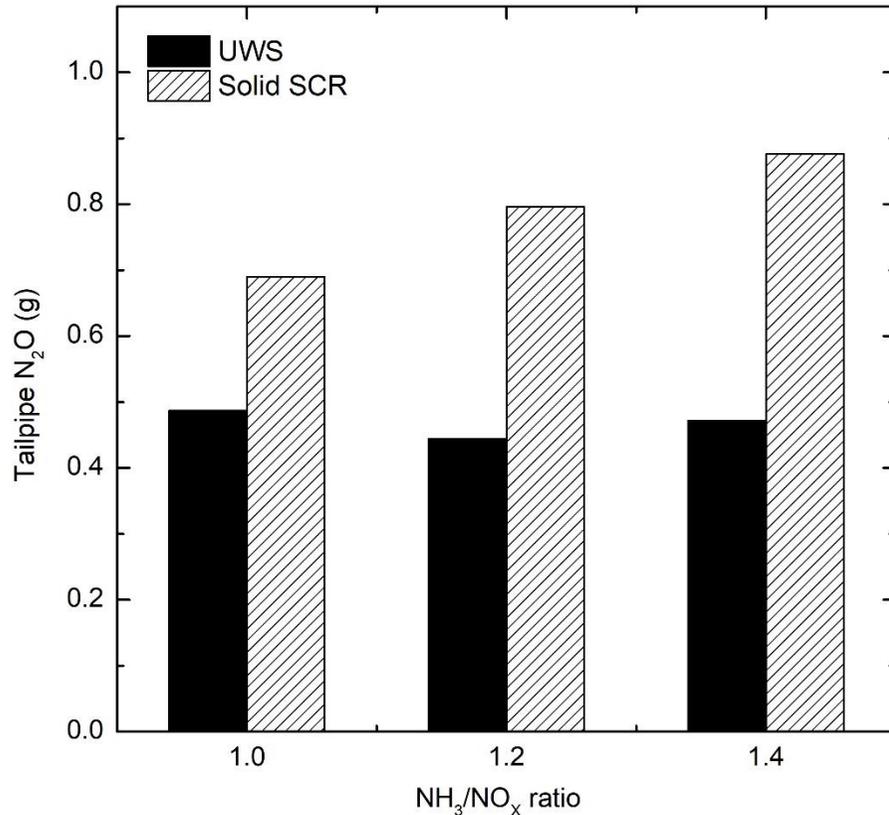


- NO<sub>x</sub> conversion efficiency of 85.6% and 99.09% was achieved during the cold and hot phase of WHTC, respectively
- Model based injection seems effective to increase the deNO<sub>x</sub> performance, especially during the cold phase of WHTC

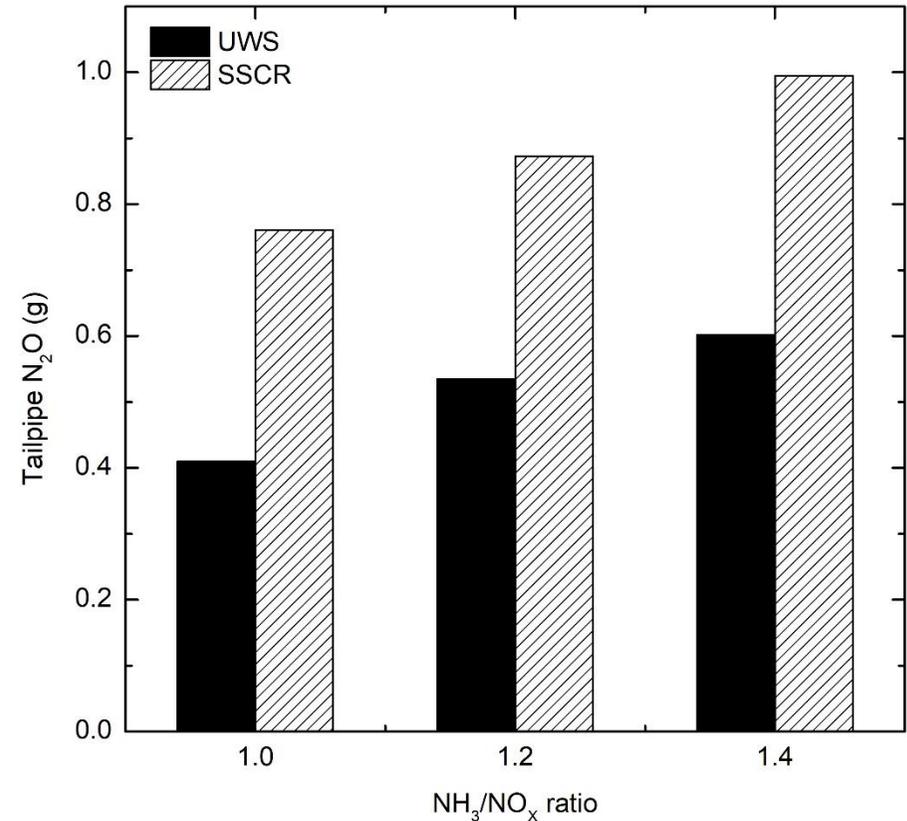
# Effect of ammonia and UWS injection on N<sub>2</sub>O emissions

**Test Conditions:** Cold phase time = 30min, Soaking time = 10 min, Hot phase = 30min,

UWS injection threshold temperature = 200°C, Ammonia gas injection threshold temperature = 100 °C



**Cold phase**



**Hot phase**

- Injection of gaseous ammonia using AC leads to more N<sub>2</sub>O emissions than UWS
- N<sub>2</sub>O emissions are sensitive to the ammonia injection amount

# Conclusion

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- SCR system using ammonium carbamate as  $\text{NH}_3$  source can be injected at an exhaust temperature of below  $200^\circ\text{C}$  and reduce more  $\text{NO}_x$  under transient conditions compared with UWS
- SCR System using ammonium carbamate is preferable to increase the  $\text{NO}_x$  conversion efficiency than UWS under WHTC and NRTC tests because of early injection and better adsorption-desorption capability
- Increasing Alpha ratio is effective to increase the  $\text{deNO}_x$  performance of AC based SCR system
- Gaseous ammonia injection leads to more  $\text{N}_2\text{O}$  emissions because of injection at low temperature compared with UWS
- Ammonia adsorption-desorption model is favorable to increase the  $\text{NO}_x$  conversion efficiency
- In future work, the system will be developed to be used for on-road vehicle tests

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**THANK YOU**  
**ANY QUESTIONS?**