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Executive Summary

This deliverable was prepared within the framework of Work Package 2 "Ammonia combustion and emission modelling" and the Task 2.2 "Detailed and reduced chemistry model of combined ammonia and diesel oil combustion". The work has been performed by Vladimir A. Alekseev and Elna Heimdal Nilsson, Lund University, and directly build on previous work in collaboration with Technical University of Denmark in the same Task, reported as Deliverable D2.1 "Validated mechanism for ammonia at high pressure and high temperature".

Using the detailed mechanism and the fundamental understanding of ammonia combustion reported as D2.1 as a starting point, a chemical mechanism suitable for use in simulation studies of real engines was constructed. These types of engine simulations are essential to the understanding of combustion and pollutant formation, and the work presented as deliverable D2.4 therefore support overall work in WP2 with the full engine simulations as the final goal.

The chemical mechanism presented here is designed to accurately represent combustion of the full range of temperatures, pressures and fuel mixtures of relevance to marine engines. It is the smallest mechanism developed for this purpose, and the only one including two plausible N_2O formation pathways. The superior performance in the aspect of N_2O pollutant formation allow the anticipated full engine simulations to be used to further elucidate these processes. The work also has a strong focus on the ignition properties of the ammonia/n-heptane mixtures, as the role of n-heptane is mainly to act as an ignition promoter. It is therefore of importance that the reduced mechanism accurately reproduce ignition events at low concentrations of the pilot fuel.

A thorough description of the work has been published as Open Access in the journal Fuel, Vol. 367 Pages 131464.

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1.   Introduction

This deliverable was prepared within the framework of Work Package 2 "Ammonia combustion and emission modelling" and the Task 2.2 "Detailed and reduced chemistry model of combined ammonia and diesel oil combustion". The work has been performed by Vladimir A. Alekseev and Elna Heimdal Nilsson, Lund University, and directly build on previous work in collaboration with Technical University of Denmark in the same Task, reported as Deliverable D2.1 "Validated mechanism for ammonia at high pressure and high temperature".

The aim of Task 2.2 is to develop detailed and reduced kinetic mechanisms for ammonia combustion for the thermodynamic regime specific to marine engines. The detailed mechanism reported as Deliverable 2.1 is suitable for increasing the detailed understanding of ammonia combustion with a hydrocarbon as co-fuel, and to use as the starting point for development of a reduced-size mechanism. The size-reduction is necessary to allow implementation of the chemical kinetics in Computational Fluid Dynamics (CFD) simulations, which is performed in Tasks 2.3 "In-cylinder modelling of ammonia injection, combustion and emission" and 2.5 "Overall ammonia engine modelling" in Work Package 2.

The first demand on the reduced mechanism presented in the present report is to predict ignition and flame propagation within the relevant range of parameters. Once achieved the next demand is to predict emissions with a particular focus on N_2O. Finally, the mechanisms have to be sufficiently compact and efficient to allow for calculations of practical engine combustion. The reduction strategy, the reduced mechanism and a thorough validation against the detailed mechanism is presented in the article "Reduced kinetics of NH_3/n-heptane: Model analysis and a new small mechanism for engine applications" published in the journal Fuel 2024 [1].

An important starting point for the work is a literature review of engine studies, presented in the introduction part of the article. To our knowledge this is the first complete review of engine studies targeting ammonia as a fuel, both neat and in combination with hydrocarbons and hydrogen co-fuels. In the review work it was found that two distinct explanations to the formation of N_2O are presented, in this work referred to as the "DeNOx" and "disrupted flame" mechanisms. The first one state that N_2O is formed during expansion and exhaust strokes where unburned NH_3 released from crevice volume is mixed with product NO_x, and N_2O is formed via the selective non-catalytic reduction mechanism (SNCR, or $DeNO_x$). The second mechanism assumes that N_2O is produced at the flame front and is not immediately consumed due to incomplete (disrupted) combustion. The disagreement in N_2O formation trends described above suggests that it is sensitive to a variety of operational parameters, and is a complex product of the effects of flow and chemistry.

A few reduced mechanisms for ammonia/n-heptane combustion have been published in recent years. However, the broad engine operating conditions reviewed here, and the $DeNO_x$ mechanism for N_2O formation were not targeted in development of these mechanisms. The new reduced scheme presented here is covering various operational strategies and the two different pathways for N_2O formation. Combustion and oxidation of NH_3/n-heptane was analyzed using 0D and 1D ideal reactor models, and the target space for reduction (including pollutants) was thoroughly constructed. During reduction, these 0D and 1D reactors were utilized simultaneously. The performance of the mechanism in engine-relevant conditions is discussed and compared to literature models. Full description and validation can be found in the Open Access journal article, and is summarized in the present report.

2.   Methodology and validation

2.1 Mechanism development strategy

An outline of the mechanism development strategy is presented in Figure 1, in which the first step is described in section 2.1.1 and the following steps are described in section 2.1.2.
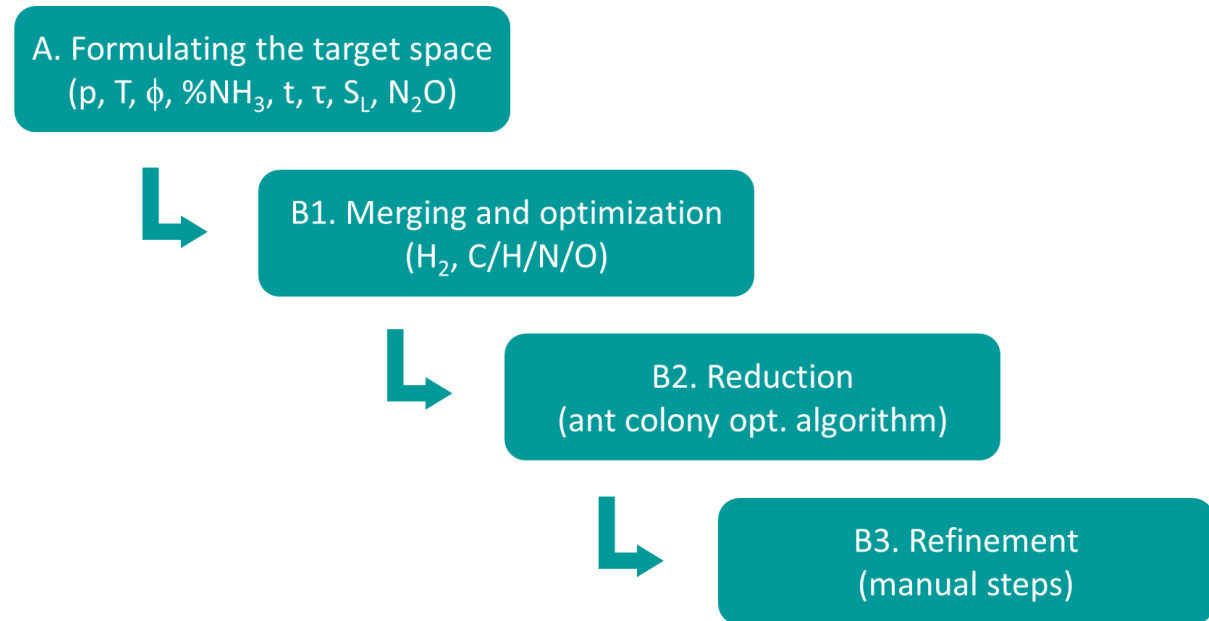
A. Formulating the target space
$(p, T, \phi, \%NH_3, t, \tau, S_L, N_2O)$

B1. Merging and optimization
$(H_2, C/H/N/O)$

B2. Reduction
(ant colony opt. algorithm)

B3. Refinement
(manual steps)

Figure 1. Outline of the mechanism development strategy.

2.1.1 Selection of parameter space

As initial steps before a mechanism reduction, a detailed target mechanism and appropriate reactor models capturing the relevant combustion targets need to be selected. Also, the reduction space must be defined in terms of initial parameters, such as NH_3/n-heptane mixture composition, stoichiometry, temperature, pressure and characteristic time scales. The selected entities must be adequate and relevant to the engine conditions since the end result is greatly affected by these initial choices.

The target mechanism selected here was the recently published mechanism by Thorsen et al. [2], developed within the ENGIMMONIA project.

To accommodate for different injection strategies, it was necessary to target both ignition and flame propagation, by using the closed homogeneous 0D reactor and 1D free-propagating flame, respectively. The corresponding target quantities are ignition delay time (IDT) and laminar burning velocity (LBV). Additional targets were selected in order to account for the two possible mechanisms of N_2O formation, therefore the 1D simulations included N_2O and NO concentrations. In addition, to account for NO formation, modelling included oxidation of $NH_3/O_2/N_2$ mixtures in presence of NO at high pressures and intermediate temperatures in adiabatic 0D reactors.

Formulation of the target space with respect to the parameters shown in part A in the graphic above, was conducted using the available engine studies and basic understanding of ammonia/n-heptane combustion obtained from simulations with detailed mechanism. The selected mixture parameters used as targets for each reactor model are found in Table 1. The big challenge with a fuel mixture with such different fuels as ammonia and n-heptane is the

difference in reactivity, meaning difference in time scales for ignition. Due to this, even small quantities of the more reactive n-heptane will trigger ignition of a mixture, which is the advantage of using a hydrocarbon to initiate combustion of ammonia. To accurately reproduce this, it is necessary to include target conditions with very small amounts if n-heptane in ammonia, as small as 0.5%.

Table 1. Mixture parameters for each of the implemented reactor models.

reactor type	0D C_v	1D flame	0D C_p
target	IDT	LBV, N_2O, NO	$N_2O(t)$
time scale, s	≤ 0.1	N/A	≤ 0.1
p, atm	10-100	10-100	10-100
T_0, K	600-1400	500	800-1400
ϕ	0.5-1.5	0.7-1.3	0.6-1
X_{NH3} (mol. %)	0-100%	0-100%	100%
No. cases	553	11	62

C_v and C_p – constant volume and constant pressure reactors, respectively

Range of pressure was determined directly from the literature review. The upper border of the characteristic timescale of ~10-1 s, is selected since it corresponds to 60° CAD piston movement in a slowly operating marine engine ~100 RPM. The lower temperature limit of 600 K for ignition cases corresponds to a pressure of ca. 10 atm at the end of compression.

2.1.2 Reduction strategy

The reduction process starts with merging of selected reaction subsets, point B1 in Figure 1, and then the second step, B2, is executed. The Ant-Colony Reduction (ACR) method is utilized, in combination with manual steps, B3. The combined methodology is motivated by the challenge to construct a compact dual-fuel mechanism for two fuels with such varying reactivity, and over wide range of conditions. ACR is a semi-stochastic build-up mechanism generating algorithm with a customizable target function that accommodates multiple reactor models, scalar and vector target quantities, and it generates mechanisms with a very low number of reactions. During reduction, performance in the whole target space acts as feedback to the mechanism-generating algorithm. This marks a difference to a more common approach where mechanisms are tested against a broader target space at the validation stage.

Predictions of the detailed mechanism were used as targets, while the starting point for the reduction was the base merged model described above. Several reactions were marked as "important" and forced to be included into all generated mechanisms. A number of reactions from the NOx subset, which do not belong to major reaction chains, were included manually. The preferred approximate range of sizes of the generated mechanisms can be selected before reduction, this was done after preliminary runs by finding an optimal trade-off between mechanisms' size and their accuracy. The final candidate mechanism was selected from the generated mechanism pool based on the overall averaged accuracy, the average accuracies of each target quantity, maximal deviations from target for each target quantity, and on the mechanism size. As ACR is a semi-stochastic build-up method, certain reactions important to a smaller subset of targets might be omitted by the algorithm. In addition to that, it is possible to manually remove species while keeping the corresponding reaction pathways by reaction lumping. These manual steps were performed by validating the test versions of the mechanism against the same target space as during the ACR reduction. After ACR reduction, optimization and manual steps were applied in several steps, to produce a final mechanism (A305) with 57 species and 158 reactions.

2.2 Validation

2.2.1 Ignition

Ignition delay time is an important property and it is very different for the two fuel components ammonia and n-heptane, with the first one igniting extremely slow. Addition of small fractions of n-heptane to ammonia rapidly increase the ignition delay time, which is the reason why heavy hydrocarbons are suitable as pilot fuels for ammonia combustion. In the mechanism reduction an ignition delay time was the main target with 553 cases spanning a wide range of temperatures, pressures and mixture fractions. Overall the agreement between the reduced and the detailed mechanism is excellent, with only some discrepancies for the low-temperature region for mixtures with lowest n-heptane content. However, the difference is less than what is commonly considered to be the range of experimental uncertainties.

2.2.2 Flame propagation

For the 1D free-propagating flames, the reduction space included laminar burning velocities in mixtures of NH_3 + air, n-heptane + air, and various proportions of NH_3/n-heptane + air. The agreement between the reduced mechanism and the detailed target mechanism was good at all conditions. Detailed analysis reveals that for laminar burning velocities, direct interactions between hydrocarbon and nitrogen-containing species are of low importance.

2.2.3 N_2O formation

To enable validation of both N_2O formation pathways it was targeted in two ways, in flame simulations and 0D reactor modelling. Not only N_2O was evaluated, but also NO since it is an important component in the nitrogen chemistry of relevance to N_2O formation. Regarding the flame simulations, the present mechanism predicts N_2O very close to the target. For NO there are small deviations in the flame zone near stoichiometric mixtures, while post-flame NO is reproduced correctly. Formation of N_2O in IC engines via the $DeNO_x$ mechanism was represented by oxidation of NH_3 in presence of NO in homogeneous constant-pressure reactors, a common configuration in kinetic studies utilized to simulate flow reactor experiments. As the goal of the present study is to reproduce conditions most relevant to IC engines, it is reasonable to investigate undiluted NH_3/NO/air mixtures. Unfortunately, there are large discrepancies between different detailed mechanisms, pointing at insufficient understanding of the underlaying chemistry. However, the reduced mechanism presented here showed good agreement with the selected detailed mechanism by Thorsen et al., developed within the ENGIMMONIA project.

3. Conclusion and Future Plans

Here a new reduced mechanism developed for use in simulations of NH_3 combustion in dual-fuel IC engines was presented. The mechanism is targeting parameters of relevance to marine engines and it is an important building block towards the final engine modelling in Work Package 2.

In particular it's necessary to point at the following novelties summarized in this report and detailed in the Open Access journal publication:

- The reduced mechanism builds on a state-of-the-art detailed chemical mechanism developed within the ENGIMMONIA project WP2.
- It is the smallest ammonia/n-heptane available, and at the same time covering the widest parameter space range, including pressures 10-100 atm, and 0-100% NH_3 in the fuel mixture.
- It is the only reduced mechanism that include two plausible pathways for N_2O formation, and can be used in CFD simulations to reveal the importance of these two mechanisms.
- The analysis shows that inclusion of interaction reactions between carbon- and nitrogen-containing species is necessary for adequate reproduction of combustion of mixtures of NH_3 and n-heptane.

4.   References

[1] V. A. Alekseev and E. J. K. Nilsson, Reduced kinetics of NH3/n-heptane: Model analysis and a new small mechanism for engine applications, Fuel 2024 Vol. 367 Pages 131464

[2] L. S. Thorsen, M. S. T. Jensen, M. S. Pullich, J. M. Christensen, H. Hashemi, P. Glarborg, et al., High pressure oxidation of NH3/n-heptane mixtures, Combustion and Flame 2023 Vol. 254 Pages 112785