AUS-32 / AdBlue / DEF Policy Mechanism & Implications

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Overview

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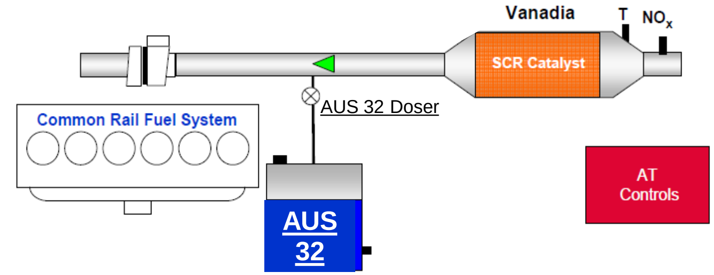
- Background
- ISO Standards
- Technical Challenges & Emission Implications
  - DEF Deposit
  - PM Mass & Number
  - PCDD/F
  - Vanadium Release
  - Nitro-PAH
- AUS32 Manufacturing & Distribution
- Policy & Implementation
- Summary

AUS-32 as Reagent in SCR System

- The means of providing ammonia (NH_3) as reagent into the exhaust for mobile applications is to use AUS32
- An aqueous urea solution made with 32.5% high-purity urea (AUS 32 – Industrial Urea) and 67.5% deionized water standardized as per ISO 22241. Required by SCR equipped vehicles for NOX reduction
- Decomposes at high T to ammonia
- Freezes at -11.5C but as 32.5% is a eutectic mixture in a part frozen state the unfrozen solution remains at 32.5%
- AUS32 consumption is expected to be approximately 3 - 5 % of fuel consumption for typical BSIV emission norms application dependent on engine tuning, vehicle duty cycle, geography, ratings etc.

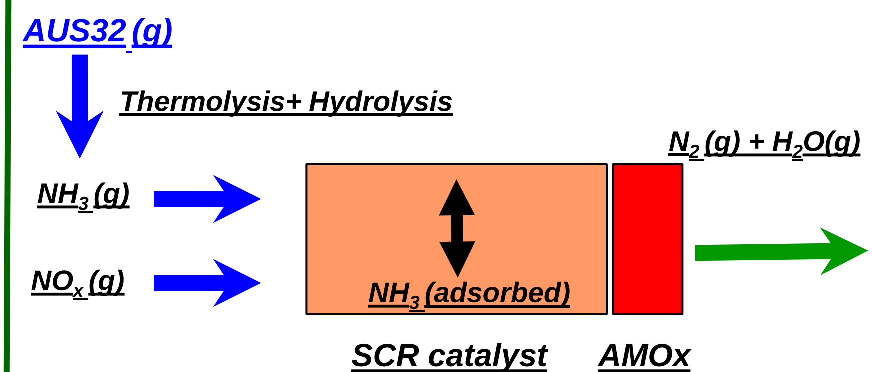


$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O$$

$$NO + NO_2 + 2NH_3 \rightarrow 2\,N_2 + 3\,H_2O$$

Fast reaction



High Efficiency SCR in Mature Market

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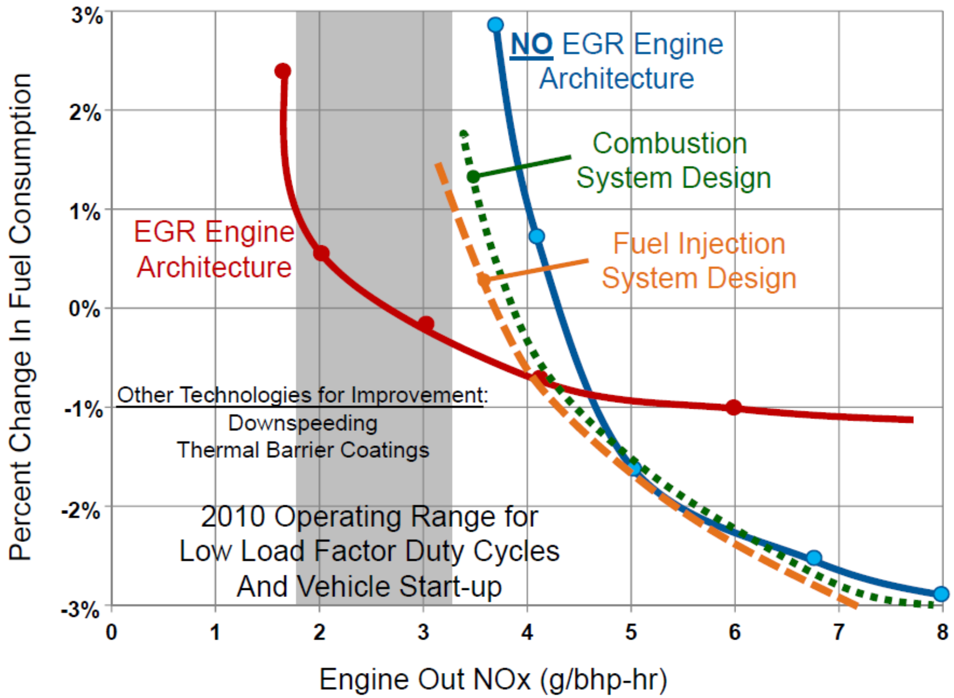
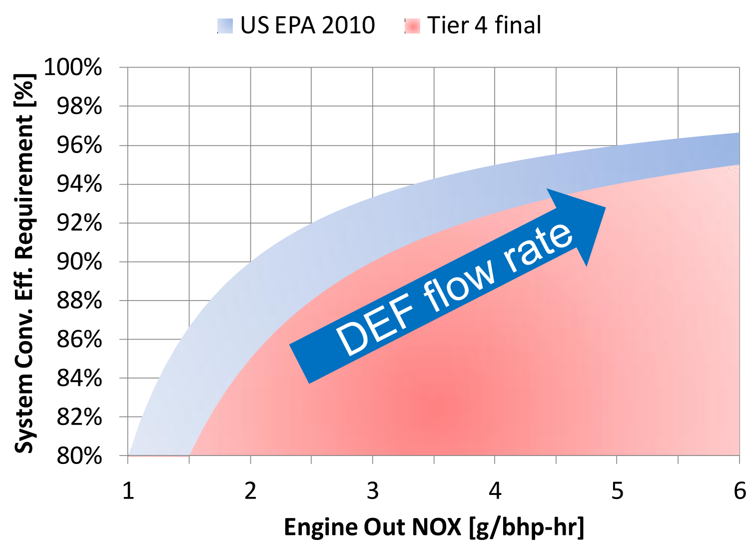
- First time in US: fuel efficiency and GHG emission standards beginning in 2014 (10-20% improvement by MY 2018)
- SCR only (no EGR) systems becoming an option, increasing fuel economy





ISO Standard

ISO22241: "Diesel Engines – NO_x reduction agent AUS32"

Specifies the quality characteristics of DEF/AdBlue

Sections

- Part 1: Quality requirements
- Part 2: Test methods
- Part 3: Handling, Transportation & Storage
- Part 4: Refilling Interface

Composition

Quality specifications from Part 1 of the ISO standard

Characteristics	Unit	Limits		Test methods
		min.	max.	
Urea content [a]	% (*m/m*) [d]	31,8	33,2	ISO 22241-2 Annex B [e] ISO 22241-2 Annex C [e]
Density at 20 °C [b]	kg/m^3	1 087,0	1 093,0	ISO 3675 or ISO 12185
Refractive index at 20 °C [c]	—	1,381 4	1,384 3	ISO 22241–2 Annex C
Alkalinity as NH_3	% (*m/m*) [d]	—	0,2	ISO 22241–2 Annex D
Biuret	% (*m/m*) [d]	—	0,3	ISO 22241–2 Annex E
Aldehydes	mg/kg	—	5	ISO 22241–2 Annex F
Insoluble matter	mg/kg	—	20	ISO 22241–2 Annex G
Phosphate (PO_4)	mg/kg	—	0,5	ISO 22241–2 Annex H
Calcium	mg/kg	—	0,5	ISO 22241–2 Annex I
Iron	mg/kg	—	0,5	
Copper	mg/kg	—	0,2	
Zinc	mg/kg	—	0,2	
Chromium	mg/kg	—	0,2	
Nickel	mg/kg	—	0,2	
Aluminium	mg/kg	—	0,5	
Magnesium	mg/kg	—	0,5	
Sodium	mg/kg	—	0,5	
Potassium	mg/kg	—	0,5	
Identity	—	identical to reference		ISO 22241–2 Annex J

Should it be necessary to add a tracer to AUS 32, it shall be ensured that the quality of AUS 32 specified in this Table is not impaired and that the tracer does not damage the SCR system.

NOTE 1 In establishment of these limit values, the terms of ISO 4259 have been applied in fixing a maximum and minimum value, a minimum difference of $4 \times R$ (R is the Reproducibility of the test method) has been taken into account. However, in case of urea content, the $4 \times R$ rule has not been applied in order to keep the high quality.

NOTE 2 The values quoted regarding urea content, density and refractive index are "true values" (see ISO 4259 for definition of true values).

NOTE 3 The manufacturer of AUS 32 should aim at the target values defined in footnotes a, b and c.

NOTE 4 Should it be necessary to clarify the questions as to whether a given urea solution meets the requirement of the specification, the terms of ISO 4259 should be applied.

[a] Target value 32,5 % (*m/m*).

[b] Target value 1 090,0 kg/m^3.

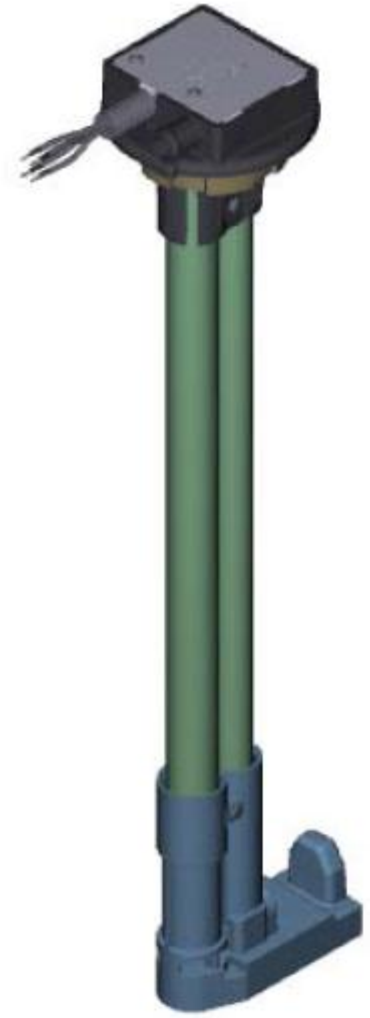
[c] Target value 1,382 9.

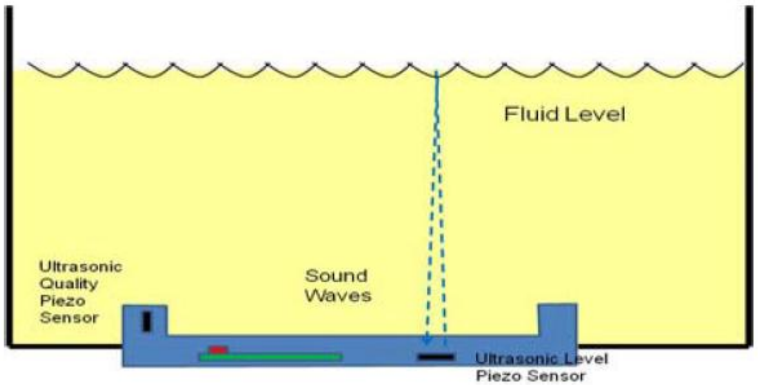
[d] For the purposes of this International Standard, the term "% (*m/m*)" is used to represent the mass fraction of a material.

[e] Calculated without subtracting nitrogen from ammonia.

Urea Quality Sensor

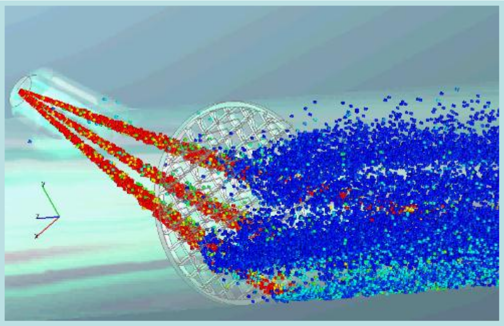
- Ultrasonic level and concentration sensor
- Currently implemented for various programs
- Capability
  - Temperature, level, and concentration detection
    - 0-55±3% DEF
  - Detects contaminants
  - RoHS compliant





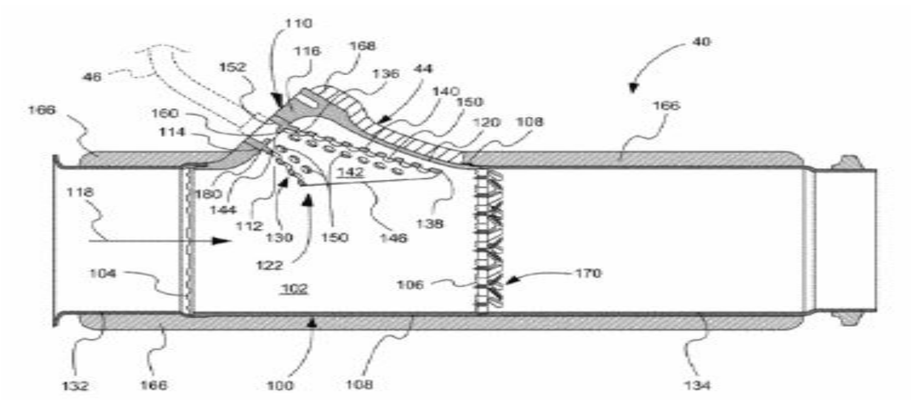
Images from SSI Technologies 2012 publication

Deposit Formation & Mitigation

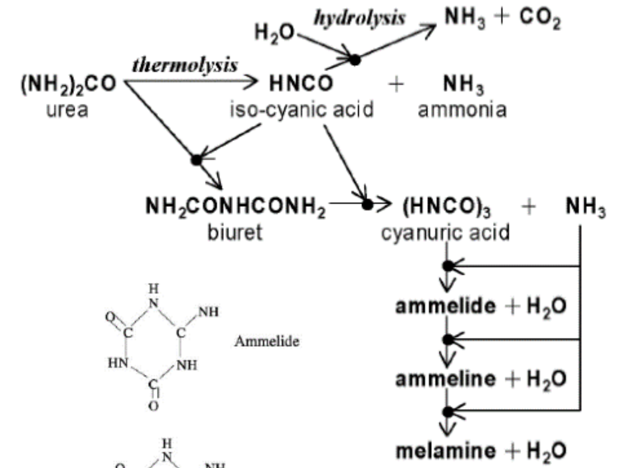


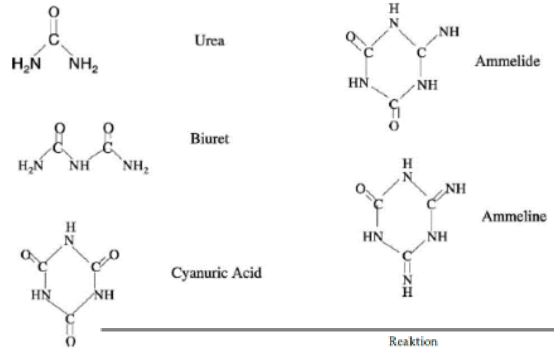
(Nishioka et al., *SAE 2006-01-0644*)
(Schaber et al., *Thermochimica Acta*, 2004)

(Munnannur, Chiruta, & Liu, *SAE 2012-01-1287*)



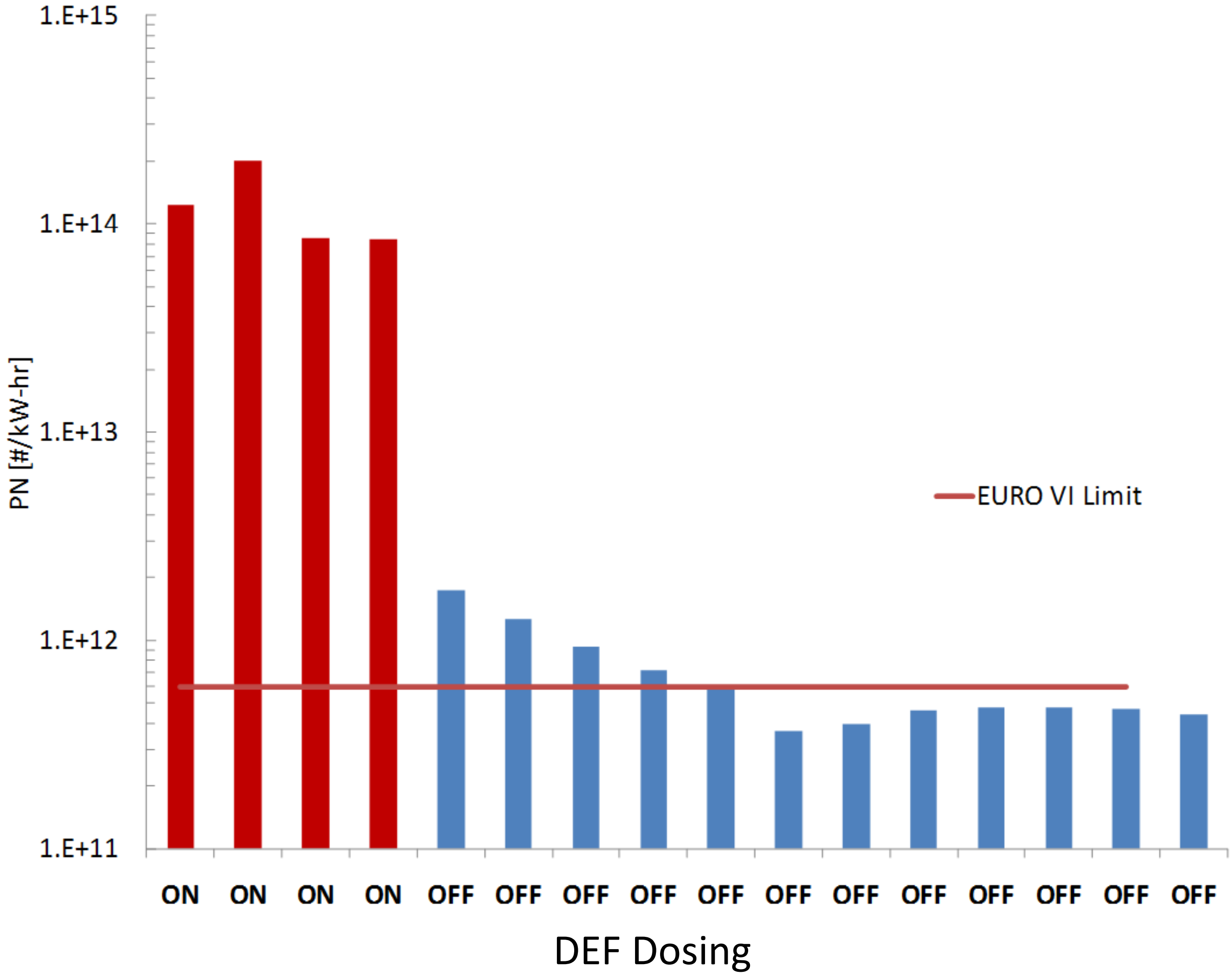
(Liu & Clerc, US Patent 8240137, 2014)





	Reaktion	γ_i	A	E_A
I	$CYA_{(s)} \longrightarrow 3\,HNCO_{(g)}$	0	$1.001 \times 10^3 \frac{mol}{s}$	$118.42 \frac{kJ}{mol}$
II	$Biuret_{(m)} \longrightarrow Harnstoff_{(m)} + HNCO_{(l)}$	1	$1.107 \times 10^{20} \frac{1}{s}$	$208.23 \frac{kJ}{mol}$
III	$Harnstoff_{(m)} + HNCO_{(l)} \longrightarrow Biuret_{(m)}$	1 / 1	$3.517 \times 10^{11} \frac{ml}{mol\,s}$	$75.45 \frac{kJ}{mol}$
IV	$Harnstoff_{(m)} \longrightarrow HNCO_{(l)} + NH_{3\,(g)}$	0.3	$2.000 \times 10^4 \frac{mol^{0.7}}{ml^{0.7}\,s}$	$74.00 \frac{kJ}{mol}$
V	$2\,Biuret_{(m)} \longrightarrow Ammelid_{(s)} + HNCO_{(l)} + NH_{3\,(g)} + H_2O_{(g)}$	2	$3.637 \times 10^{26} \frac{ml}{mol\,s}$	$257.76 \frac{kJ}{mol}$
VI	$Biuret_{(m)} + HNCO_{(l)} \longrightarrow CYA_{(s)} + NH_{3\,(g)}$	1 / 1	$9.397 \times 10^{20} \frac{ml}{mol\,s}$	$158.68 \frac{kJ}{mol}$
VII	$Biuret_{(m)} + HNCO_{(l)} \longrightarrow Triuret_{(s)}$	1 / 1	$1.091 \times 10^{15} \frac{ml}{mol\,s}$	$116.97 \frac{kJ}{mol}$
VIII	$Triuret_{(s)} \longrightarrow CYA_{(s)} + NH_{3\,(g)}$	1	$1.238 \times 10^{18} \frac{1}{s}$	$194.94 \frac{kJ}{mol}$
IX	$Harnstoff_{(m)} + 2\,HNCO_{(l)} \longrightarrow Ammelid_{(s)} + H_2O_{(g)}$	1 / 2	$1.274 \times 10^{20} \frac{ml^2}{mol^2\,s}$	$110.40 \frac{kJ}{mol}$
X	$Biuret_{(m)} \longrightarrow Biuret_{(matrix)}$	1	$8.193 \times 10^{26} \frac{1}{s}$	$271.50 \frac{kJ}{mol}$
XI	$Biuret_{(matrix)} \longrightarrow Biuret_{(m)}$	1	$3.162 \times 10^9 \frac{1}{s}$	$122.00 \frac{kJ}{mol}$
XII	$Biuret_{(matrix)} \longrightarrow 2\,HNCO_{(g)} + NH_{3\,(g)}$	1	$5.626 \times 10^{24} \frac{1}{s}$	$266.38 \frac{kJ}{mol}$
XIII(a)	$T > 403$ K: $Harnstoff_{(s)} \longrightarrow Harnstoff_{(m)}$	1	$1.000 \times 10^{15} \cdot T^{1.5} \frac{1}{s}$	$160.00 \frac{kJ}{mol}$
XIII(b)	$T < 403$ K: $Harnstoff_{(s)} \longrightarrow Harnstoff_{(m)}$			siehe Anhang B
XIV	$Ammelid_{(s)} \longrightarrow Ammelid_{(g)}$	1	$1.000 \times 10^{14} \frac{1}{s}$	$201.67 \frac{kJ}{mol}$
XV	$HNCO_{(l)} \longrightarrow HNCO_{(g)}$			Herz-Knudsen-Geleichung

Effect of AUS Dosing on PM Emissions

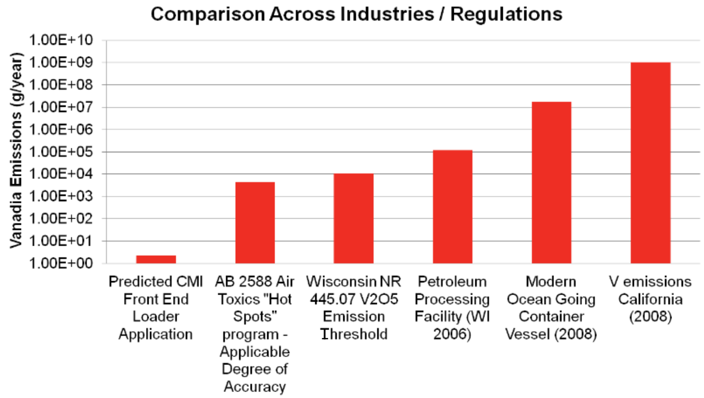


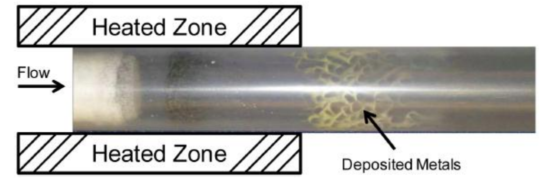
Vanadium and Tungsten Release

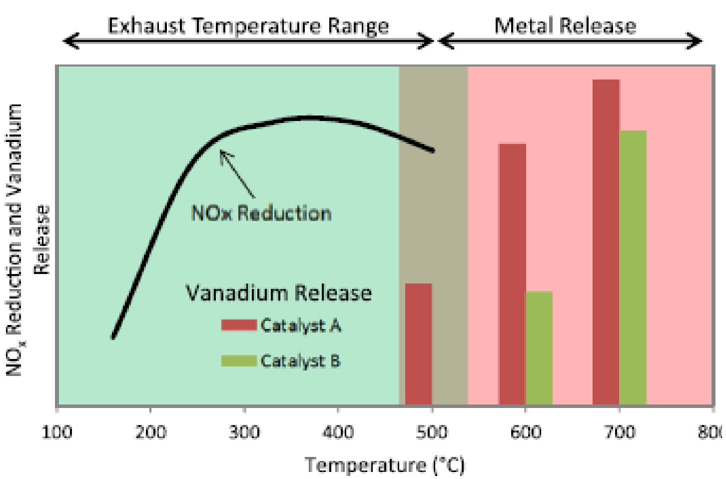
Emission Solutions

Outcome/Results:

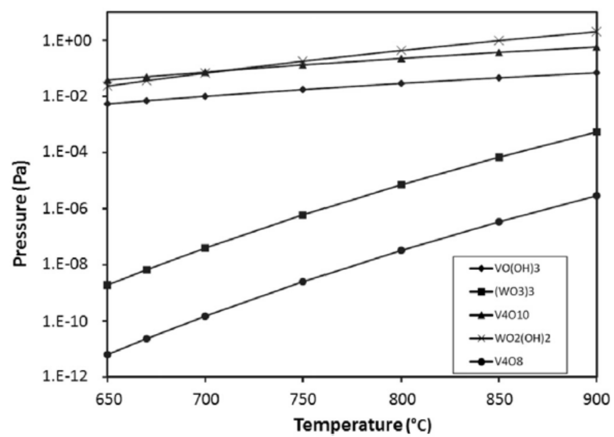
- Developed robust reactor method that measures vapor-phase release
- Determined emissions levels
- Published reactor method







(Liu et al., *SAE Int. J. Engines*, 2012)



(Liu et al., *Atmos. Environ.* 2015)

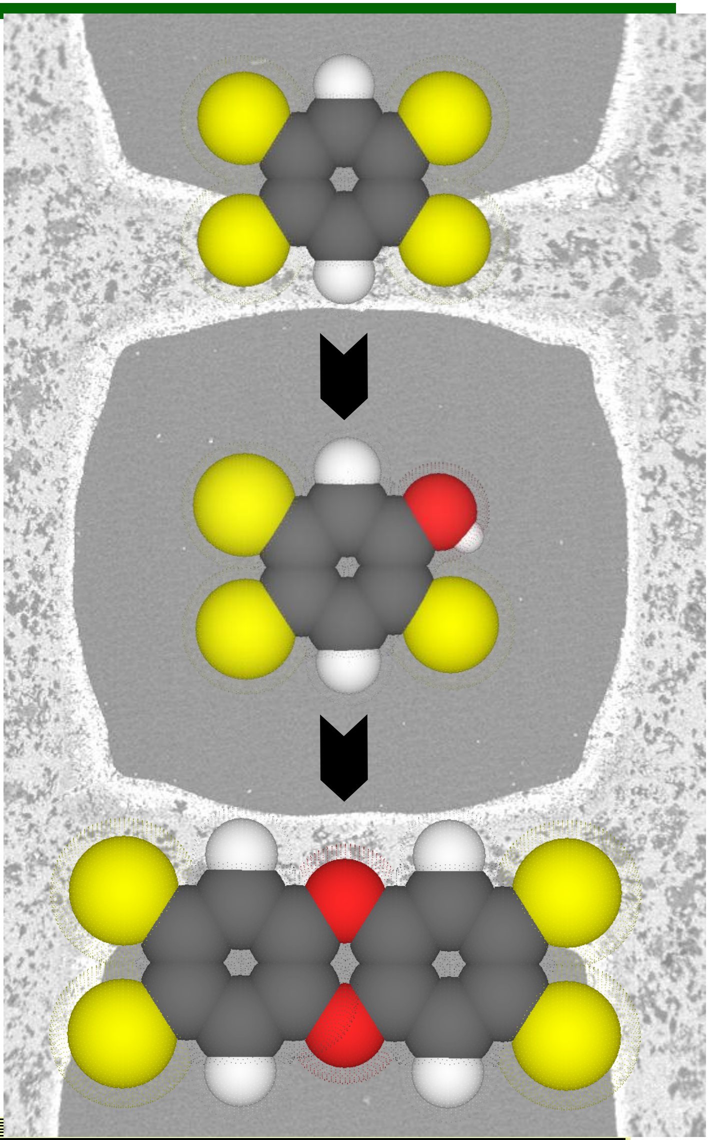
Polychlorinated Dibenzodioxins/Furans

The dioxin problem

- Highly toxic
- Persistent, ubiquitous
- Bioaccumulating
- Unwanted side product of uncontrolled combustion processes

Properties:

- Thermally stable up to 440°C
- Solid, non-volatile, particle-bound
- Should be trapped in DPFs unless they are formed *de novo*

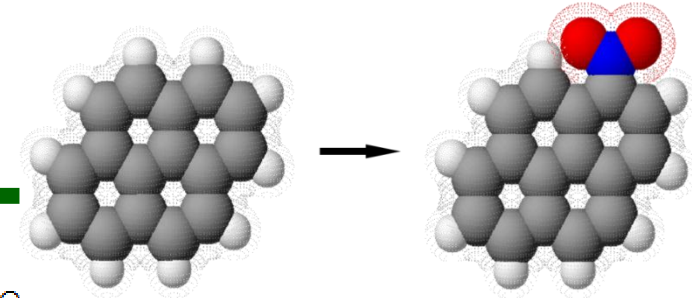


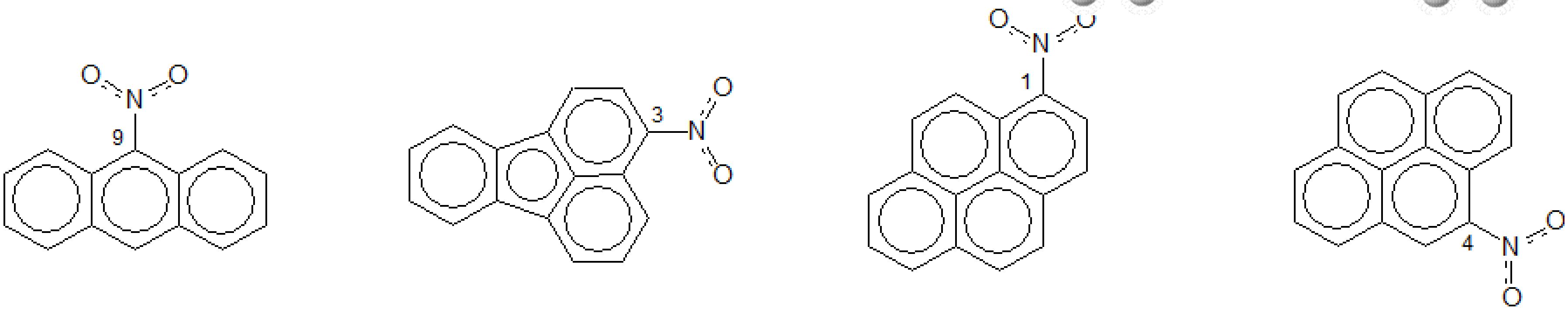
Heeb et al. ES&T, **2007**, 42, 3773-3779

(Liu et al., *SAE Trans. 2011-01-1158*)

(Liu, Wall, Barge, *Environ Sci. & Technol*., 2011)

Nitration of PAHs



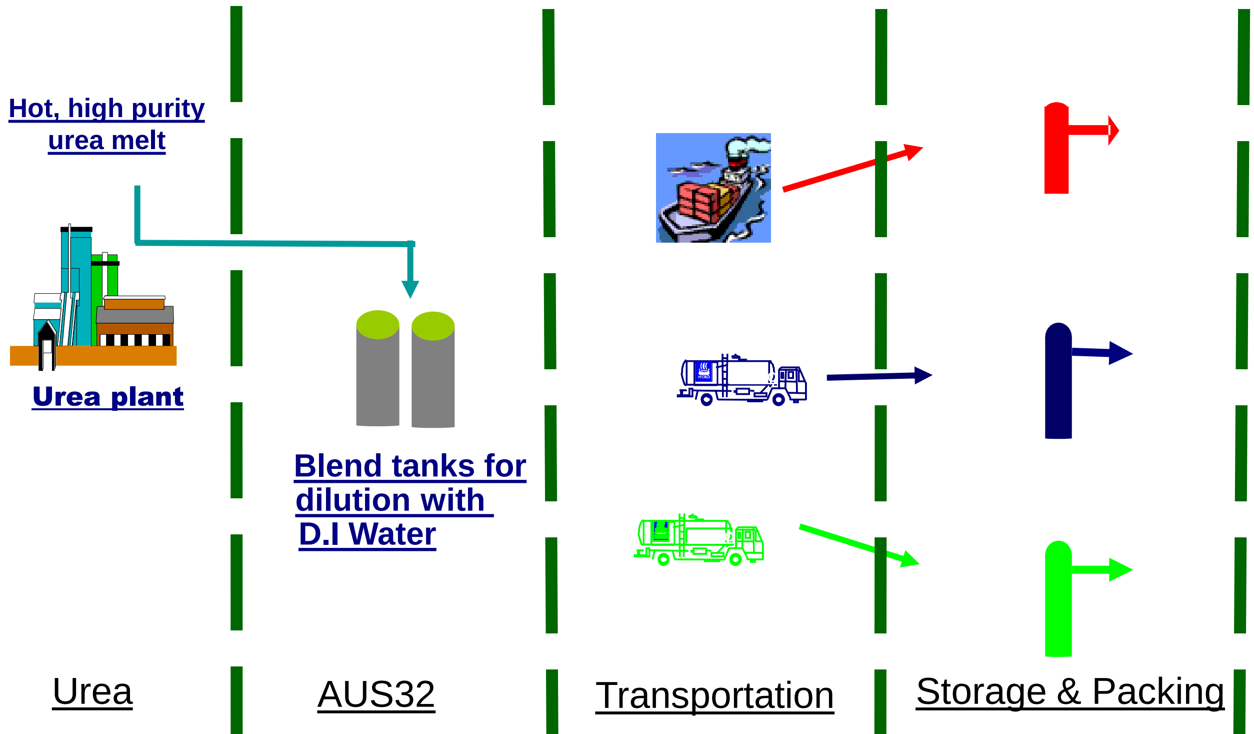


- There are multiple reaction pathways that may lead to nitrated PAHs including electrophilic and free radical nitration, photolysis in the atmosphere, and de novo formation.
- There is evidence that points toward nitration via N_2O_4 and NO_2 radicals.
- Nitration of PAHs can take place in SCR or DPF systems if not designed properly.

(Heeb et al. ES&T, 2008, 42, 3773-3779)

(Liu et al., *Environ. Sci. Technol.*, 2015)

AUS32 Manufacturing & Distribution



Decant and Distribute

- Stored in bulk tanks (SS/MS(coated)/HDPE)
- Can be distributed in bulk, totes, drums and small packs

Policy & Implementation

- Availability of Industrial Urea locally for manufacturing AUS 32 in India to provide best TCO to the customer
  - Subsidized (agricultural) vs commercial stream maintenance
  - Additional capacity requirement

- Clarity on Industrial Urea imports policy for automotive application

- Educating drivers and operators in field
  - How much AUS32 consumption to expect
  - Importance of high quality AUS32 solution usage
  - OBD-II diagnostics capabilities that will deter substitutes / dilution
  - Cleanliness aspects.

Emission Solutions

Questions?

Thank You