Crack, Reform, Recover: Optimising alternative marine fuels

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MariNH3 — Clean, green ammonia engines for maritime

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Introduction

Ammonia is a carbon-free fuel with high hydrogen density, making it a strong candidate for decarbonising internal combustion engines. However, direct ammonia substitution often leads to **unburnt NH_3 (ammonia slip)** and **N_2O emissions**. To improve combustion and reduce emissions, **onboard catalytic cracking** is used to generate hydrogen-rich reformate gas.

In this study, a **dual-fuel strategy** is applied, combining gasoline with NH_3/H_2 blends. A **multi-stage aftertreatment system**—including a TWC, ammonia slip catalyst (ASC), and deN_2O catalyst is used to mitigate tailpipe emissions under various operating conditions.

Why Ammonia Cracking?

2012 – Assessing the Effects of Partially Decarbonising a Diesel Engine by Co-fuelling with Dissociated Ammonia

2013 – Ammonia as Hydrogen Carrier for Transportation; Investigation of the Ammonia Exhaust Gas Fuel Reforming

2015 – Increased NO_2 Concentration in the Diesel Exhaust for Improved Ag/Al_2O_3 Catalyst NH_3-SCR Activity

2021 – Exhaust Energy Recovery via Catalytic Ammonia Decomposition to Hydrogen for Low Carbon Clean Vehicles

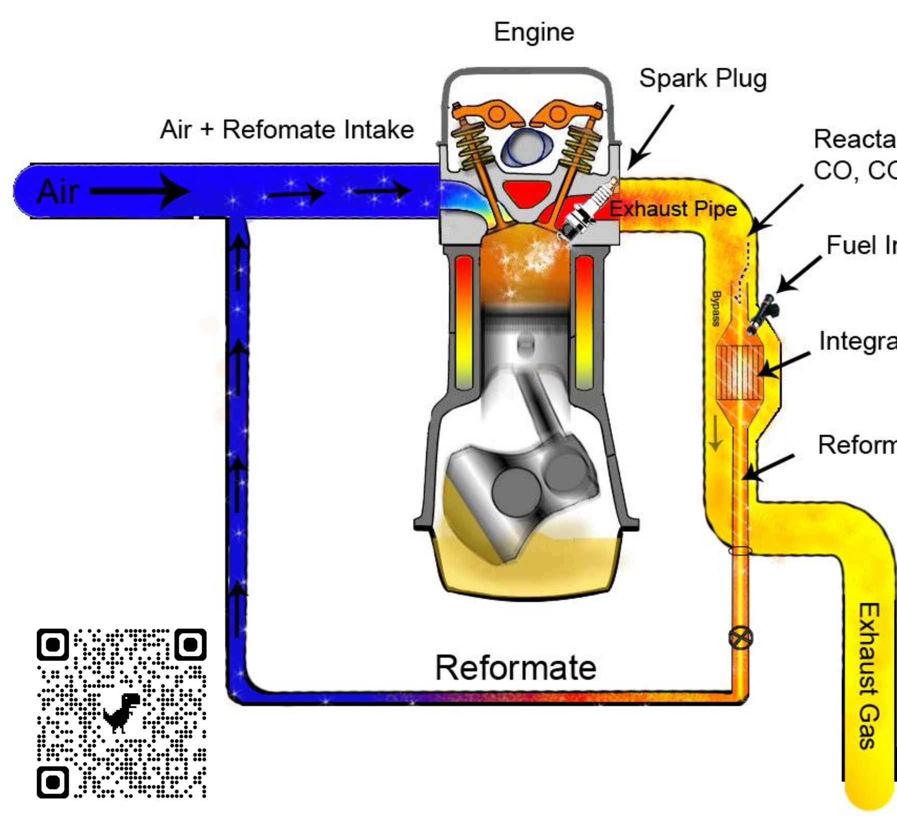
Key Points

- NH_3 slip increases as gasoline is replaced by ammonia
- H_2 from cracked NH_3 enhances combustion stability
- Tailpipe NH_3 and N_2O are controlled using advanced catalysts

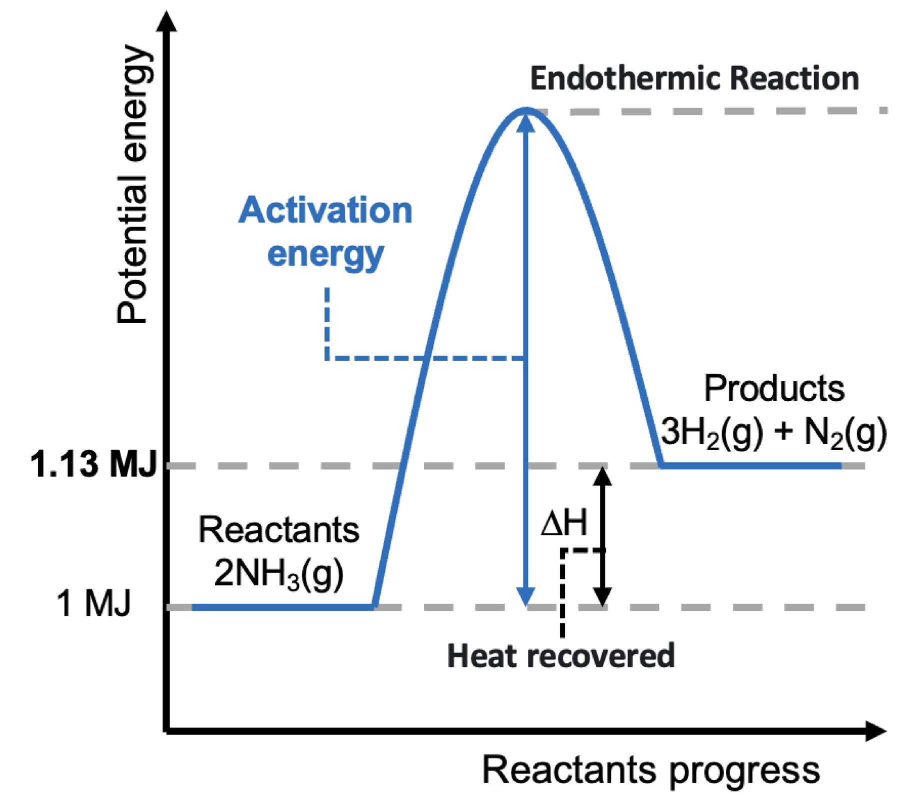
Ammonia as a fuel & Ammonia/Methanol cracking with Heat Recovery

Why Ammonia/Methanol Cracking with Exhaust Heat Recovery?

- Recover energy waste heat in the form of "H_2 - Fuel" (Ammonia/Methanol)
- Hydrogen enables the efficient combustion of Ammonia and reduces Ammonia Slip
- Reduce all the GHG emissions
- Potential to reduce regulated and unregulated emissions (NH_3, NO_X, N_2O, CO, HC)

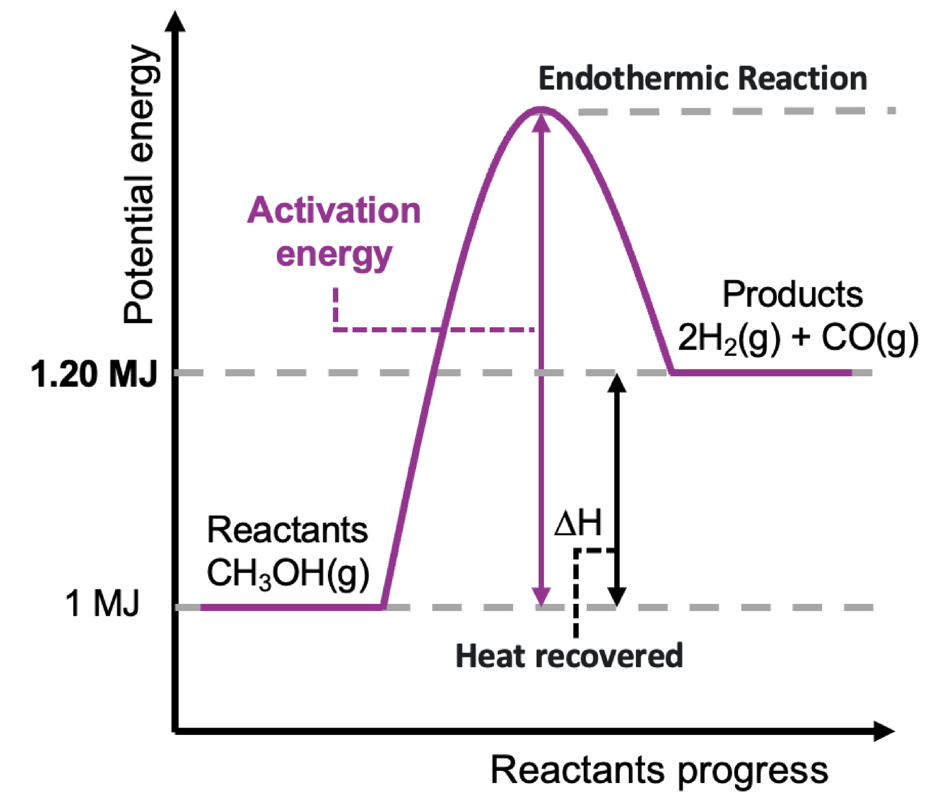


Option 1. Use only the Heat of the hot exhaust gas
Option 2. Use the Heat, Water (H_2O) and Carbon Dioxide (CO_2) of the exhaust gas to produce H_2



Ammonia Cracking

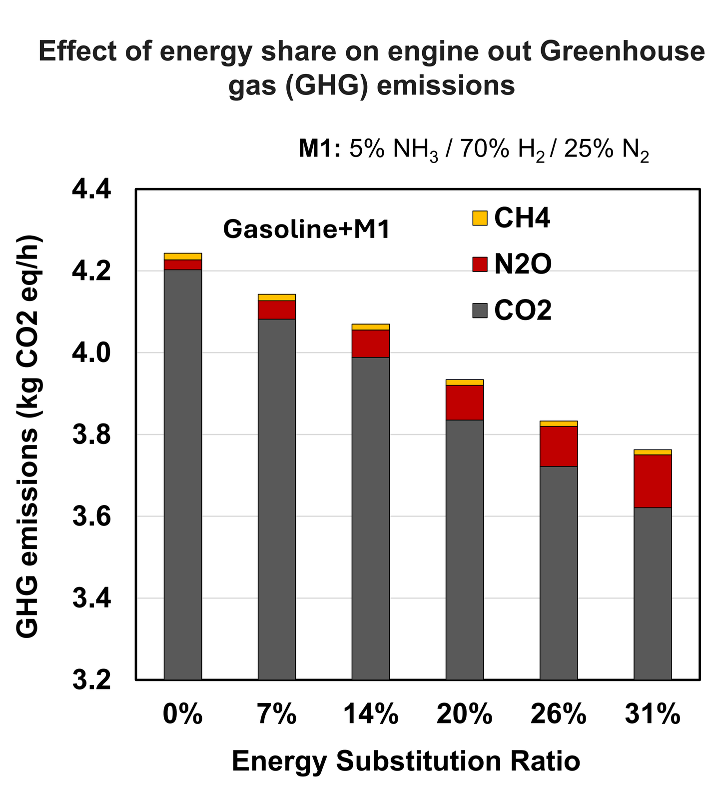
$$2NH_3 \rightarrow N_2 + 3H_2,\ \Delta H_{298} = +46\ kJ\ mol^{-1}$$

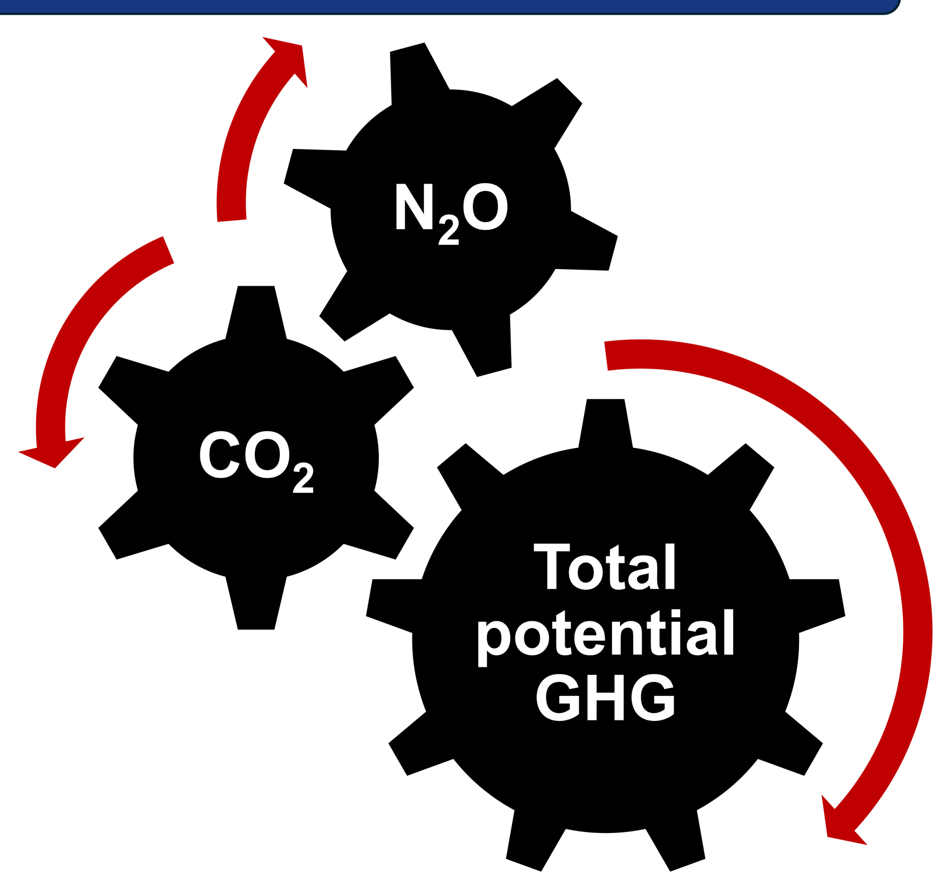


Methanol Cracking

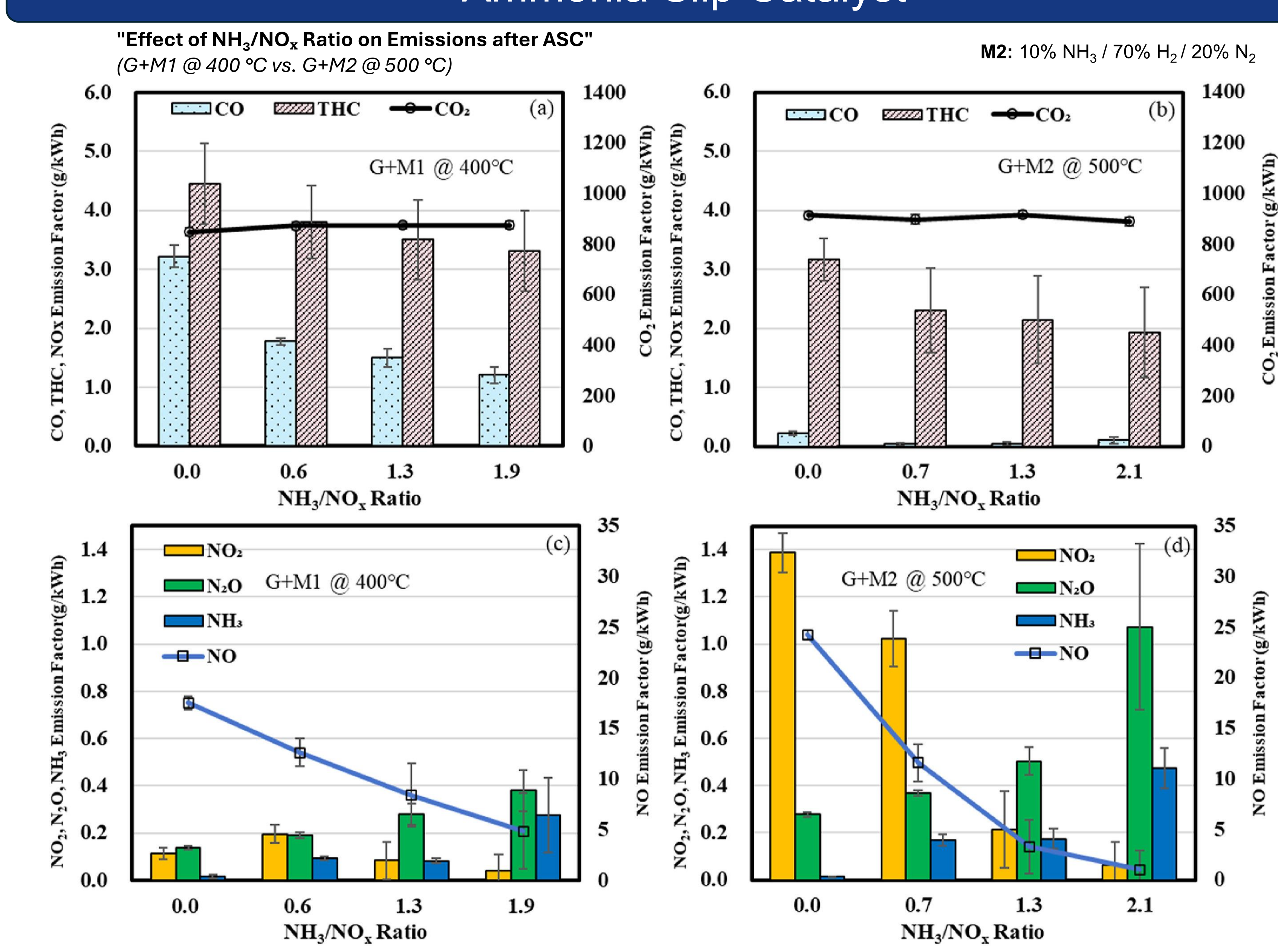
$$CH_3OH \rightarrow CO + 2H_2,\ \Delta H_{298} = +90\ kJ\ mol^{-1}$$

Engine GHG Emissions



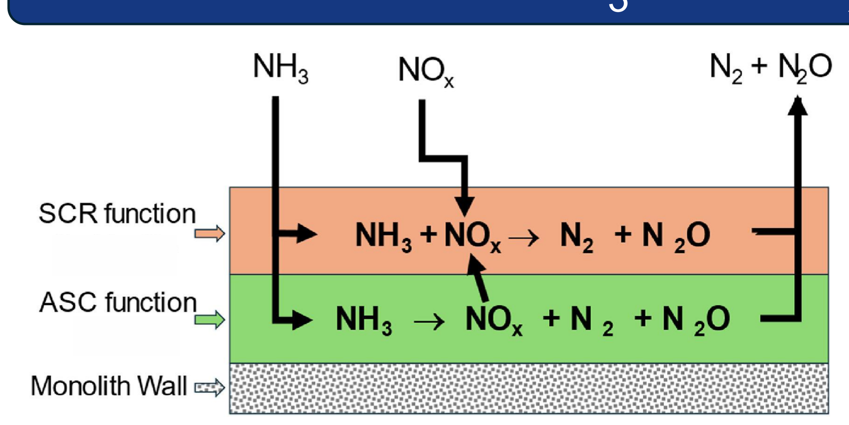


Ammonia Slip Catalyst

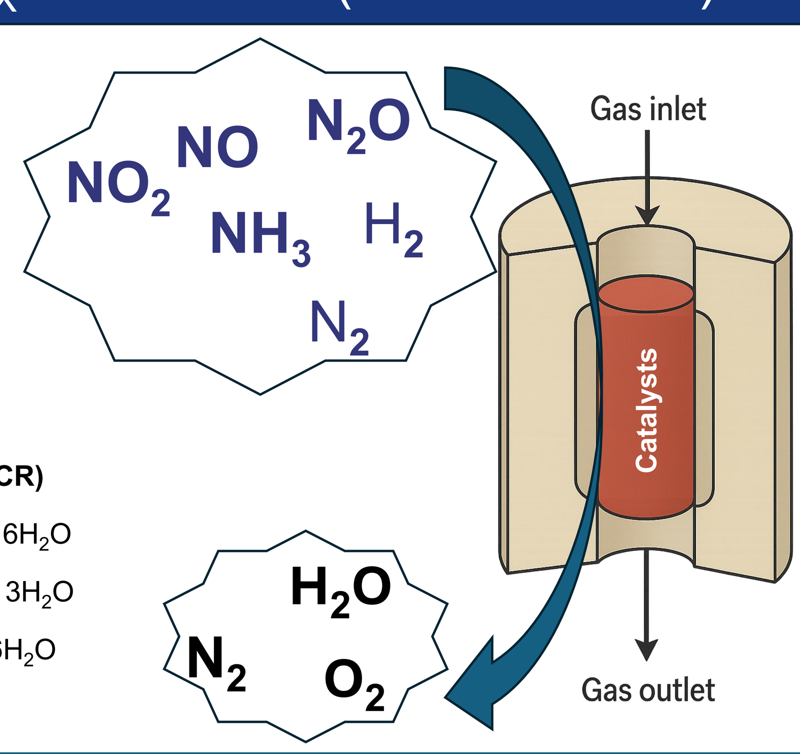


- NO_X↓: NH_3/NO_X > 0.7 enhances fast SCR, reducing NO & NO_2
- NH_3 Slip↑: Excess NH_3 (≥1.3) exceeds ASC oxidation capacity
- N_2O↑: Linearly increases with NH_3/NO_x due to side reactions → need deN_2O catalyst
- CO & THC↓: Improved oxidation at 500 °C via PGM activation
- Best Temp: ASC optimal in 400–500 °C range (typical SI exhaust)

Schematic of NH_3 and NO_X conversion (Dual-function)



Oxidation reactions (ASC)	Reduction reactions (SCR)
$4NH_3+3O_2 \rightarrow 2N_2+6H_2O$	$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$
$2NH_3+2O_2 \rightarrow N_2O+3H_2O$	$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$
$4NH_3+5O_2 \rightarrow 4NO+6H_2O$	$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$
$4NH_3+7O_2 \rightarrow 4NO_2+6H_2O$	



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