Safe and compact ammonia storage/delivery systems for SCR-DeNO$_X$ in automotive units

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Catalytic NO$_X$ reduction

- Selective Catalytic Removal of NO$_X$:
  \[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 6\text{N}_2 + 6\text{H}_2\text{O} \]

- Needed for diesel and lean-burn engines (3-way catalyst)
- Main problem: Safe and compact NH$_3$-storage on-board for dynamic dosing into tail pipe.

*Urea solves the safety issue…*

*but is not a simple plug’n’play technology*
Challenges of using urea

- Freezing
- Moderate storage capacity
- Complex system
- Droplet conversion and mixing in exhaust line
- Hydrolysis catalyst (?)
- No dosing at idle
- Solid deposits
  - undesired products of decomposition
  - droplet impaction
- Enforcing / OBD
Components in the urea system

- Tank (incl. heater)
- Temperature sensor
- Level sensor
- Urea quality sensor
- Compressed air (some are airless)
- Heated urea transport flow tubes
- Supply module with filter
- Pump
- Supply line purging
- Spray nozzle
- Internal mixers in exhaust line
A couple of important questions:

- Is urea the only SCR enabler?
- Do OEMs have to wait for an AdBlue infrastructure?

Ammonia is there!

[source: US DOE ammonia report]
Dense and safe ammonia storage: Controlled release from metal ammine complexes

The ammonia content

- Mg(NH$_3$)$_6$Cl$_2$: 38.1 mol NH$_3$/l
- Liquid ammonia: 40.1 mol NH$_3$/l

Reversible ammonia storage:

MgCl$_2$ + 6NH$_3$ $\rightleftharpoons$ Mg(NH$_3$)$_6$Cl$_2$
Volatile-to-toxicity ratio*

- 1 liter liquid ammonia
  - => 1.1 liter storage material
  - => 1.3 kg storage material
  - => 4000 times lower volatility

* Vapor pressure divided by IDLH (NIOSH) partial pressure

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Details on the ammonia capacity

kg NH$_3$/m$^3$

- **AdBlue:**
  - 3.1 times higher volume needed;
  - 2.7 times higher mass needed

Liquid ammonia | Amminex technology | AdBlue
---|---|---
680 | 620 | 200
Getting NH$_3$/H$_2$ out of dense rods: a self-generated nanoporosity

Symmetry axis

NH$_3$

Heat

Porous front

R=R$_0$

Ammine salt unit

NH$_3$ 2-4nm 15-40nm

Porous front

15-40nm

Pore Volume (cm$^3$/g)

Pore Diameter (nm)

54.3%

28.2%

91.7%

0.0%

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A simple, low-cost ammonia delivery system

Storage canister

Ammonia release control

ECU

Exhaust line

Limited “free” $\text{NH}_3(\text{g})$ at all times
Example of system dynamics

46 hrs

>99% NH$_3$-release

Buffer pressure

Set-point

Buffer pressure

Set-point

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Driving cycle dynamics demonstrated
Retrofit or new vehicles – both possible

SCR catalyst

Diesel

Buffer

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Also very suitable for light duty

- 6-8 liters ammine-canisters equals 18-24 liters of AdBlue
- No extensive infrastructure and end-user intervention

7 liter canister: 22,000 km
7 liter AdBlue: 7000 km

1 kg NO$_X$ removed $\iff$ 1 kg “AdAmmine” (0.9 liter)
Light-duty test system

0.5-1 gall. sized prototypes

Ammonia release control

Storage canister

ECU

Exhaust line

Buffer

Dosing valve

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Recharging of canisters: Demonstrated

- Existing infrastructure for ammonia distribution
- Canisters can be recharged with storage material inside

Example of some of the ammonia pipelines in US
[source: US DOE ammonia report].

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Enforcing / compliance

• No end-user intervention → less risk of neglecting
  – No end-user handling; no false urea refill
  – Easy to detect empty ”AdAmmine” system
  – Simpler OBD
Urea infrastructure

An example urea production and distribution pathway

Slide from DEER proceedings (available on-line)

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The storage capacity of “AdAmmine” is as high as solid urea. AdBlue is urea and approx. 70% water. The transported volume (in retail) of AdBlue is three times higher than “AdAmmine”
Prices and production: bulk chemicals

• Ammonia: 300-350$/ton
• MgCl$_2$: 250$/ton in bulk quality
• Solid ammonia storage material:
  – Combination of existing bulk production technology.
• No tank station infrastructure
• Canister re-saturation: Anhydrous ammonia

• Will always be competitive with the price of distributed AdBlue.
Value propositions – both soft and hard

- **Car/truck**: Low cost of storage/dosing system (low impact on vehicle cost)
- **Car/truck**: High capacity (lower impact on design)
- **Driver/user**: No end-user intervention (user-friendly)
- **Driver/user**: Low raw-material cost (inexpensive for end-users)
- Authorities: Easier to enforce!
Summary

• Higher capacity than AdBlue (factor 3 by volume; 2.7 by mass)
• Fewer moving parts in the Amminex dosing system
• No complex urea chemistry
  – Long-term storage possible (no decomposition in tank)
• No issues of freezing
• Flexibility in dosing point; fast mixing with exhaust gas
• No drop in exhaust temperature due to water evap.
• A simpler infrastructure: “car dealers, repair shops and fleet-operators”.
  – Storage canisters replaced at service intervals. No end-user intervention. Avoiding the need for AdBlue at every gas station
• Lower price of raw materials (lower than AdBlue).
  – OEM canister: salt (MgCl$_2$) + ammonia + steel
  – recharging: anhydrous ammonia
• Ammonia is available worldwide. MgCl$_2$ is 10% of sea salt.

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