The role of carbon-nitrogen interactions in the low-temperature oxidation of NH_3/CH_3OH fuel blends

Francesco Roman Artioli, Giuseppe D'Amato, Alessandro Stagni*
*alessandro.stagni@polimi.it

Abstract

Ammonia/methanol (CH_3OH) blends are gaining increasing attention due to methanol's capability to offset the most important chemical limitation of ammonia, such as its high autoignition temperature and low flame speed. This study aims to understand the binary interactions between ammonia and CH_3OH at low temperatures. The related reactions were added to a detailed kinetic mechanism for description of the pyrolysis and oxidation behavior of such fuel mixtures. It was found that the interactions impact the simulations of experimental conditions decreasing the ignition delay time. Sensitivity analysis was utilized to understand the most important reactions in the system.

Introduction

There is a growing trend towards making internal combustion engines more environmentally friendly, low-carbon, and energy-efficient. In this regard, ammonia (NH_3) has gained attention as a zero-carbon fuel [1]. However, ammonia has to be coupled with other fuels to overcome its poor combustion features [2]. Among the candidate co-fuels, methanol (CH_3OH) has recently emerged as a promising enhancer: compared to ammonia, it has a higher laminar flame speed, is easier to ignite, and has been widely tested as a fuel for spark-ignition internal combustion engines [3]. A noteworthy application of these blends in the marine sector has also been explored [4]. The objective of this work is to show and discuss the effect of the interactions between ammonia and methanol at low temperatures.

Methodology

As a first step, a literature review was performed on the available reaction rates studies recently evaluated through first-principles approaches [5], [6]. Building on these findings, the kinetic mechanism was developed using a hierarchical and modular approach. For the description of the ammonia oxidation chemistry, the work by Stagni et al. [7] was used as reference. The core mechanism describes the chemistry of C_0-C_4 species, where methanol reactivity is included, starting from the work by Dong et al [8]. The rate constants for the two H-abstractions by NH_2 on CH_3OH, forming either CH_2OH or CH_3O, were added to the mechanism following the recommendations by Li et al. [5].

Results

Fig. 1a shows the measured and predicted ignition delay times using a rapid compression machine (RCM), whose experimental data were taken from the work by Li et al. [5]. The effect of the equivalence ratio and pressure is comprehensively shown. An earlier ignition is observed at higher pressures and equivalence ratios. To identify the key reactions responsible for this behaviour, a sensitivity analysis was performed (Fig. 1b), while a flux analysis was carried out and is shown in Fig 2 to gain a further insight into these reactive pathways.

One significant pathway involves methanol reacting with oxygen and hydroperoxyl radicals to produce OH radicals, which initiate the reactivity of ammonia. The interaction between CH_3OH and NH_3 opens an alternative reaction pathway through the formation of CH_3O, which rapidly decomposes into formaldehyde, generating H radicals. The amino radical subsequently participates to the consumption of formaldehyde, leading to the formation of HCO. Flux analysis (Fig. 2) confirms these findings, highlighting the two reaction routes enabled by ammonia. All of these interactions have a tangible impact on the reactivity of ammonia-methanol mixtures at such low temperatures, decreasing the overall ignition delay time.

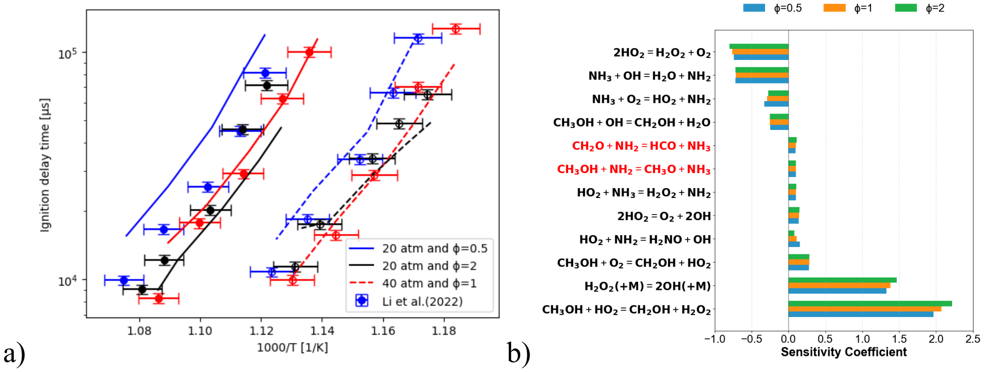

Figure 1. a) RCM experiment with 20/80 CH_3OH/NH_3 mixture at intermediate temperature. b) Sensitivity analysis on OH radical at 900 K and 20 bar.

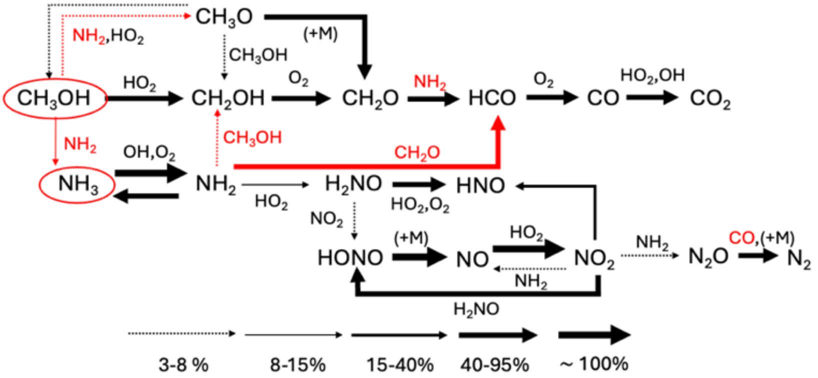

Figure 2. C (CH_3OH) and N (NH_3) flux analysis at 1% CH_3OH conversion.

Conclusions

In summary, this study represents a step forward in understanding the low-temperature combustion behaviour of CH_3OH/NH_3 mixtures. The focus on direct interaction reactions, particularly hydrogen abstractions, highlights their role in enhancing the combustion. Sensitivity analysis identified the most influential reactions, and the flux analysis confirmed the presence of alternative pathways. Furthermore, the kinetic model showed good agreement with experimental ignition delay times in a wide range of operating conditions.

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