A Kinetic Study of $NH_3/H_2/CH_3OH$ Fuel Mixture

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Summary

This study analyses how the addition of methanol (CH3OH) and hydrogen (H2) affects ammonia (NH3) oxidation, improving its reactivity and reducing the ignition temperature. The impact of stoichiometry and mixture composition on evaluated through species profiles.

Introduction

Currently, climate change and the imperative to reduce greenhouse gas emissions are prompting the pursuit of sustainable alternatives to fossil fuels. NH_3 is emerging as a promising energy vector due to its high volumetric energy density, well-developed storage and transport infrastructure, and the possibility of being produced from renewable sources. However, its low reactivity and calorific value, as well as the potential formation of nitrogen oxides (NO_x) during combustion, limit its direct use as a fuel.

In order to address these limitations, the strategy of co-combustion (co-firing) with more reactive fuels such as CH_3OH [1] and H_2 [2] has been demonstrated to significantly enhance the combustion characteristics of ammonia. Methanol, which is carbon-neutral and easy to obtain from biological resources, contributes to lowering the ignition temperature and improving NH_3 oxidation conversion. Hydrogen, due to its high efficiency and clean combustion, promotes a complete and more efficient oxidation. Previous studies have shown that a $[NH_3]/[CH_3OH] = 1$ ratio favours the complete oxidation of NH_3, and consequently reduces the ignition temperature and NO_x emissions [3].

Experimental

The experiments were carried out using a homogeneous quartz tubular flow reactor, with an internal diameter of 8.7 mm and a length of 200 mm. All reactions were conducted under isothermal conditions, with the reactor placed inside an electric furnace equipped with three electric heating elements.

The composition of the outlet gases was analysed using a micro gas chromatograph (μGC) for O_2, N_2, CH_3OH, NH_3, H_2, CO_2, and CO. A continuous gas analyser was employed for N_2O and NO, as the μGC had difficulties in detecting these nitrogen-containing compounds.

During each experiment, temperature (873–1423K), oxygen excess ratio (λ = 0-3), and the $[NH_3]/[CH_3OH]$ and $[NH_3]/[H_2]$ mixture ratios (0.5-2) were modified, maintaining a standardised total flow rate of 1 $L \cdot min^{-1}$ (STP). The O_2 concentrations were calculated based on the following stoichiometric reactions:

$$NH_3 + \tfrac{3}{4}\, O_2 \rightarrow \tfrac{1}{2}\, N_2 + 1\tfrac{1}{2}\, H_2O \quad \text{(r1)}$$

$$CH_3OH + 1\tfrac{1}{2}\, O_2 \rightarrow CO_2 + 2\, H_2O \quad \text{(r2)}$$

$$H_2 + \tfrac{1}{2}\, O_2 \rightarrow H_2O \quad \text{(r3)}$$

Additionally, calculations were performed using Chemkin-Pro software [4], employing a plug-flow reactor module with the same specifications as the experimental setup to validate the laboratory results. The mechanism by Glarborg et al. [5] was used as a starting point, with minor updates as explained by Alzueta et al. [6]. Furthermore, reactions from the CH_3OH subset, based on the mechanism proposed by Ruiz-Gutiérrez et al. [3], were added.

Results and discussions

Figure 1 shows the behaviour of NH_3 as a function of temperature for different λ values. It can be observed that for pyrolysis conditions (λ = 0), ammonia conversion is practically negligible throughout the entire temperature range studied, confirming that NH_3 oxidation requires the presence of oxygen, without its thermal decomposition playing a relevant role.

As λ increases, ammonia conversion occurs at lower temperatures. For λ = 0.5, conversion begins near 1100 K, while for λ = 1 and higher, complete NH_3 oxidation is achieved at temperatures around 1100 K or even lower. This behaviour indicates that increasing the oxygen concentration boosts the formation of radicals (OH, and O), which are key in the ammonia oxidation pathways, as described in the literature, $NH_3 + OH \rightleftharpoons NH_2 + H_2O$ (r4), and $NH_3 + O \rightleftharpoons NH_2 + OH$ (r5). Thus, fuel-lean conditions not only shift the ignition temperature to lower values but also increase the efficiency of NH_3 conversion.

Under stoichiometric conditions (λ = 1), repeatability experiments were performed, and the results show excellent reproducibility of the conversion curves, validating the reliability of the experimental methodology used.

Conclusions

The increase in λ favours ammonia conversion, shifting the onset of its oxidation to lower temperatures. Under pyrolysis conditions (λ = 0), NH_3 is not appreciably consumed, whereas for λ ≥ 1, nearly complete conversion is achieved at temperatures around 1100 K. These results confirm that the presence of oxygen is crucial for ammonia reactivity. The excellent repeatability observed at λ = 1 validates the reliability of the experimental methodology.

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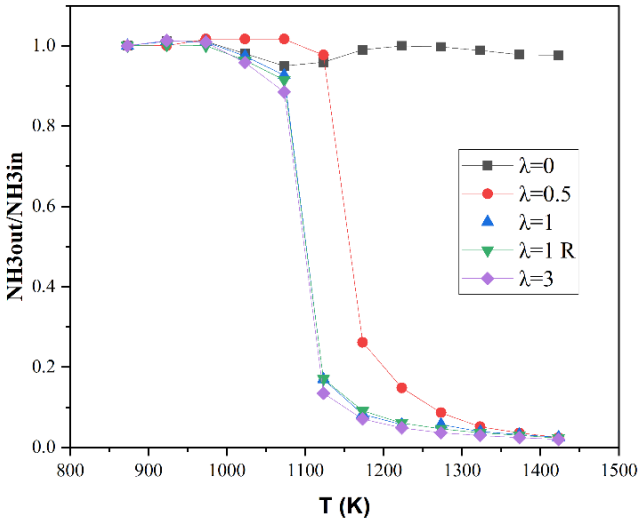

Figure 1. Ammonia profile comparisons for different λ and NH_3/CH_3OH, NH_3/H_2 = 1 mixture ratio.