XIII JONADA DE JÓVENES INVESTIGADORES DEL I3A

High-pressure study of ammonia/dimethyl-ether conversion in a flow reactor

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Objective:
- Extending the knowledge of NH_3/DME oxidation at high pressure under different operating conditions.
- Development of a detailed reaction kinetic model.

Introduction

Ammonia (NH_3)

Growing **interest:** climate change and **energy transition**
Applications: Security of **energy supply and storage, transportation** and combustion in **gas turbines**.

Carbon-free fuel: Combustion with **no CO_2 emissions** [1].

$$NH_3 + \frac{3}{4}O_2 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2O \quad r1$$

Implementation drawbacks: lower burning velocity and higher autoignition temperature compared to fossil fuels [2].

Promising solution **DME as an additive [3]**
- Excellent autoignition properties [4]
- Miscibility with hydrocarbons [4]
- High cetane number [4]

Methodology

Experimental Conditions:
Pressure: 1, 10, 20, 40 bar
Temperature: 350 – 1225 K; λ = 0.7, 1 and 3
$[NH_3]$ = 1000 ppm; [DME] = 0, 50 and 300 ppm
$[O_2]_{\lambda=0.7}$ = 630 ppm
$[O_2]_{\lambda=1}$ = 900, and 1650 ppm
$[O_2]_{\lambda=3}$ = 2700 and 4950 ppm
Quartz tubular reactor: 153.8 cm long, inner diameter of 0.6 cm. Ar as a bath gas
Simulation software: Chemkin pro [5]

Residence time:

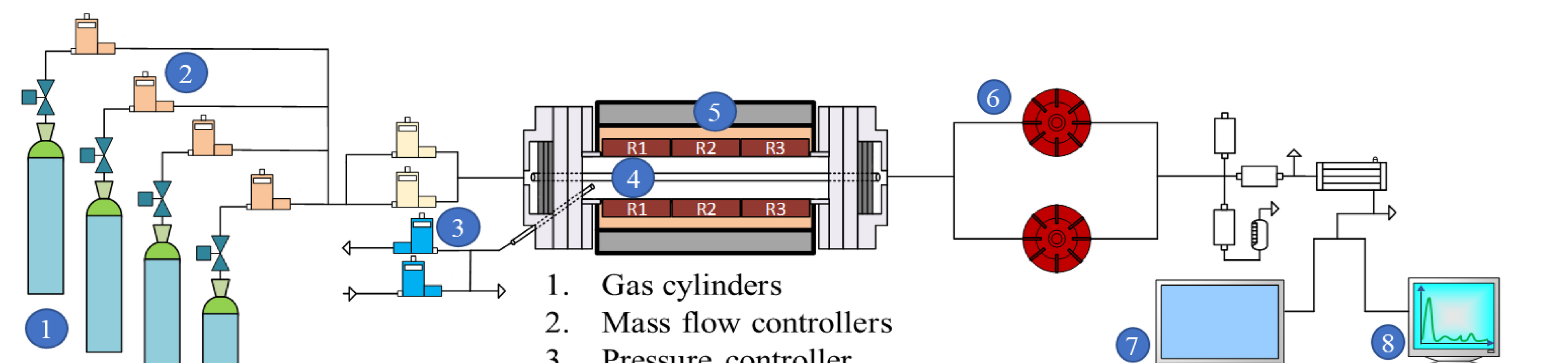
$$t_r(s) = 231.6 \cdot \frac{P\ (bar)}{T\ (K)}$$

Oxygen excess ratio, Lambda:

$$\lambda = \frac{O_{2\,inlet}}{O_{2\,stoichometic}}$$

$$NH_3 + \frac{3}{4}O_2 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2O \quad r1$$

$$CH_3OCH_3 + 3O_2 \rightleftharpoons 2CO_2 + 3H_2O \quad r2$$



1. Gas cylinders
2. Mass flow controllers
3. Pressure controller
4. Reactor
5. Electrically heated oven
6. Depressurization valve
7. $NH_3/NO_2/NO/N_2O$ analyzer
8. Micro-GC

Experimental Results

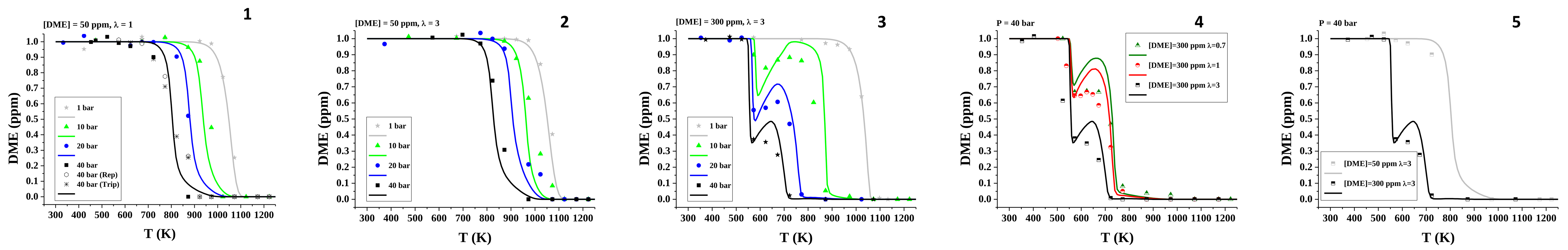


Figure 1 to 5: DME concentration as a function of temperature at 1, 10, 20 and 40 bar of pressure, for DME/NH_3 mixture oxidation and λ=0.7, 1 and 3 respectively.

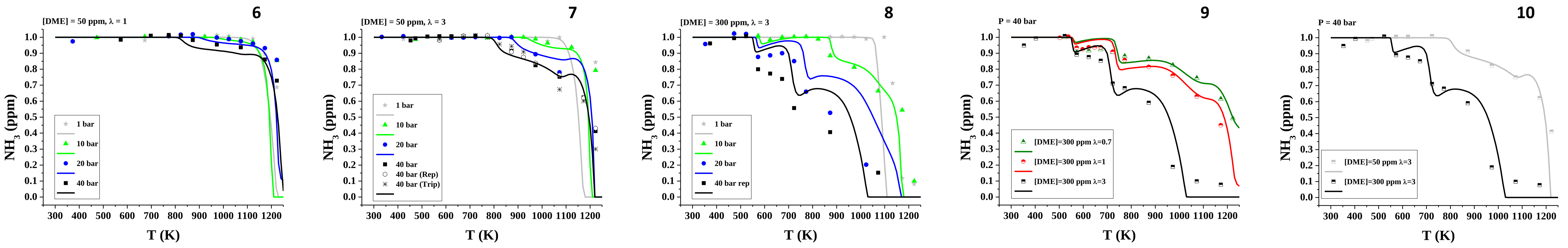
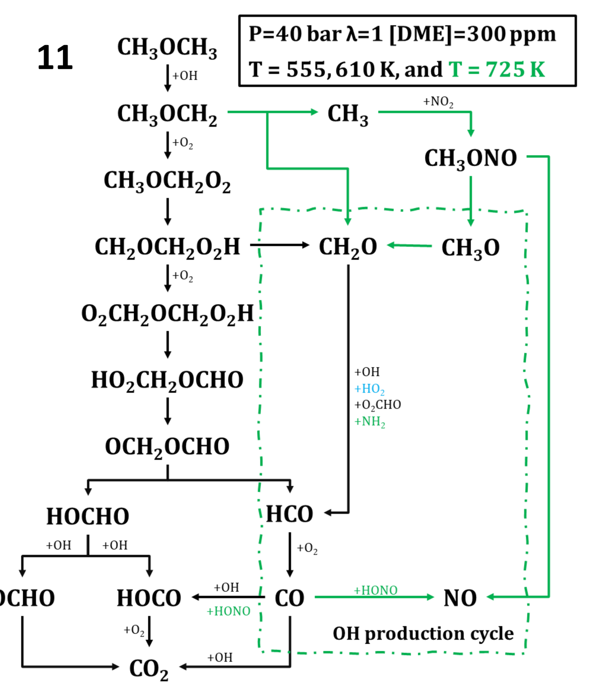


Figure 6 to 10: NH_3 concentration as a function of temperature at 1, 10, 20 and 40 bar of pressure, for DME/NH_3 mixture oxidation and λ =0.7, 1 and 3 respectively.



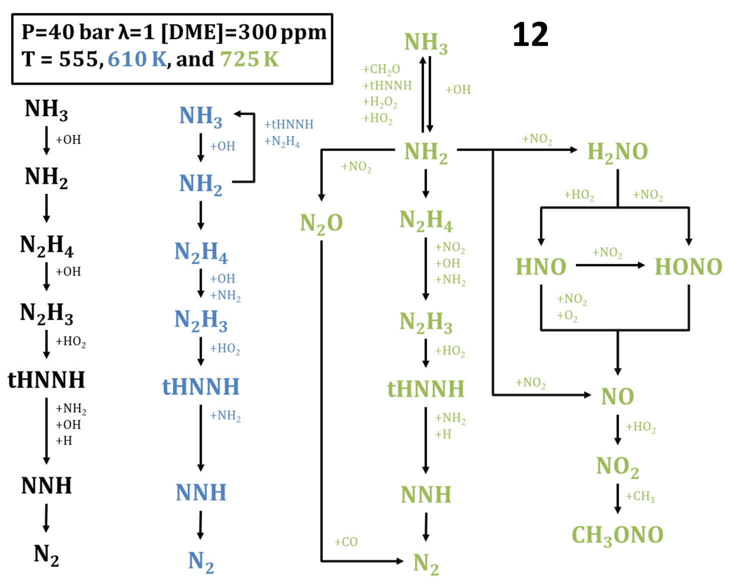


Figure 11 and 12: DME and NH_3 reaction pathway in pre-, during and post-NTC behaviour at 40 bar of pressure, for DME/NH_3 = 0.3 and λ =1.

- **NH_3 Reaction onset** occurs at a lower temperature as pressure increases.
- **DME addition** (50 and 300 ppm) enhances the NH_3 conversion respectively (up to 250 K and 600 K) compared to pure NH_3 at 40 bar.
- **Oxygen availability** is a key variable: NH_3 and DME conversion occurs at lower temperatures under oxidizing conditions, slightly more remarkable for NH_3 than for DME.
- A negative temperature coefficient (**NTC**) is observed for NH_3 and DME conversion with higher DME/NH_3 ratios.
- CH_2O is an important intermediate product of the DME/NH_3 combustion and is involved in the NTC behavior.
- NH_3/DME oxidation produces **N_2O** in significant quantities under almost all conditions and **NO** only under certain conditions, while pure NH_3 combustion does not produce NO and N_2O. **CO**, **CO_2**, and **CH_4** (in some cases) were found as carbon species in significant amounts.
- **Calculations** show good reproducibility and do follow the same trends as observed experimentally.

Conclusions

1º The main products of NH_3/DME oxidation are N_2, N_2O, CO, and CO_2. H_2, CH_4, NO, and HCN are only produced under certain conditions, and NO_2 is negligible. This is a positive result compared to NH_3/CH_4 mixtures.

2º DME addition improves the NH_3 combustion properties starting its consumption at minor temperatures than pure NH_3.

3º Pressure and oxygen availability have an important influence on the NH_3/DME oxidation regime. NH_3 and DME conversion occurs at lower temperatures under oxidising conditions, for all the pressures considered.

4º High pressure seems to favour the NH_3 and DME conversion compared to atmospheric conditions, which is an advantage for the use of NH_3 as a fuel in pressure applications such as turbines.

5º The kinetic model reproduces the main trends of the experimental results under the studied conditions. In some cases with a very good reproducibility.

References:

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