Nitrogen-based Fuels: Renewable Hydrogen Carriers

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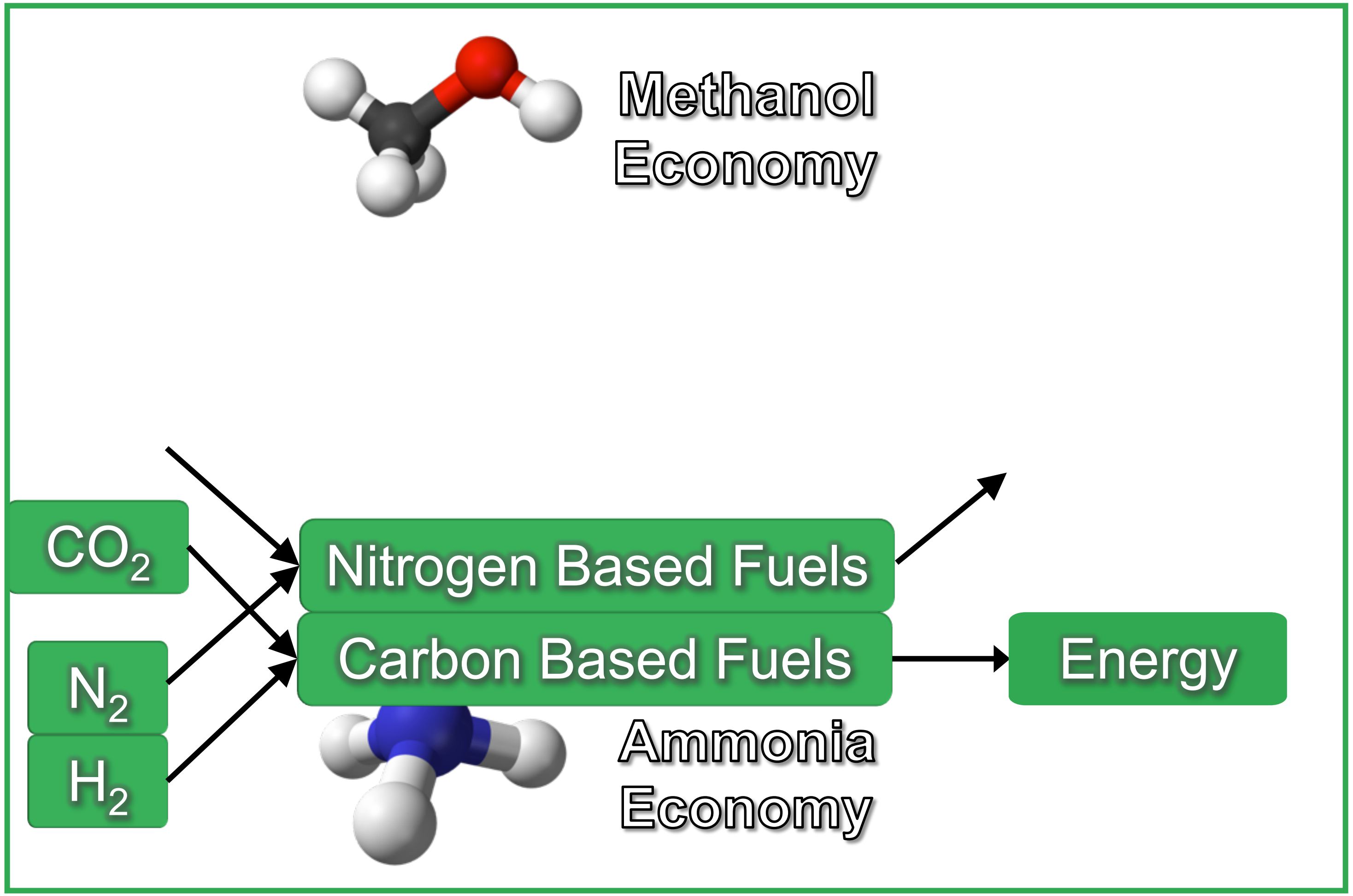
Motivation

- Economic renewable H_2 is getting closer
- H_2 is incompatible with large scale fuel transport infrastructure
- Chemical fuels are attractive H_2 carriers since they are safer and easier to transport
- Chemical fuels offer higher volumetric energy densities than pure H_2

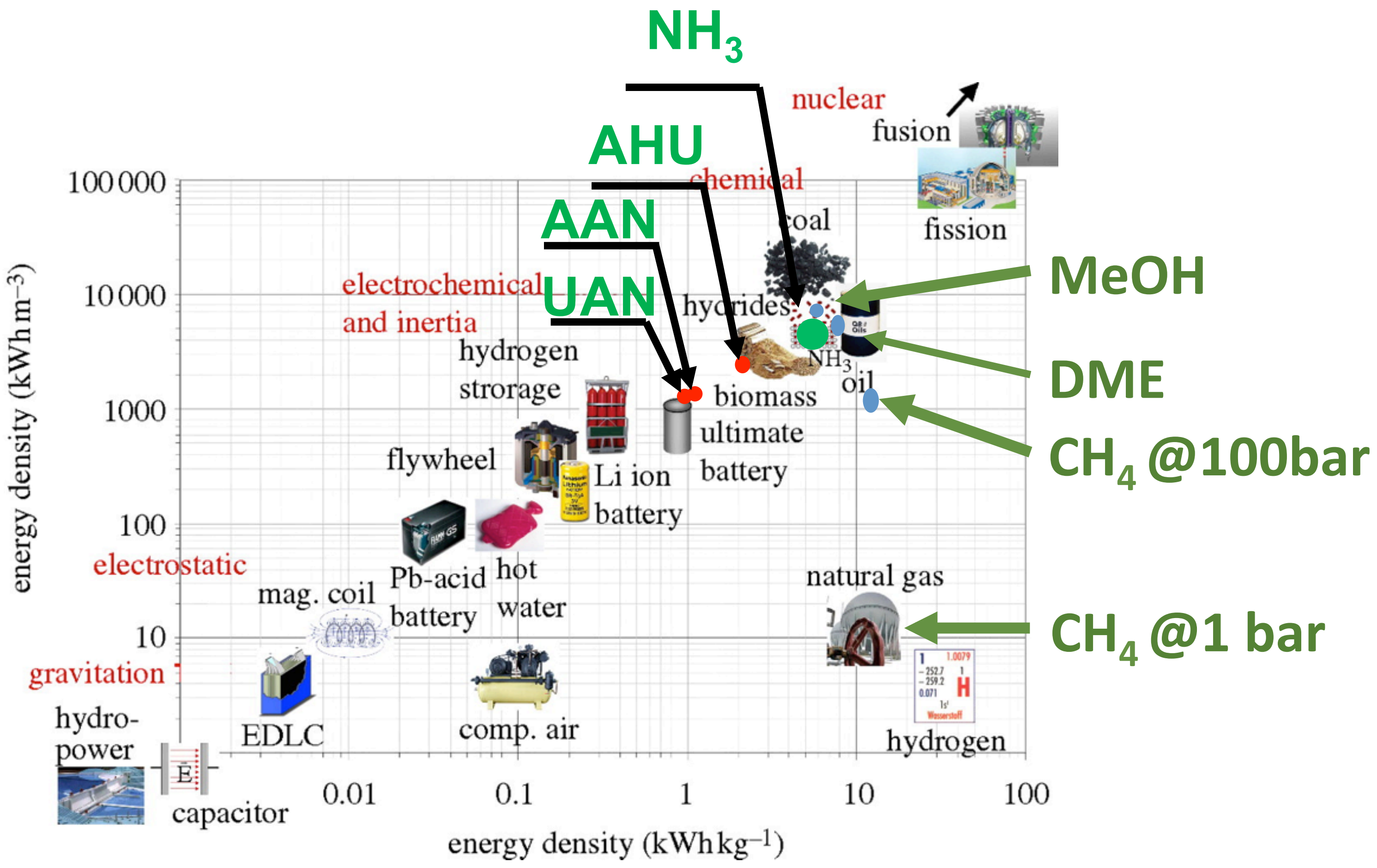
But what fuels can we choose from?



Motivation

- Synthetic fuels from N_2 & H_2 can be gases, liquids or solids.
- N2-based fuels are competitive with carbon-based fuels.

Energy Density?



R. Lan et al., *Int. J. Hydrogen Energy*, **37**, 1482-1494, 2010.

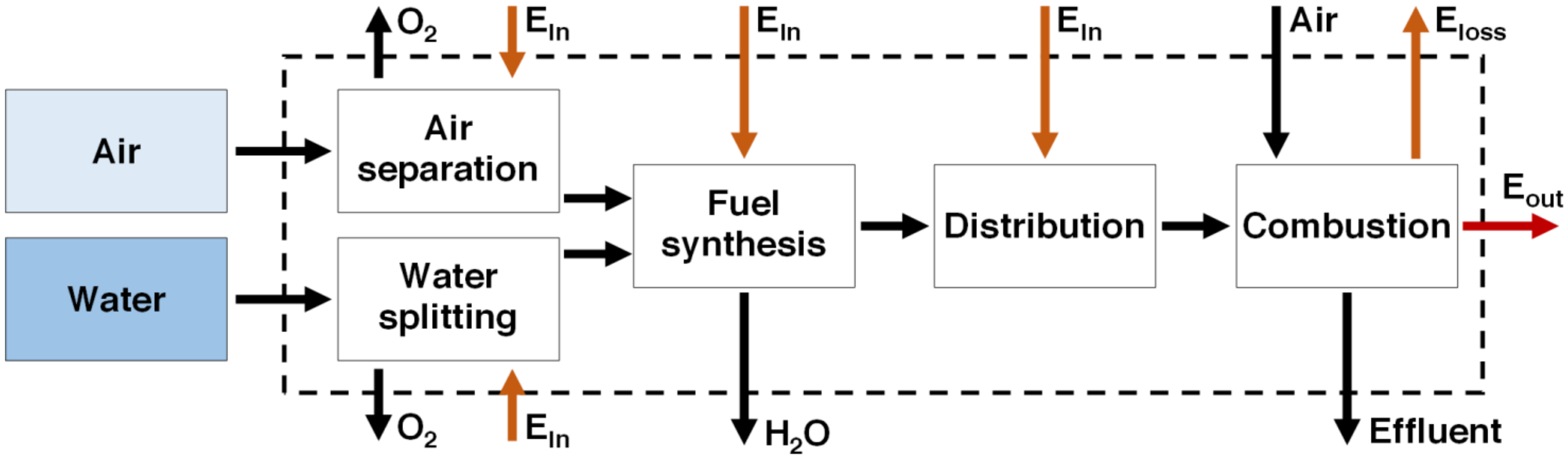
Any Special Applications?

- High pressure gas (e.g. EOR)
- Ammonia to power: ammonium nitrate in-situ ignition agent.

Feasibility of Nitrogen-based Fuels

Power to Fuel to Power Analysis – PFP index

For any synthetic fuel the ratio of the useful energy output and the synthesis energy from stock materials can be calculated giving rise to the PFP index:



A. Grinberg Dana et al., *Angew. Chem. Int. Ed.*, **55**, 8798-8805, 2016.

Feasibility of Nitrogen-based Fuels

Power to Fuel to Power Analysis – PFP index

For any synthetic fuel the ratio of the useful energy output and the synthesis energy from stock materials can be calculated giving rise to the PFP index:

$$PFP_{atm} = (energy\ density) \cdot \eta_{combustion} / (water\ splitting) + (air\ seperation) + (synthesis) + (dist$$

A. Grinberg Dana et al., *Angew. Chem. Int. Ed.*, **55**, 8798-8805, 2016.

Feasibility of Nitrogen-based Fuels

<u>Power to Fuel to Power Analysis – PFP index</u>

For any synthetic fuel the ratio of the useful energy output and the synthesis energy from stock materials can be calculated giving rise to the PFP index:

Fuel	Air Separation (CO_2/N_2) (GJ ton^{-1})	Water splitting (GJ ton^{-1})	synthesis energy (GJ ton^{-1})	Distribution (GJ ton^{-1})	Energy Density (HHV) (GJ ton^{-1})	Combustion efficiency	PFP index
CH_4	18.1	90.8	1.2	1.51	55.5	54%	27%
MeOH	9.1	34.1	4.8	0.13	23.7	54%	27%
DME	12.6	47.4	8.7	0.15	31.7	50%	23%
NH_3	0.18	32.1	1.6	0.19	22.5	53%	35%
Aq.AHU	2.56	14.6	1.5	0.10	9.2	50%	27%
Aq.ANA	0.06	115	0.9	0.08	3.7	47%	14%
Aq.UAN	0.79	10.9	1.3	0.07	3.3	48%	12%

Angewandte Chemie International Edition — A. Grinberg Dana et al., *Angew. Chem. Int. Ed.*, **55**, 8798-8805, 2016.

Effect of ϕ on AAN ignition

- Ammonium nitrate is a net oxidizer, decomposing into ammonia (reducer) and nitric acid (oxidizer)

$$3NH_4NO_{3(aq)} + 2NH_4OH_{(aq)} + XH_2O_{(l)} \rightarrow 3HNO_{3(g)} + 5NH_{3(g)} + (X+2)H_2O_{(g)} \rightarrow 4N_{2(g)} + (X+11)H_2O$$

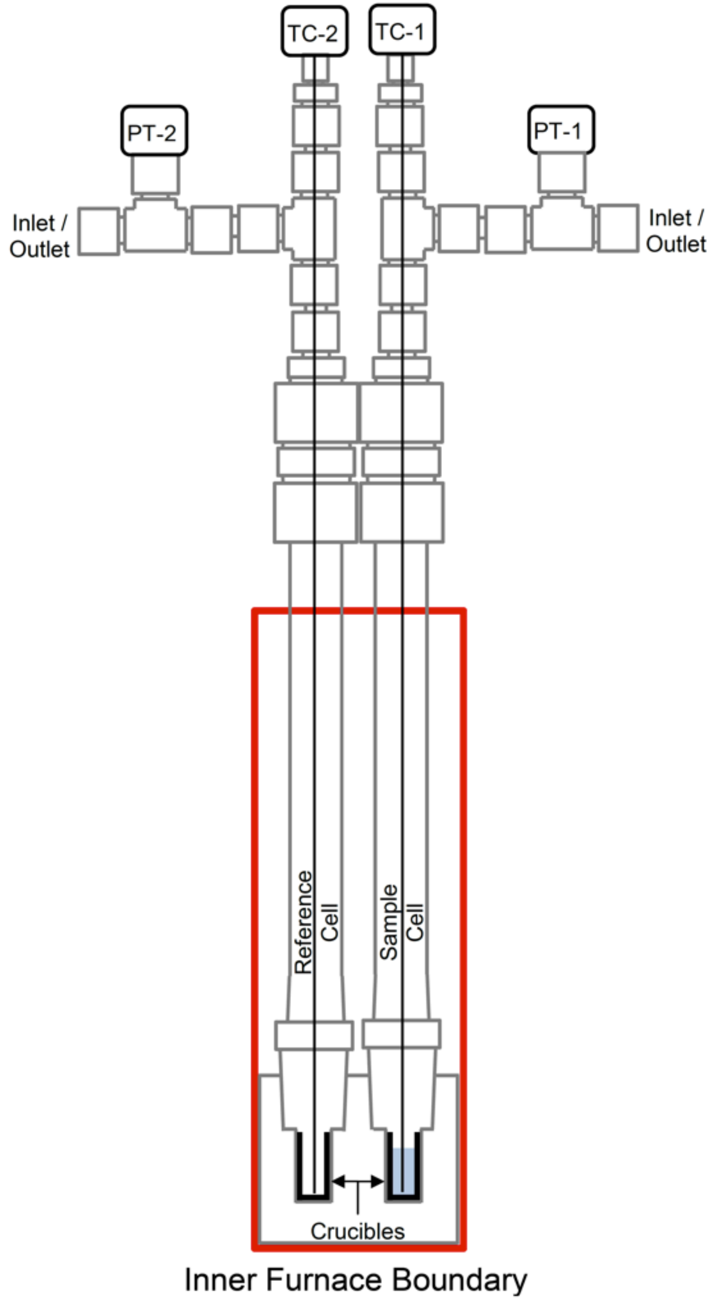
- The combustion of AAN does not require an external oxidizer (i.e. O_2/Air)
- For AAN, the equivalence ratio (the fuel to oxidizer ratio) is as follows:

$$\phi = fuel\ to\ oxidizer\ ratio/(fuel\ to\ oxidizer\ ratio)\downarrow sto. = n\downarrow fuel\,/n\downarrow oxi.\,/5/3$$

- **Hence, fuel rich and lean mixtures correspond to Φ>1 and Φ<1**

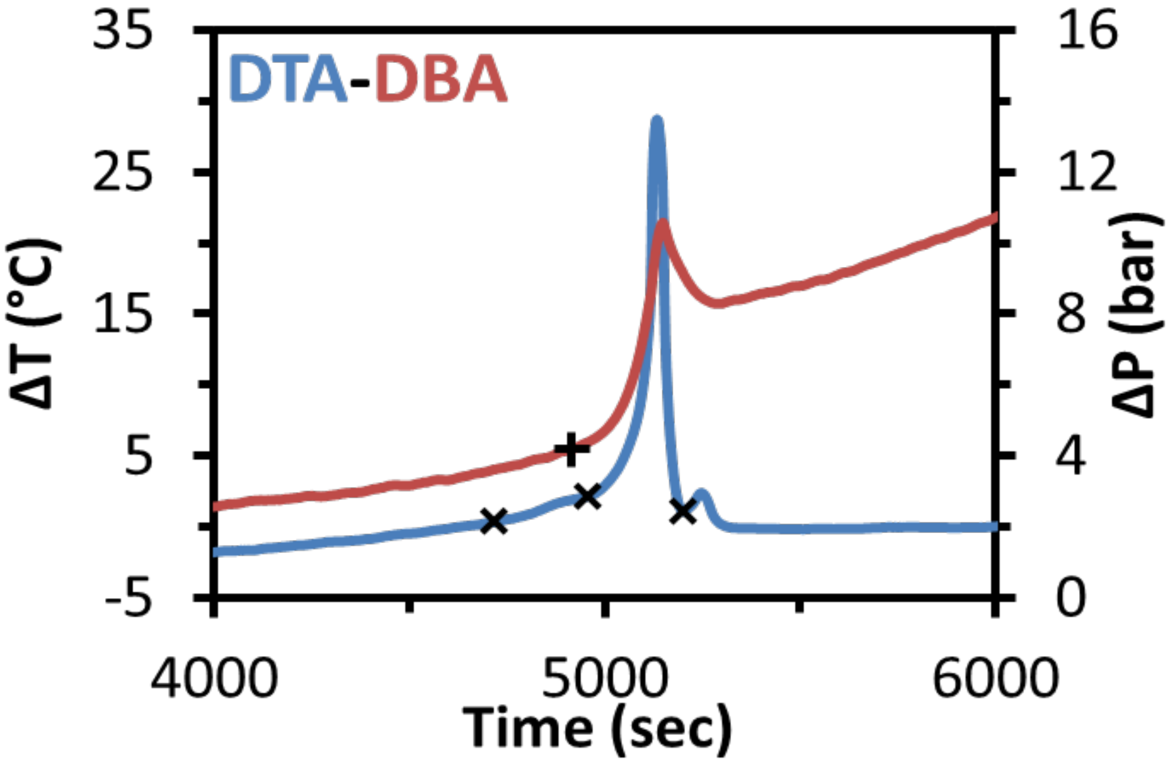
Experimental

- Testing rig: a dual chamber reactor
- Simultaneous differential thermal / barometric analysis (DTA/DBA)
- Heating 30^{o}C → 450^{o}C @ 5^{o}C min^{-1}
- Parameter of interest: the AIT - the **Auto Ignition Temperature**



FUEL A. Grinberg Dana et al., *Fuel*, **159**, 500-507, 2015.

Autoignition Data

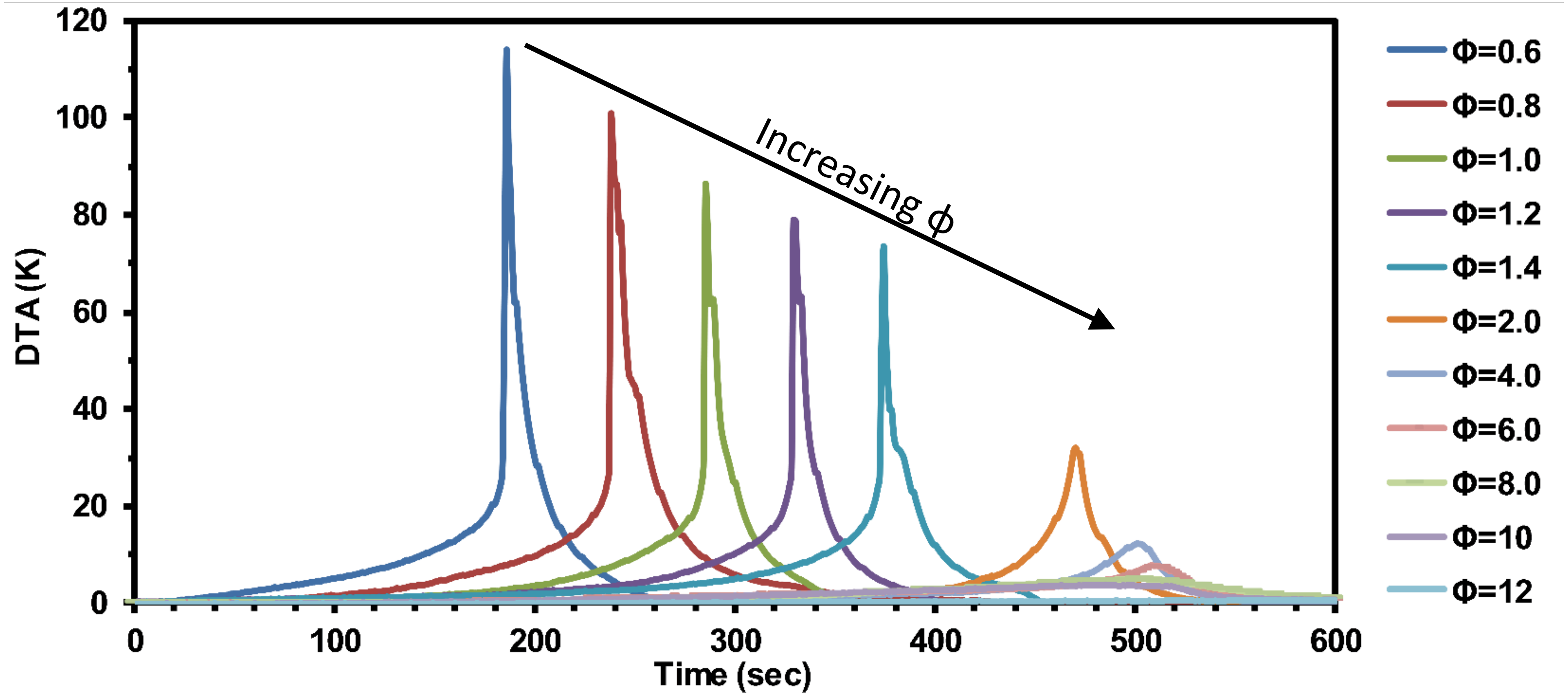


Effect of ϕ on AAN ignition
ΔT (K) vs. time starting from 250ºC

Increasing ϕ:

Delays the auto ignition

Reduces the peak DTA value



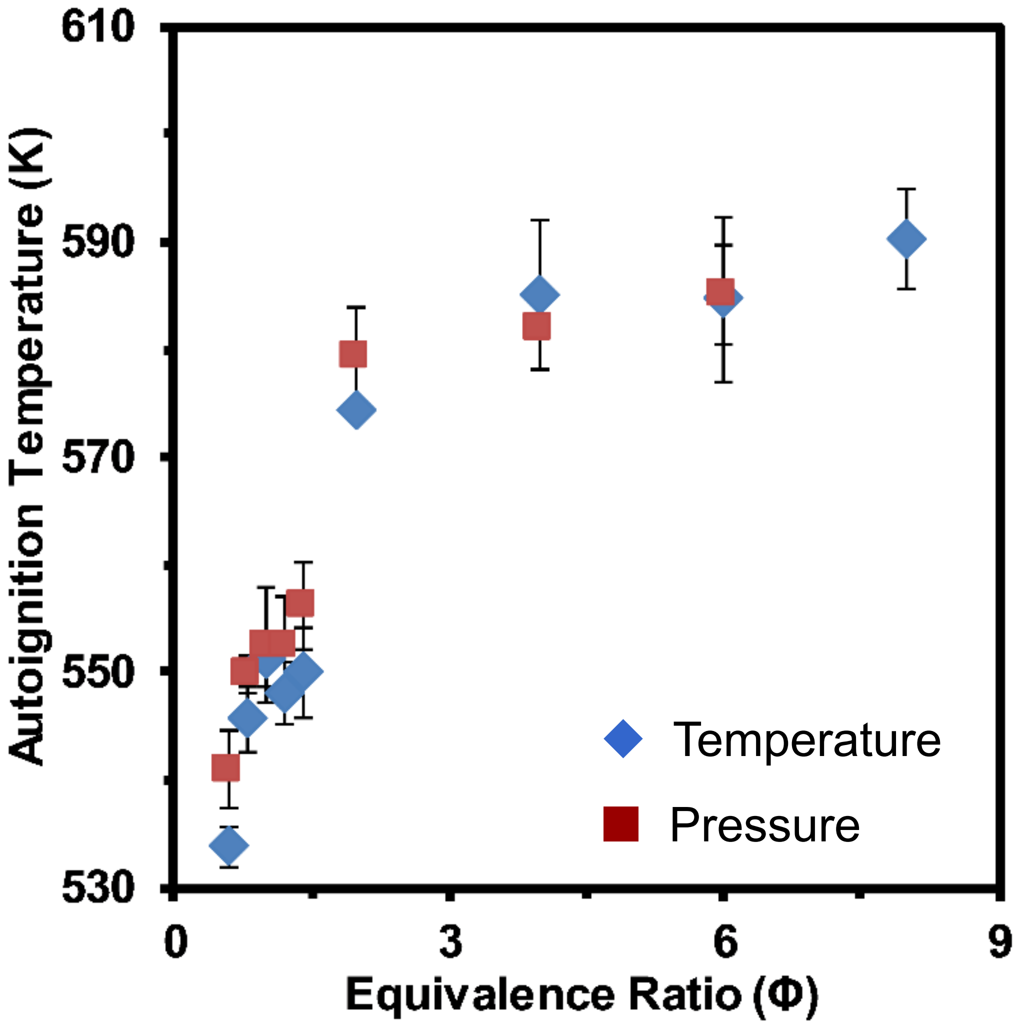
Combustion and Flame

B. Mosevitzky et al., *Combust. Flame*, 188, 142-149, 2018.

Effect of ϕ on AAN ignition

- The AIT increased with Φ
- Autoignition is not detected above Φ=6 and Φ=8 using DBA and DTA,
- What happened between

  Φ=1.6 and Φ= 2.0



Combustion and Flame

B. Mosevitzky et al., *Combust. Flame*, 188, 142-149, 2018.

Effect of ϕ on AAN ignition – Reaction Mechanism

- As ϕ is increased, more ammonia is present in the gas phase, thereby increasing the rate of re-formation of AN, and delaying the thermal autoignition:

$$NH_4NO_{3(aq)} \leftrightarrow NH_{3(g)} + HNO_{3(g)}$$

- Nitric acid mostly reacts to form dinitrogen tetraoxide, which in turn easily decomposes to nitrogen dioxide, generating small amounts of nitrogen trioxide:

$$HNO_{3(g)} + HONO_{(g)} \rightarrow N_2O_{4(g)} + H_2O_{(g)}$$

$$N_2O_{4(g)} \rightarrow 2NO_{2(g)} \qquad 2NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$$

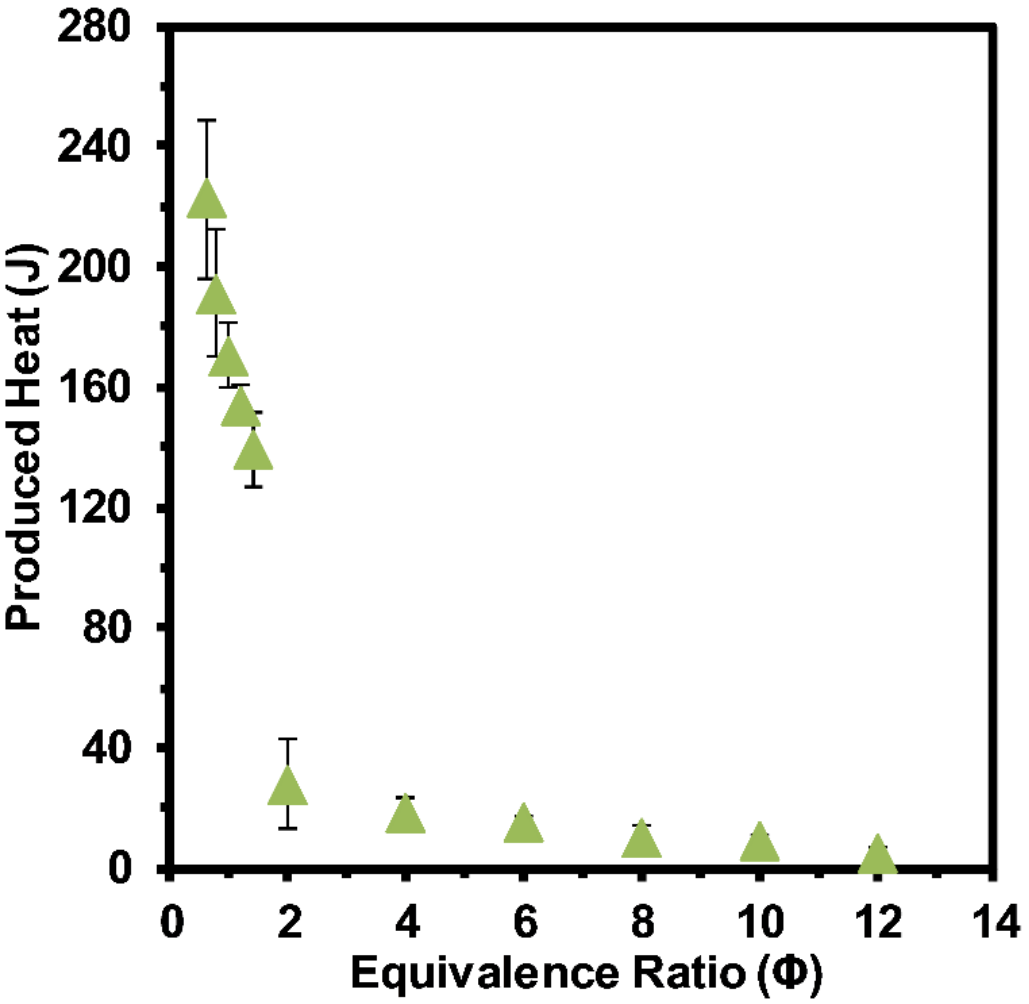
- Since **amidogen generation** is the ignition rate limiting step, higher ϕ values delay the thermal autoignition of AAN:

$$NH_{3(g)} + NO_{2(g)} \rightarrow NH_{2(g)} + HONO_{(g)} \qquad NH_{3(g)} + NO_{3(g)} \rightarrow NH_{2(g)} + HNO_{3(g)}$$

B. Mosevitzky et al., *Combust. Flame*, 188, 142-149, 2018.

Effect of ϕ on AAN ignition

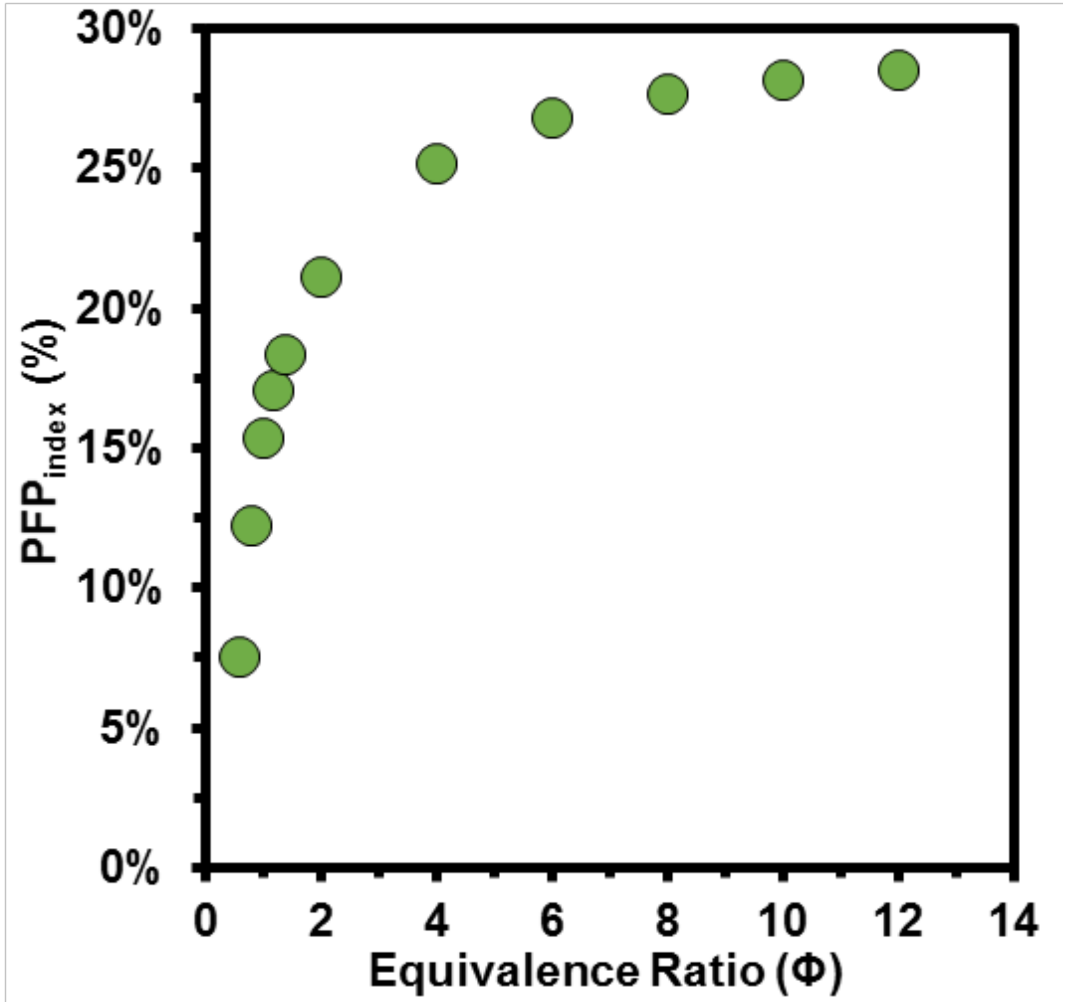
- The decreasing DTA peaks with increasing Φ suggests a smaller exothermic ignition
- To confirm this, the heat produced from 250^0C to the ignition peak was calculated
- Generated heat drops with increasing Φ
- This suggests the ignition is limited by AN content



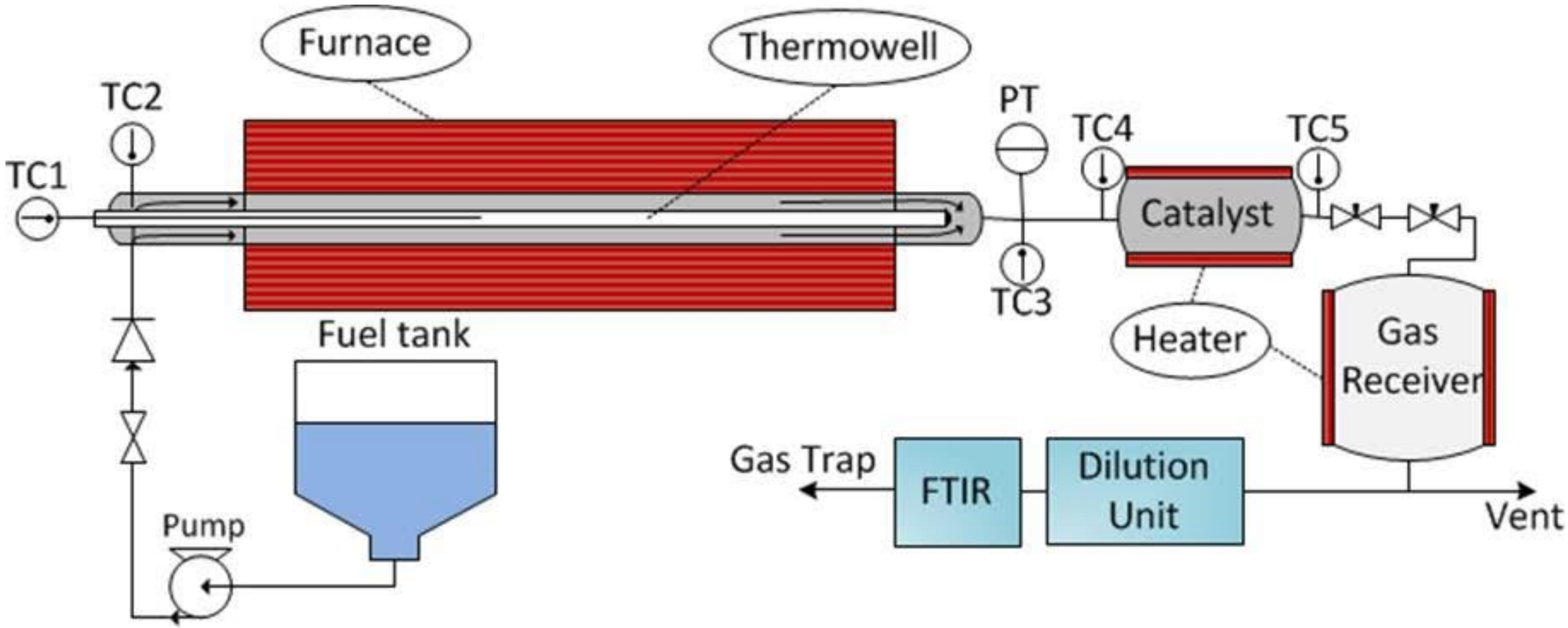
Combustion and Flame B. Mosevitzky et al., *Combust. Flame*, 188, 142-149, 2018.

Effect of ϕ on AAN ignition

- Increasing large ϕ can lead to higher PFP_{index} if the remaining NH3 is oxidized with air.
- Ammonium nitrate can be a catalyst for ammonia ignition at large ϕ.



Combustion Pollutant Abatement (UAN)



ACS OMEGA A.K. Deepa et al., *ACS Omega*, accepted, 2017

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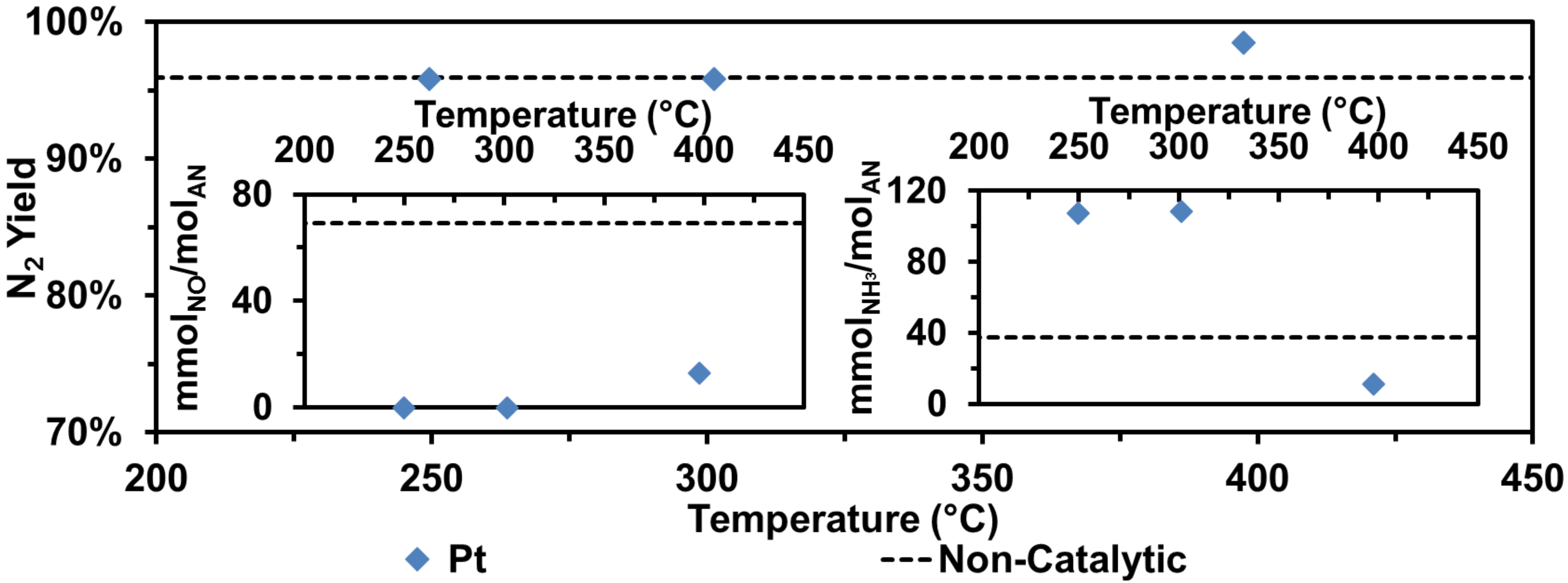

- Platinum can eliminate NO_X at temperatures as low as 250°C
- But ammonia is generated

ACS OMEGA A.K. Deepa et al., *ACS Omega*, accepted, 2017

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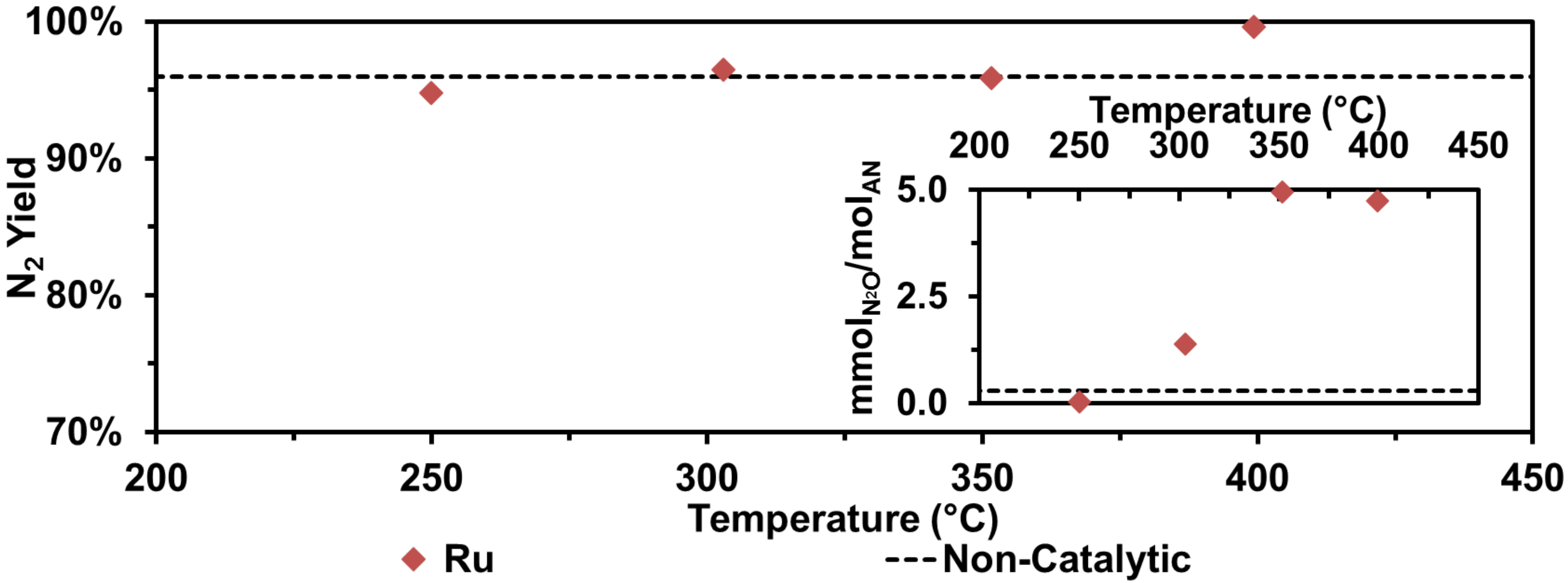
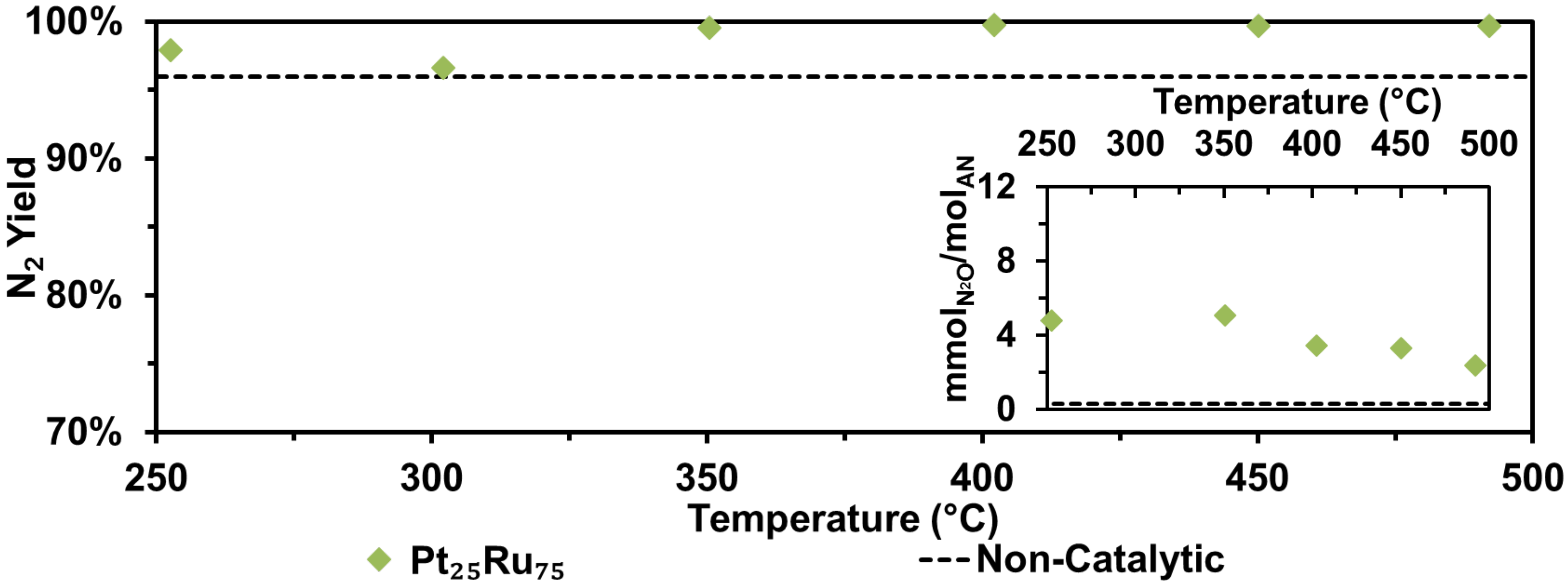


- Ruthenium shows good pollutant abatement activity only above 350°C
- However, it produces N_2O rather than NO_X and ammonia

A.K. Deepa et al., *ACS Omega*, Minor Revisions.

Combustion Pollutant Abatement (UAN)

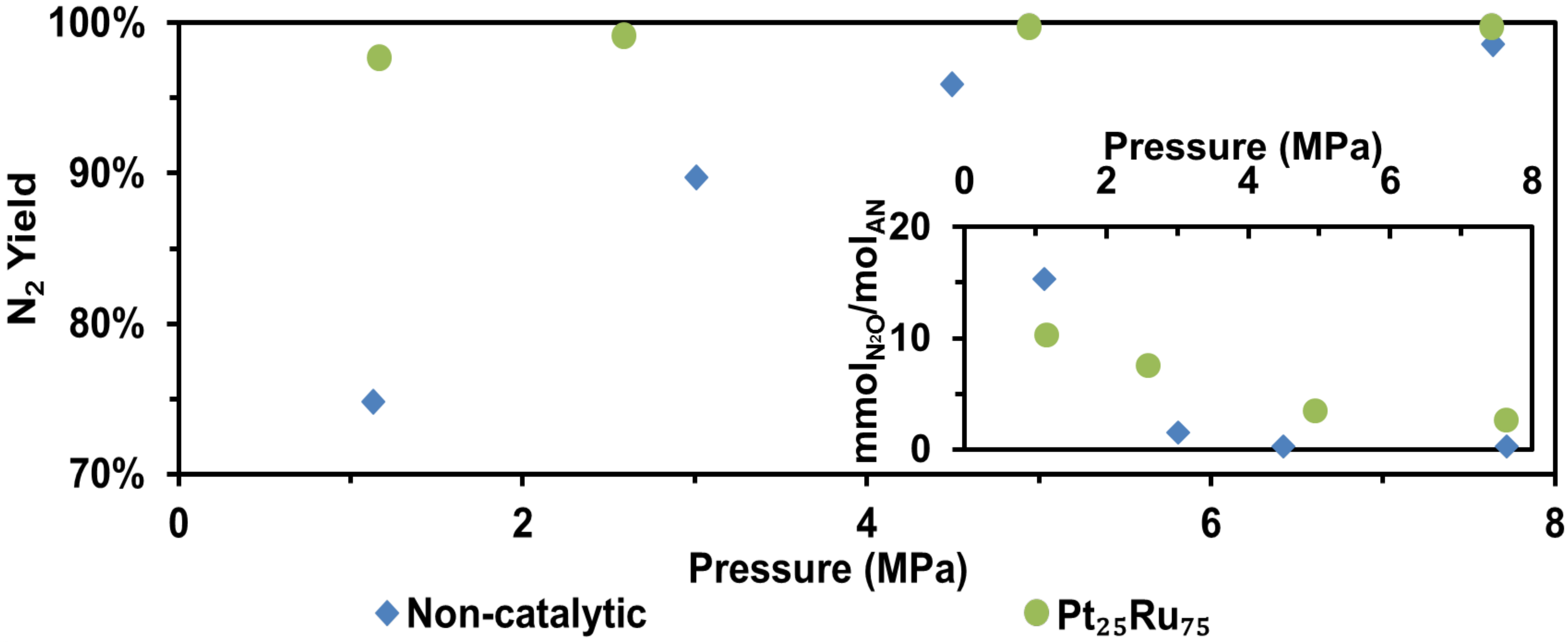


- Combining Pt and Ru produces an effect similar to pure Ru
- However, it requires lower temperature (T>300°C) and increases N_2 yield

A.K. Deepa et al., *ACS Omega*, Minor Revisions.

Combustion Pollutant Abatement (UAN)

With proper catalysts even **lower** pollutant levels can be reached



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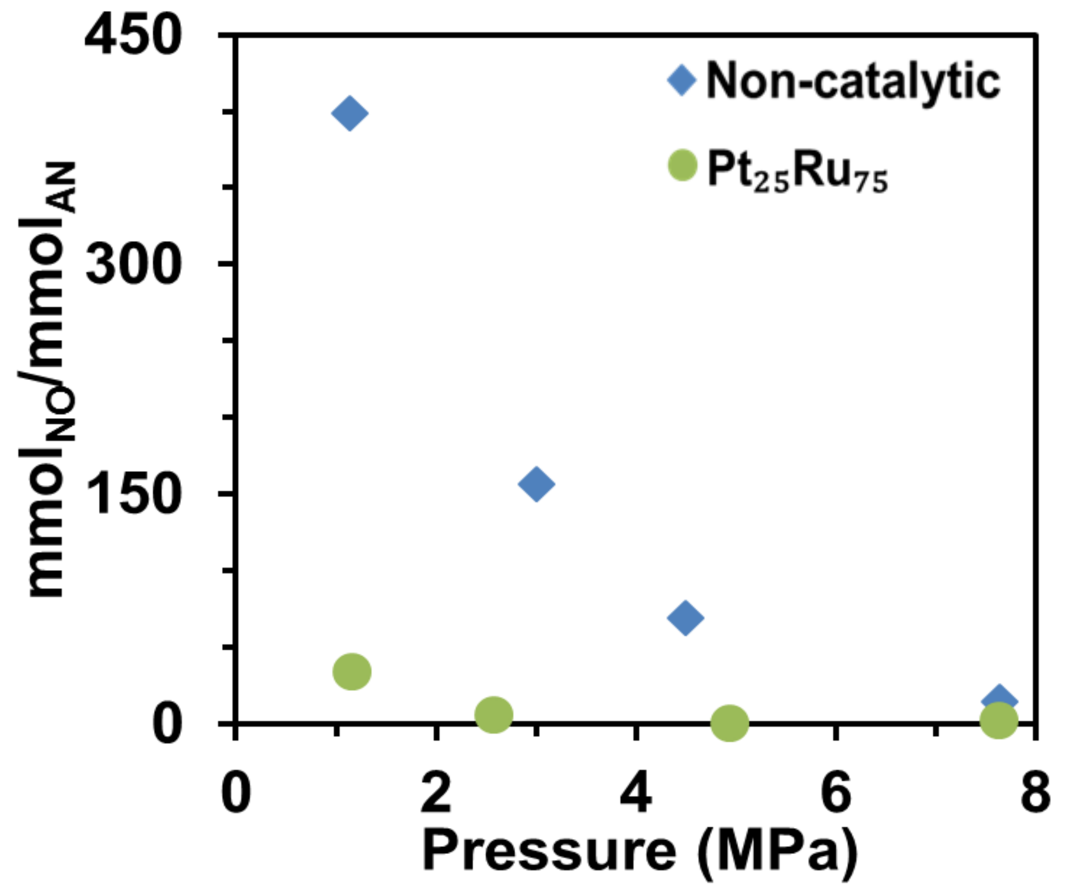

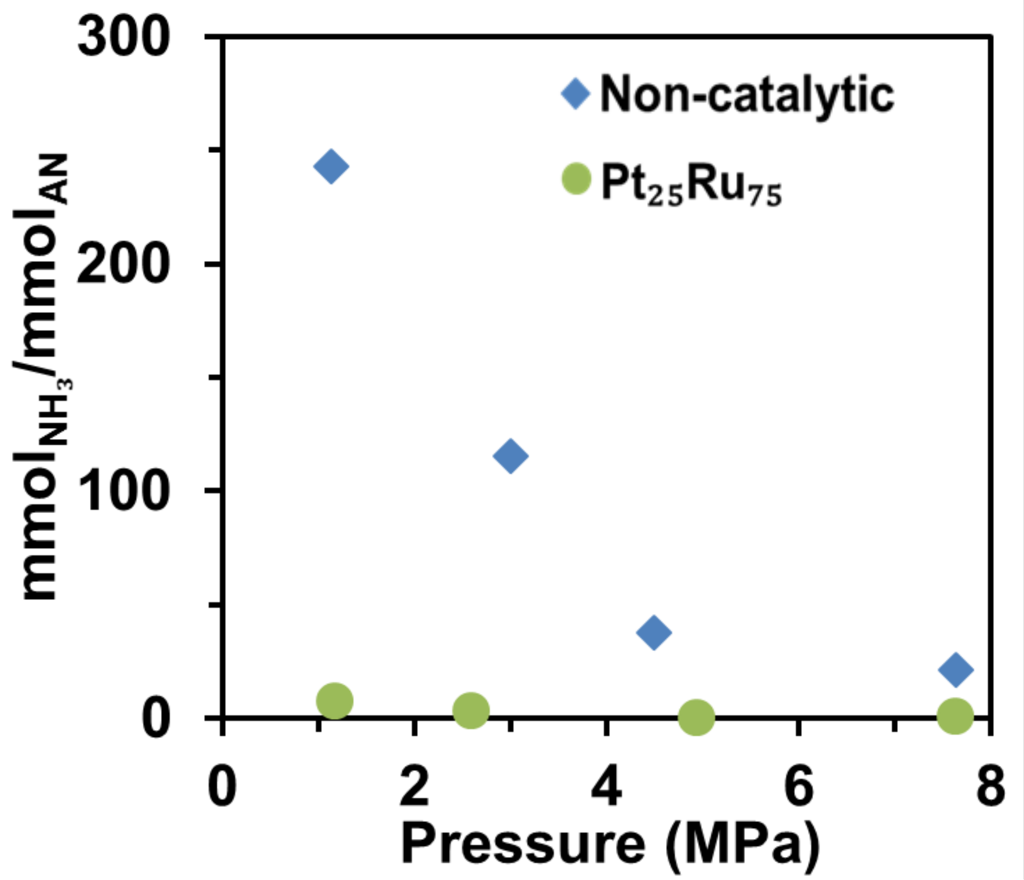

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Conclusions

- **PFP index:**
  - **NH_3 ranks higher than CH_4, CH_3OH or DME on an energy basis**
  - **UAH (Urea Ammonium Hydroxide) is comparable with HC fuels**
  - **AN can be used as an initiator for NH_3 combustion**
- **The ignition point of AAN increases with Equivalence ratio,**
- **AN limits the extent of reaction**
- **Mixed metal catalyst of $Pt_{25}Ru_{75}$ reduces the pollutant emission to a minimum even at 5 MPa**

Acknowledgements

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Thank You