

# ASSESSING THE COMBUSTION BEHAVIOR OF DIMETHYL ETHER AND AMMONIA: A COMPARATIVE STUDY

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## Abstract

The mixtures of ammonia/dimethyl ether (DME) are increasing in importance because DME can compensate for the limiting properties of ammonia (like autoignition temperature and flame speed).

This work aims to develop a comprehensive kinetic mechanism describing the pyrolysis and oxidation of the mixtures of the two species. The critical aspects are the binary interactions, which are the focus of this investigation.

Different experimental sets were used to validate the mechanism proposed. The model works reasonably well considering the uncertainty intervals. In addition, different models were used to make a comparison considering the same experimental data.

## Introduction

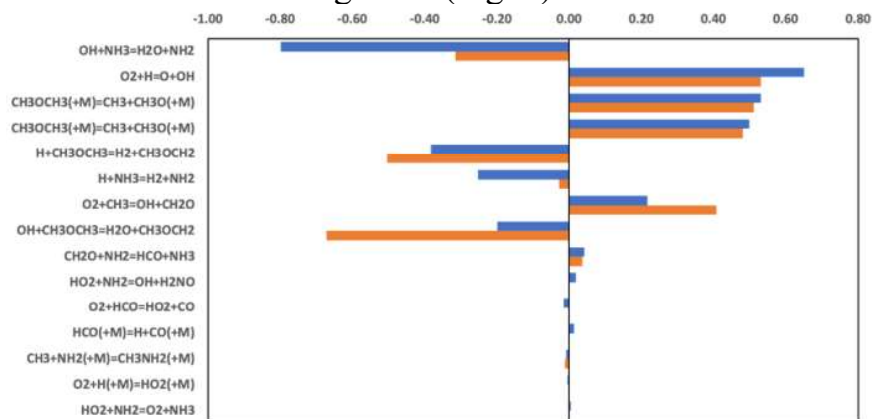
There is a growing interest in utilizing ammonia ( $\text{NH}_3$ ) as an alternative fuel to mitigate greenhouse gas emissions associated with conventional fossil fuels. However, ammonia presents challenges such as a significantly lower burning velocity [1] and higher autoignition temperature [1] compared to traditional fuels.

The aim is to achieve a mixture that performs comparably to existing fuels, thereby enabling the proper utilization of ammonia. It is crucial to select co-fuels that meet specific requirements for burning velocity and ignition behavior.

Oxymethylene ethers (OMEs), as environmentally friendly co-fuels, show great potential in enhancing the oxidation kinetics of  $\text{NH}_3$  for various reasons. Firstly, they can be manufactured within a sustainable carbon cycle, thereby facilitating zero-net  $\text{CO}_2$  emissions. Additionally, OMEs exhibit desirable characteristics such as high cetane numbers and oxygen content, without containing any carbon-carbon bonds. When blended with conventional fuels, they have been observed to notably decrease soot emissions [2]. Furthermore, OMEs are non-toxic, further highlighting their suitability as sustainable co-fuels. The simplest of the OMEs is DME (or  $\text{OME}_0$ ). In the literature, many mechanisms and experimental studies on the combustion of the mixtures  $\text{DME}/\text{NH}_3$  are present [3,4]. The objective of this work is to describe the development of a mechanism with predictive features comprehensive of both the pure compounds and mixtures.

## Methodology

This work is based on a hierarchical and modular approach. The starting point is to use what has already been developed by Stagni et al for both pure NH<sub>3</sub> and DME [5,6]. The modules have been validated in the respective works. They must be updated with the newest aspects investigated in literature both reactions and reaction paths. Therefore, a new model for the interactions between the two species must be created. Following the hierarchical approach, the first aspect investigated was the C<sub>0</sub>-C<sub>1</sub> module starting from the work by Dong et al [7]. The reason was that the combustion of both DME and NH<sub>3</sub> is based on the reactivity of the species included in this module. The effects of this change are very relevant in the case of flame speed because the chemistry of the species up to C<sub>1</sub> is the main in the combustion of dimethyl ether [8]. The single modules about ammonia and DME were slightly changed as mentioned before. The main modifications were made to the module concerning dimethyl ether. The reactions added to the original mechanism are reported in the table below (Table 1). The first two reactions became part of the module due to the sensitivity analysis done for ignition delay times simulations at high temperatures. The mechanism used for this simulation (Dai-Zhang) was proposed by Yin [3]. The sensitivity coefficients of the reactions are not the highest, but these reactions are still present changing the conditions of the system. For this reason, these reactions cannot be ignored (Fig. 1).



**Figure 1.** Sensitivity analysis at P=0.14 MPa, φ=1 and 5% DME/95% NH<sub>3</sub> (blue bars) and 30% DME/70% NH<sub>3</sub> (orange bars). [9]

The two successive reactions were added by looking at reaction paths not considered, like the ones from Guan et al [10]. After all these modifications, the changed module was used to perform several simulations to prove the validity of the changes. The results of this analysis are not reported here to focus on the results of the mixtures DME-NH<sub>3</sub>. The module for the interaction of DME and ammonia is described by two reactions (reported in the last two rows of Table 1). The first reaction has the expression presented in the work of Yin et al [3]. It is shown to be an important reaction through sensitivity analysis. Instead, the second reaction has an expression derived from ab initio calculations. Different studies are available in the literature for this specific reaction. The one chosen is from the work of Cavallotti et al [11]. The reason for this choice is that the rate proposed has been developed considering

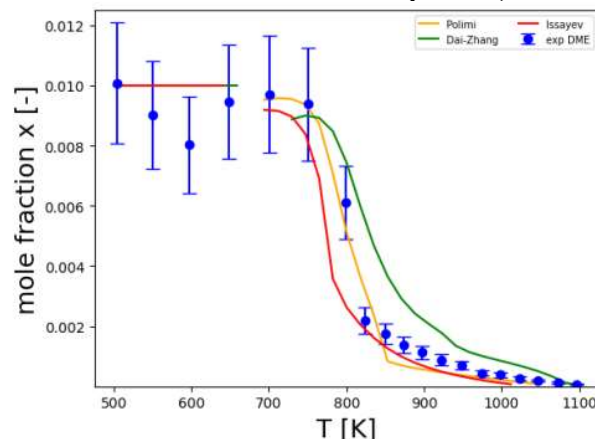
a very wide range of temperature conditions (between 300 and 2500 K). The rate was evaluated using an automatic code, for the derivation of kinetics parameters, called EStokTP [11].

**Table 1.** New interaction reactions were added in the module for DME and DME/NH<sub>3</sub> with references. [9]

Reactions	Reference
$\text{CH}_2\text{O} + \text{NH}_2 \rightarrow \text{HCO} + \text{NH}_3$	[12]
$\text{CH}_3 + \text{NH}_2 (+\text{M}) \rightarrow \text{CH}_3\text{NH}_2 (+\text{M})$	[13]
$\text{CH}_3\text{OCH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{OCH}_2 + \text{HONO}$	[10]
$\text{CH}_3\text{OCH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{OCH}_2 + \text{HNO}_2$	[10]
$\text{CH}_3\text{OCH}_2 + \text{NH}_2 (+\text{M}) \rightarrow \text{CH}_3\text{OCH}_2\text{NH}_2 (+\text{M})$	[3]
$\text{CH}_3\text{OCH}_3 + \text{NH}_2 \rightarrow \text{CH}_3\text{OCH}_2 + \text{NH}_3$	[11]

## Results

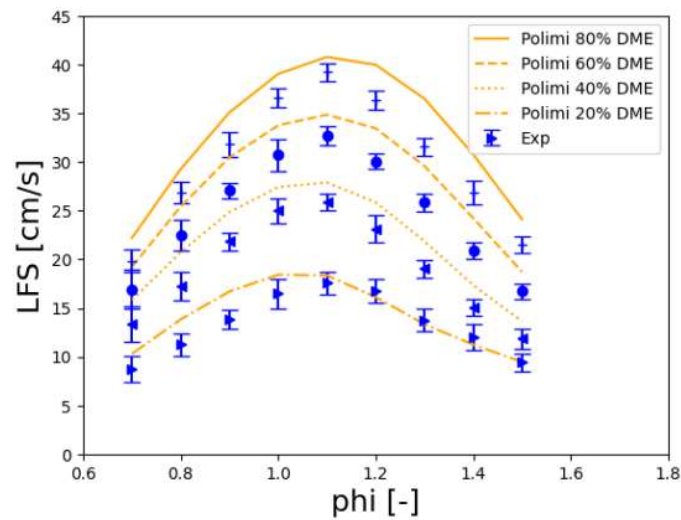
The first result is about a simulation of a Jet Stirred Reactor (JSR). The mixture, at stoichiometric condition, analyzed has the following composition: 50% DME/50% NH<sub>3</sub>. In Fig. 2, the plot represents the mole fraction of DME varying the temperature of the reactor (the pressure is constant and atmospheric).



**Figure 2.** Mole fraction of DME changing the temperature of the JSR. Each color expresses a different mechanism: Polimi (orange), Dai-Zhang (green), and Issayev (red) [4]. The experimental points are from [14].

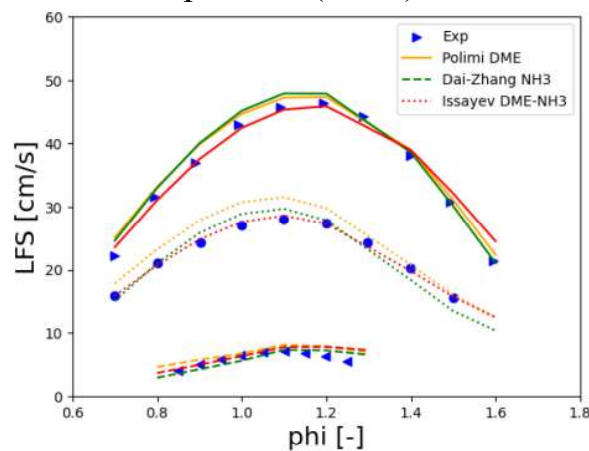
The curves present some missing points because, as seen in other cases [15], the oscillation issues can affect the low-temperature combustion in a perfectly stirred reactor. This phenomenon does not let the system converge to the steady-state solution, as detailed in the work by Stagni et al [15]. The problem is observed experimentally, and it is reproduced in the numerical simulations.

The laminar flame speed cases are another type of simulation to understand the validity of the mechanism. The first case simulated is about a system with a pressure of 1 bar and an initial temperature of 300 K. Different mole fractions of DME are considered (Fig. 3).



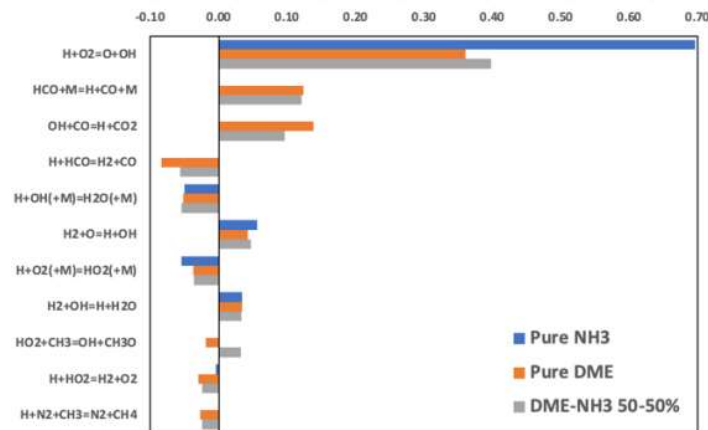
**Figure 3.** LFS (Laminar Flame Speed) changing the mole fraction of DME. Polimi mechanism (orange). The experimental points are blue [16].

The higher the mole fraction of DME the higher the distance between the model and the experimental data. The results overall have a relative error of around 10%. The successive case analyzed is about the combustion of pure  $\text{NH}_3$  and DME and a mixture of 50% DME/50%  $\text{NH}_3$  (Fig. 4). The flames studied are at atmospheric pressure and initially at room temperature (298K).



**Figure 4.** LFS (Laminar Flame Speed) changing the equivalence ratio. Polimi (orange), Dai-Zhang (green), and Issayev (red). The experimental data are from [3].

The curves are different based on the model. The mixtures come from a superposition of the effects related to single components. The important difference in the models is the reactivity of the pure ammonia. This explains the difference also in the mixture of DME- $\text{NH}_3$ . Dai-Zhang and Issayev models have a lower speed in the mixtures mainly due to a lower speed of the pure ammonia. A sensitivity analysis was performed for each type of mixture shown (Fig. 5).



**Figure 5.** Sensitivity analysis, on the mass-flowrate, of the eleven most important reactions for the mixture 50% DME/50% NH<sub>3</sub>.

The sensitivity analysis emphasizes the importance of the reactions in the C<sub>0</sub>-C<sub>1</sub> module. The most important reactions, after the main branching reaction, regard the chemistry of carbon. The carbon in the mixture is given by the DME. Therefore, the flame cases are strongly influenced by the DME. This was expected because the addition of DME to ammonia helps in overcoming the lower flame speeds of pure NH<sub>3</sub>.

## Conclusions

To summarize, this work represents a further stride in advancing the comprehension of combustion of DME/NH<sub>3</sub>. The peculiar properties are the base methodology (use of hierarchical and modular approach) and the generality regarding the conditions of development. At the same time, it offers a mechanism applicable with reasonably good results for both the mixtures and the pure components. In fact, new reactions and reactive paths were added based on the sensitivity analysis. In addition, sensitivity analysis was performed on the results that supports the superposition effects mentioned before.

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