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Executive Summary

This deliverable (D2.1) corresponds to task 2.1 in which a "Validated mechanism for ammonia at high pressure and high temperature" is developed and validated by DTU, in collaboration with Lund University and Princeton University.

In parallel work, DTU has developed a detailed reaction mechanism for ignition and oxidation of ammonia at high pressure and medium to high temperature. In the present WP, the focus has been on developing a reaction mechanism for ignition and oxidation of ammonia/n-heptane mixtures, where n-heptane is a surrogate for diesel. Due to the poor combustion properties of ammonia, it is challenging to operate diesel engines on ammonia without a co-fuel / pilot flame, and due to its availability and combustion properties diesel is considered to the most attractive co-fuel. In this deliverable, the NH_3/n-heptane oxidation is characterized experimentally at pressures of up to 100 atm and temperatures of 450-900 K, in both a laminar flow reactor (at DTU) and a jet-stirred reactor (Princeton University). A detailed kinetic model is developed in collaboration with Lund University by combining the best available ammonia and n-heptane mechanisms, adding a subset describing the chemical coupling between the mechanisms. The resulting model provides a good prediction of the ignition delay measurements by Yu et al. (2020) at elevated pressure from rapid compression machine experiments as well as the high-pressure reactor results obtained in the present work.

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1.   Introduction

The deliverable D2.1 corresponds to task 2.1 in which a "Validated mechanism for ammonia at high pressure and high temperature" is developed and validated by DTU, in collaboration with Lund University and Princeton University. More details about the work can be found in: Lauge Sven Thorsen[1], Malene Stryhn Thestrup Jensen[1], Mille Stub Pullich[1], Jakob Munkholt Christensen[1], Hamid Hashemi[1], Peter Glarborg[1], Vladimir Alekseev[2], Elna Heimdal Nilsson[2], Ziyu Wang[3], Bowen Mei[3], Ning Liu[3], Yiguang Ju[3]: "High pressure oxidation of NH_3/n-heptane mixtures", in preparation (1: Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Lyngby DK-2800, Denmark; 2: Division of Combustion Physics, Lund University, Sweden; 3: Department of Mechanical and Aerospace Engineering, Princeton University, NJ 08544, USA).

The feasibility of using ammonia in engines and gas turbines is being investigated extensively [1–3]. The use of NH_3 as an engine fuel is challenging due to its poor combustion characteristics such as a long ignition delay time and a low flame speed. This shortcoming can be partly or fully overcome by use of a co-fuel mixture such as hydrogen or diesel fuel addition into ammonia [4].

In terms of compression-ignition engines, using diesel as a pilot- or co-fuel is considered a promising approach. Co-combustion of diesel and ammonia has been tested in diesel engines [5–10]. Results indicate that this fuel mixture has a significant potential, allowing operation with up to 95% NH_3 energy input. However, there are challenges related to comparatively low combustion temperatures, unburned ammonia, and N_2O emissions, and advanced diesel injection strategies may be required to alleviate these problems [6].

Use of computational fluid dynamics (CFD) is an attractive option in the design and optimization of ammonia/diesel-fuelled engines. However, knowledge of the detailed kinetics of ignition and oxidation of this fuel mixture is limited. Results on ignition delay times have been reported from Rapid Compression Machines (RCM) [11]. A blended mechanism was used to interpret the data, but analysis was made difficult by the complexity of the diesel fuel. To facilitate modelling and interpretation of the behavior of ammonia/diesel mixtures, it is of

interest to study the ignition and oxidation of NH_3 mixed with n-heptane; a common diesel surrogate.

Several studies of the high-pressure chemistry of ammonia and n-heptane, respectively, are available in the literature. Results include ignition delay measurements for ammonia [12–15] and n-heptane [16–19], as well as flow reactor results for the oxidation of each of the two fuels [20, 21]. Experimental results are scarce for ammonia/n-heptane mixtures, but data at elevated pressure have been reported for ignition delays in RCM (635-945 K, 10-15 bar) by Yu et al. [22]. In addition, results at lower pressure are available for flame speeds [23] and species profiles in jet-stirred reactors [24]. A number of models for n-heptane ignition have been reported [19, 25–29] that generally predict the ignition behavior well, with the mechanism of Zhang et al. [19] providing the best agreement also for oxidation in high pressure flow reactors [21]. For ammonia, several mechanisms have been published in recent years. Models by Mathieu and Petersen [12], Li et al. [30], Otomo et al. [31], Glarborg et al. [32], Mei et al. [33, 34], Stagni et al. [35], and Jiang et al. [36] were tested by Valera-Medina et al. [3] who concluded that none of them provided accurate predictions over a wider range of conditions.

Available mechanisms for n-heptane/ammonia mixtures are based on merging subsets for n-heptane and ammonia, assuming little direct interaction. Yu et al. [22] combined the n-heptane mechanism of Zhang et al. [19] with the amine subset from Glarborg et al. [32]. Compared to experiment, their modelling showed substantially longer ignition delay times at lower temperatures and overestimated the negative temperature coefficient (NTC) initiation temperature, possibly due to omitting reactions of n-heptane or its derived radicals with amines. Lubrano Lavadera et al. [23] adopted the model developed at Polimi [35, 37], which provided a good description of the measured flame speeds. They concluded that for flame propagation, direct chemical coupling effects could be disregarded.

Due to the scarcity of both experimental data and modeling studies, the importance of the chemical coupling for high pressure ignition and oxidation of mixtures of NH_3 with n-heptane is still an open question. The C/H/N/O chemistry has been studied extensively for C1-C2 hydrocarbons [32], but few studies are available for larger hydrocarbons. Interactions include H abstraction from hydrocarbons by radicals such as NH_2 and CN, as well as reactions involving NO and NO_2 with hydrocarbon and peroxide radicals. These steps may affect ignition as well as pollutant emissions. Reported experiments for ignition and oxidation of n-heptane/ammonia fuel mixtures were conducted at pressures well below those of engines and gas turbines.

In T2.1, experiments were conducted at pressures up to 100 atm in the DTU laminar flow reactor and the Princeton jet-stirred reactor to characterize the high-pressure features of this fuel mixture. A detailed chemical kinetic model for the ignition and oxidation of n-heptane/ammonia was established. Similar to Yu et al. [22], we based the mechanism on merging the n-heptane mechanism of Zhang et al. [19] with the amine subset from Glarborg et al. [32]. However, we included a novel subset for the chemical coupling reactions, based on analogy with similar reactions for smaller fuels. Furthermore, the H_2-O_2 and amine subsets were updated to include newly published elementary reactions involving HO_2 chemistry. The revised model was validated against the present experimental results, as well as the ignition delay times reported by Yu et al. [22].

2. Experimental

2.1 High pressure laminar flow reactor

The DTU high pressure flow reactor is designed to operate at pressures up to 100 bar. A brief description is given here as the setup is described in detail elsewhere [21, 38, 39]. The reactor is a 154 cm long quartz tube with 8 mm ID (inner diameter) and 10 mm OD (outer diameter). A steel container surrounds the quartz tube and the cavity between the steel container and quartz tube is pressurized to form a pressure shell preventing high pressure gradients over the quartz tube. A moveable thermostat is placed inside the steel container to estimate the temperature inside the reactor. Heating trace (~ 373 K) is used downstream to prevent product condensation. High pressure mass flow controllers are used to control the feed of the reactant gasses (ammonia, heptane and O_2) and nitrogen (for dilution). Gas bottles from Air Liquid with certified concentrations of ±2% were used. The total mass flow was maintained around 1500 Nml/min, allowing a good plug flow approximation in the laminar flow regime [38]. Temperature profiles in the reactor were measured at inert conditions. We define the isothermal zone to be the length of the reactor where the temperature is within ±6 K. The isothermal zone was measured to be 45-48 cm at 21 bar and 39-45 cm at 100 bar, corresponding to residence times of 6-10 s at 21 bar and 28-57 s at 100 bar, decreasing with temperature.

The downstream was analysed for products using a Trace 1300/1310 gas chromatograph (GC) from Thermo Fisher for hydrocarbons, O_2, CO and CO_2, and ammonia levels were measured using either an FTIR analyser (MKS multigas 2030) or a dedicated NH_3 analyzer (ABB AO2020). The GC uses a Flame Ionization Detector (FID) with a capillary column Rtx-5, and a Thermal Conductivity Detector (TCD) with three micro packed columns; Rt-XLSulfur, Molsieve-5A, and HS-N (HayeSep). For every measuring temperature, two to five GC samples were collected to determine the species mole fractions with a measuring uncertainty within 10%. The GC was calibrated for heptane, butane, iso-butene, propane, propene, ethane, ethene, methane, methanol, acetaldehyde, CO, CO_2, and O_2.

2.2 High pressure jet-stirred reactor

The supercritical pressure jet-stirred reactor (SP-JSR) recently developed at Princeton was employed to conduct oxidation studies of NH_3/n-C_7H_{16} mixtures at low and intermediate temperatures and at 100 atm. The core part of the SP-JSR was a quartz sphere with an internal volume of 0.4 cm3. The centre of the sphere had eight perpendicular nozzles with 0.2 mm inner diameter on four jet fingers. This geometry generates homogeneous mixing [40]. The reactor was placed inside a stainless-steel shell with several segments of electric heating wires. The axial temperature profiles were within ± 5 K under the experimental conditions. The velocity distribution profiles of the sphere cross section and the temperature profile measurements are provided in an earlier publication [40]. The gas flow rates were controlled by several high-pressure mass flow controllers (Brooks, SLA5800). The liquid fuel (n-C_7H_{16}, Sigma-Aldrich, ≥99.5%) was injected into a vaporization line by a high-pressure syringe pump (Harvard PHD). The products at the exit of the sphere were sampled through a quartz sonic nozzle into a vacuum environment created by a dry pump. The NH_3 mole fractions were measured by a multi-pass Herriot cell for tunable diode laser absorption spectroscopy (TDLAS) at 1726.4 cm^{-1} wavenumber. The other gas samples were quantified with a micro gas chromatography (μ-GC). The uncertainty of the measurements was less than 5%. The schematic of the entire setup and the detailed descriptions are available elsewhere [40]. The oxidation experiments were performed at temperatures between 450 and 850 K at 100 atm. The nominal residence time was defined as the ratio of the reactor volume to the volume flow rate at the specific temperature and pressure. The inlet volume flow rate was fixed to reduce the error in flow control and perturbation. Therefore, the flow residence time of the experiment

changed with the temperature. Each measurement was repeated at least twice to minimize the experimental uncertainty [41].

3.   Detailed chemical kinetic model

The chemical kinetic model consists of subsets for n-heptane, ammonia, and interactions between the amine and hydrocarbon species. The full mechanism and thermodynamic data are available from the authors.

The n-heptane subset was drawn from Zhang et al. [19], since this mechanism provides the best overall agreement with high-pressure ignition delay and flow reactor experiments [21]. In the Zhang et al. scheme, the H_2-O_2 subset was replaced by the updated Princeton high pressure mechanism [42], which involves the most recent fitting of experimental results or theoretical calculations for several key reactions involving HO_2 chemistry. The H_2O_2 subset, including the singlet/triplet competing channels, was updated based on the recent study of Klippenstein et al. [43]. The new channel $HO_2 + HO_2 = 2OH + O_2$ enhances the intermediate temperature chemistry, especially for high pressure conditions.

The amine subset was adopted without change from Glarborg [44]. This part of the mechanism draws mainly on the review of nitrogen chemistry by Glarborg et al. [32], but includes updates for $NH_2 + H$ (+M) [45, 46], $NH_3 + HO_2$ [35], $NH_2 + HO_2$ [45, 47], amine + NO_2 [44], and steps in the diazene subset [48].

An important objective of the present work was to establish a subset for the chemical coupling between the n-heptane and the amine chemistry. Of particular interest was the H-abstraction from n-heptane by NH_2,

n–$C_7H_{16} + NH_2 = C_7H_{15} + NH_3$ (R1-R4)
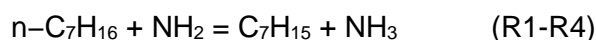
where the heptyl radical could be any of the four isomers (C_7H_{15}-(1,2,3,4)). Fuel + NH_2 type reactions are known to be of major importance for ignition of binary mixtures of ammonia with small hydrocarbon fuels [49–51]. The rate constants for R1-R4 were estimated by analogy to similar reactions of smaller hydrocarbons. Siddique et al. [52, 53] employed CBS-QB3 methodology and conventional TST to calculate rate constants for H-abstraction by NH_2 from different C-H sites for a number of aliphatic (up to C4) and aromatic molecules. Their calculated total rate constants for C_3H_8 were shown to agree well with experimental values from Demissy and Lesclaux [54] (300-500 K), Ehbrecht et al. [55] (550-1070 K), and Hennig and Wagner [56] (1500-2100 K). Figure 1 shows the variation in the rate constant for primary and secondary alkyl radicals, as reported by Siddique et al. [52, 53], together with the values calculated by Mebel and Lin [57]. In the present model, the values from Siddique et al. [52, 53] were taken directly or extended by analogy, scaling for the correct degeneracy level, for all n-alkane and n-alkene molecules present in the mechanism. As discussed below; while predicted ignition delay times are very sensitive to the presence of the n-heptane + NH_2 reaction, the A-factor sensitivity is not substantial. For this reason, the uncertainty associated with using the analogy approach for this reaction is not expected to affect significantly the modelling predictions.

It is known that hydrocarbon/NO_x interactions may promote or inhibit reaction, depending on the fuel and the reaction conditions [58]. Reaction classes include,

$ROO + NO = RO + NO_2$

$ROO + NO$(+M) $= RONO_2$(+M)

$RH + NO_2 = R + HONO$
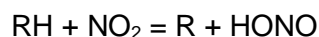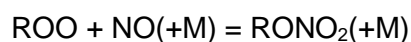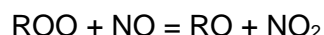
Reactions of the type $ROO + NO = RO + NO_2$ may inhibit ignition of large hydrocarbons in systems with initial presence of NO [59]. Chen et al. [60] studied autoignition of n-heptane/NO

mixtures and summarized hydrocarbon/NO sub-mechanisms available in literature. In binary mixtures with NH_3, where no or little NO is present among the initial reactants, the hydrocarbon/NO_x interactions are expected to have lower importance, but we include them in the present model for completeness. Recommended values for methyl, ethyl-, n-propyl and i-propyl peroxy radicals with NO do not deviate from each other by more than 25% [61], and the rate constants for $C_7H_{15}OO + NO$ are estimated by analogy to $CH_3O_2 + NO = CH_3O + NO_2$. Formation of nitrate from $C_7H_{15}OO + NO$ (+M) is presumably insignificant at elevated temperatures and was not considered further. For the C_7H_{15}-3 + NO_2 reaction, the rate constants were adopted from the recent study of Almodovar and Goldsmith [62]; following Fang et al. [59], the other heptyl isomers were assumed to have analogous rate constants. Other reactions of the NOx subset involving C3-C7 hydrocarbons were adopted from Fang et al. [59], but were found to be of low importance for the conditions of the present work. For the smaller hydrocarbons, the C/H/N/O subset was drawn from the review of Glarborg et al. [32].
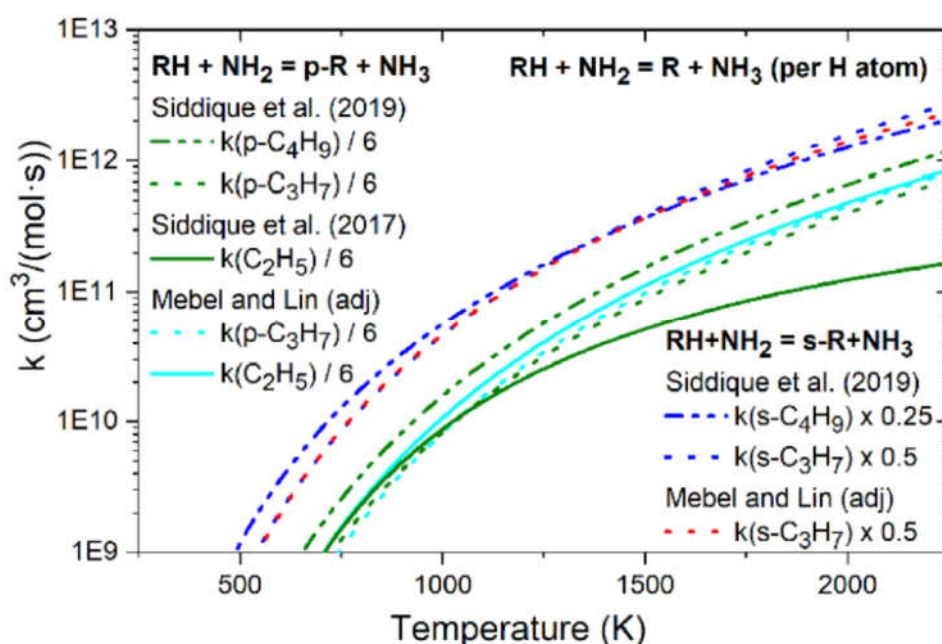

Figure 1: Rate constant of the H-abstraction reaction by NH2 forming primary and secondary alkyl radicals (per H atom): p-C3H7 and s-C3H7 (dotted lines) [53, 57]; p-C4H9 and s-C4H9 (dash-dot-dot lines) [53] and C2H5 (solid lines) [52, 57]. Note that Mebel and Lin [57] adjusted the theoretically calculated values within the method accuracy for better agreement with available experimental data.

4.   Results and discussion

The revised NH_3/n-heptane mechanism has been validated by comparison with high-pressure experiments from literature (the ignition delay measurements from Yu et al. [22]) and from the present work. In addition to evaluating the predictive capabilities of the revised model at high pressure, the importance of the chemical coupling is discussed.

4.1 Ignition delay

Figure 2 presents simulations of ignition delay measurements in RCM of Yu et al. [22] for a selected case of a stoichiometric 90/10 (mole fraction) $NH3$/n- C_7H_{16} mixture at 15 bar. In the modeling, volume profiles obtained by Yu et al. [22] from pressure histories, are implemented. First and main ignition events were determined at pressure inflection points, as done in the experiments [22].
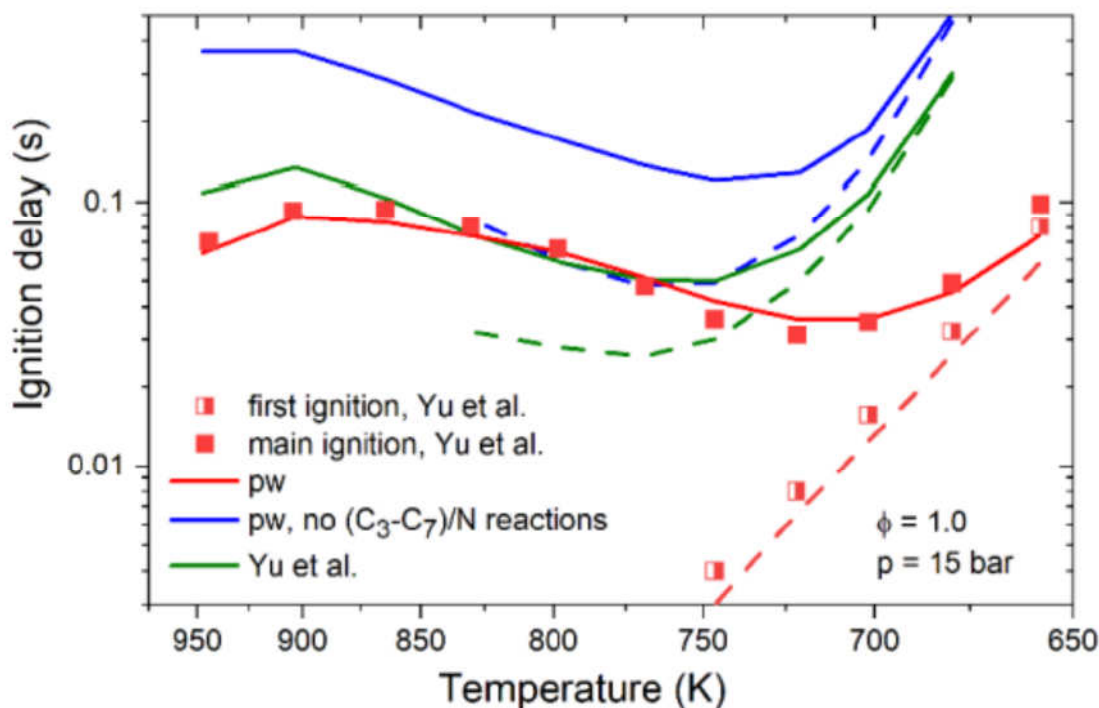
Figure 2: Comparison of experimental (symbols, from Yu et al. [22]) and predicted (lines) ignition delay times for a fuel mixture of 9.6% n-C7H16 and 90.4% NH3 in 10.5% O2 and 88.5% Ar with a fuel-air equivalence ratio $\phi = 1$ and a pressure of 15 bar. Solid lines, filled symbols – main ignition; dashed lines, open symbols – first ignition. Simulations using the measured RCM compression histories [22] were conducted with the model developed in the present work (red), with that excluding the C3-C7/N interaction subset (blue), and with the model of Yu et al. [22] (green).

Predictions with the mechanism developed in the present work are compared to calculations with the model of Yu et al. [22] who merged the n-heptane model of Zhang et al. [19] with the mechanism of Glarborg et al. [32]. Even though we adopted a different merging approach in the present work, we found that combining the mechanisms of Zhang et al. and Glarborg et al. yielded predictions (not shown in Figure 2) almost identical to those of Yu et al. Due to the influence of the updated H_2/O_2 subset, the present model predicts considerably faster ignition for pure n-heptane at intermediate temperatures, compared to the mechanism by Yu et al. For the 90% NH_3 fuel mixture in Fig. 2, the present mechanism (red lines) closely follows the experimental results [22] in terms of both first and main ignition. The results are significantly improved compared to the merged model of Yu et al. [22] (green), which predicts a qualitatively different profile for the first ignition and overestimates both the main ignition at T < 750 K and the NTC initiation temperature.

In order to illustrate the influence of the updates in different subsets of the mechanism on ignition delay, predictions the present mechanism without the interaction reactions between nitrogen-containing and C3-C7 species is shown as a blue curve in Fig. 2. It can be seen that the updates in the amine subset (primarily, the novel rate constant for the $NH_2 + HO_2$ reaction [47]) slow down the ignition; still, the interval between the first and the main ignition is comparable to that predicted by the mechanism of Yu et al. [22]. Inclusion of R1-R4 into the interaction subset accelerates the initial n-heptane consumption, enhancing the first ignition and subsequently affecting the chemistry leading to the main ignition. Also for other NH3/n-heptane mixtures, good agreement between predictions with the present mechanism and the

experimental results from Yu et al. was obtained. It can be concluded that the modifications in the different subsets of the mechanism were essential for correct prediction of ignition of NH_3/n-heptane binary mixtures.

4.2 High pressure laminar flow reactor

The high pressure plug flow reactor experiments were conducted at both 21 bar and 100 bar, and stoichiometric and oxidizing conditions. The n-heptane/NH_3 ratio was maintained at 10%. The residence time in the isothermal zone, which depends on the temperature and pressure, is measured to be 6-10 s at 21 bar and 28-57 s at 100 bar. The model predictions are conducted using Chemkin Pro by ANSYS v. 19.1 [63] by assuming plug flow conditions in the reactor and including the full temperature profile.

The measured NH_3 and n-heptane mole fractions are compared with modelling predictions in Fig. 3. Predictions are shown for both the present mechanism (solid lines) and the mechanism by Yu et al. [22] (dashed lines). The conversion of n-heptane exhibits a low temperature region from 500 K to 700 K and a high temperature region above 700 K. An increase in pressure or O_2 level promotes the low temperature n-heptane conversion and lowers the onset temperature. A pronounced NTC region is only observed at 21 bar and stoichiometric conditions, whereas at higher oxygen levels and/or higher pressure, a transition region is detected as a plateau in the n-heptane mole fraction. Low temperature conversion of NH_3 is only observed at high pressure and lean conditions. At 100 bar and stoichiometric conditions, as well as at 21 bar and lean conditions, the NH_3 conversion has an onset temperature of 700 K, coinciding with the high temperature onset of n-heptane oxidation. For 21 bar and stoichiometric conditions, no NH_3 conversion is observed. The increasing levels of NH_3 observed in the low temperature region and just before the full conversion of n-heptane for the conditions at 21 bar, and 100 bar stoichiometric, is assumed to be an analyser cross interference with some of intermediates formed in the n-heptane oxidation. Comparison of the present results with previous high-pressure flow reactor studies on ammonia [20] and n-heptane [21] allows an assessment of the mutual interaction between the two fuels. The presence of n-heptane lowers the onset temperature for ammonia about 100 K compared to pure NH_3 oxidation under similar conditions. The promoting effect of n-heptane is consistent with reported ignition delay measurements. For n-heptane, the oxidation behavior with a low temperature region of roughly 500-700 K and high temperature region starting at 700 K is the same with and without presence of NH_3. However, ammonia addition has an inhibiting effect on the low temperature n-heptane oxidation; the conversion in the NTC region is reduced by a factor of two, and the onset temperature is increased by up to 50 K. The present model provides a satisfactory prediction of the n-heptane and ammonia profiles. The NTC behavior for n-heptane at lean conditions and 21 bar is captured, even though the width of this region is slightly underpredicted. The main discrepancy is the overprediction of the NH_3 conversion at higher temperatures for lean conditions at 21 bar. Predictions with the model from Yu et al. [22] are less accurate. Notably, this model does not predict NTC behavior for n-heptane at lean conditions and 21 bar. This discrepancy can be attributed mostly to the failure to describe direct interactions between the ammonia and n-heptane, in particular omission of the reaction between NH_2 and n-heptane (R1-R4). The model from Yu et al. also tends to overpredict the reactivity of ammonia at higher temperatures. The improved performance of the present model in terms of NH_3 consumption is facilitated by the updates in the amine subset compared to Glarborg et al. [32], mainly the use of the recent theoretical rate constants for NH_2 + HO_2 from Klippenstein and Glarborg [47].
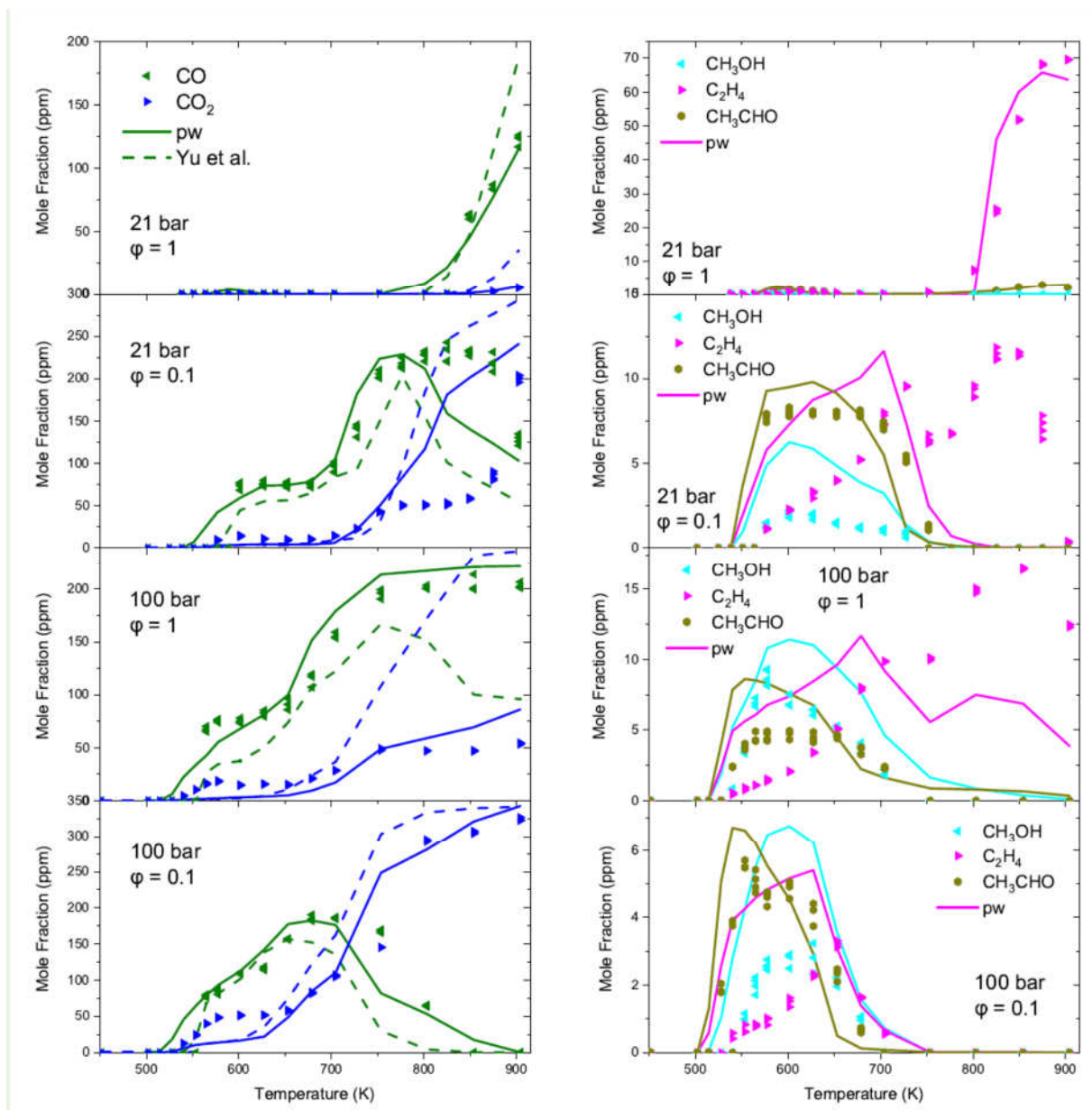
Figure 3: Comparison of measured and predicted mole fractions of n-heptane and ammonia in oxidation of a NH3/heptane mixture at high-pressure flow reactor conditions. Experimental results are shown as symbols. Modelling predictions are shown as solid lines (present model) or dashed lines (model from Yu et al. [22]). The residence times in the isothermal zone are 6-10 s at 21 bar and 28-57 s at 100 bar, respectively, decreasing with temperature.

4.3 High pressure jet-stirred reactor

The supercritical pressure jet-stirred reactor (SP-JSR) experiments were conducted at 100 atm, and fuel-air equivalence ratios of 0.1 and 1.0. The n-C_7H_{16}/NH_3 ratio was maintained at 10%. Figure 4 shows a comparison of measured and predicted species mole fractions as a function of temperature. The residence times were 0.52-0.28 s at 100 atm and the equivalence ratio was 0.1. The experimental results show that n-C_7H_{16} starts to be oxidized at a temperature around 550 K. The consumption of NH_3 is negligible at this temperature; it is initiated around 600 K, significantly below the onset temperature for pure NH_3 oxidation. This can be explained by the active radicals produced by the low temperature oxidation of n-C_7H_{16}.

Similar to the flow reactor results discussed above, the experimental n-C_7H_{16} mole fraction profile exhibits a narrow shoulder, here from 625 to 700 K. The plateau represents the remnant of the negative temperature coefficient (NTC) behavior, where the n-C_7H_{16} consumption slows down with increasing temperature. The species profiles for CO_2 and H_2O in Fig. 4 also exhibit a shoulder in the same temperature region as the n-C_7H_{16} profile.

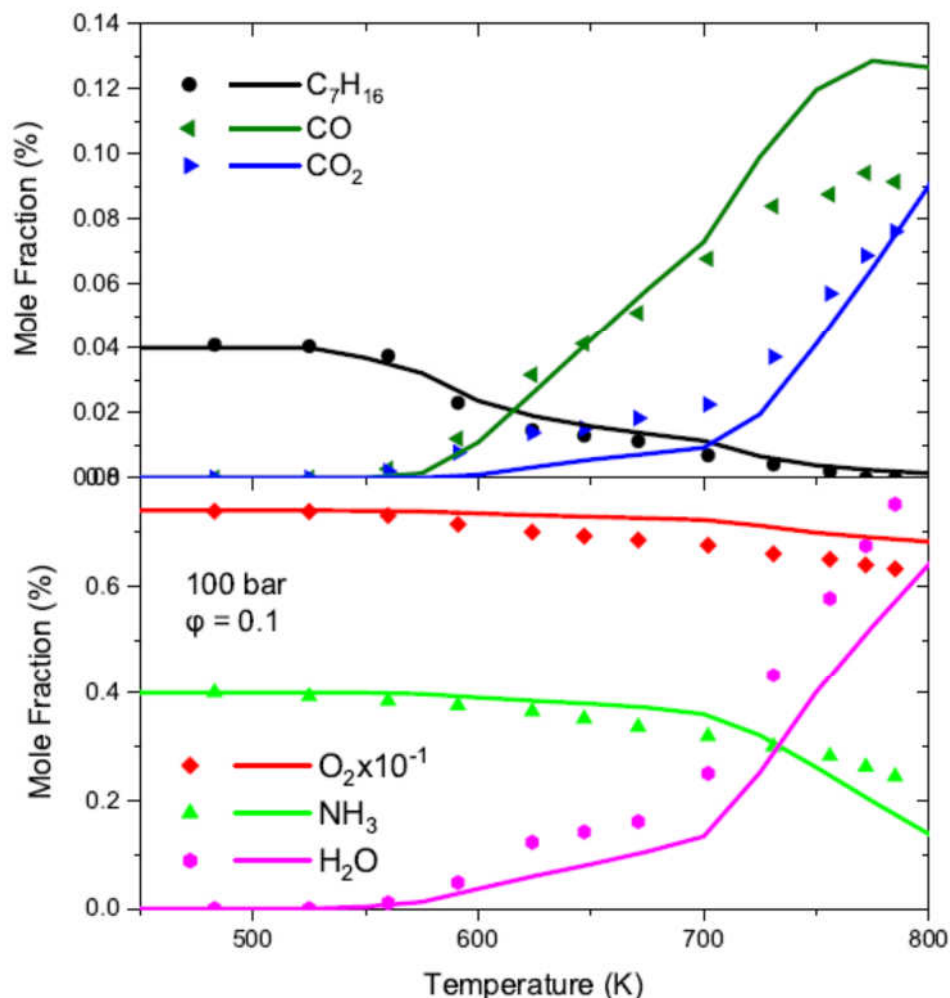*Figure 4: Comparison of measured and predicted mole fractions in oxidation of a fuel-lean (ϕ = 0.1) NH_3/n-heptane mixture at 100 atm in a jet-stirred reactor. Experimental results are shown as symbols and modelling predictions with the present model are shown as solid lines.*

The modelling predictions show good agreement with experimental data, especially for n-C_7H_{16}. However, the model slightly underpredicts the NH_3 consumption at lower temperatures, while it overpredicts the NH_3 consumption in the intermediate temperature region. The increased OH radical production via the H_2O_2 (+M) = 2OH (+M) and $2HO_2$ = 2OH + O_2 reactions at high pressure shifts the intermediate temperature chemistry to lower temperature.

5. Conclusion and Future Plans

The present work has provided an updated model for the NH_3/n-heptane mixture oxidation. The model was compared to ignition delay time measurements in the literature, and novel experiments using a laminar flow reactor and jet-stirred reactor. The flow experiments were conducted at intermediate temperatures (T=450-900 K) and high pressures up to 100 atm, relevant for engine conditions. The model predictions were in good agreement with the experimental data, providing significant better predictive capabilities than models in the literature [22]. The reaction mechanism provides a good starting point for subsequent systematic reduction, which will give compact mechanisms suitable for use in engine simulations in CFD.

Future work in WP2 includes work on formation and decomposition of nitrogen oxides, with focus on the strong greenhouse gas N_2O.

6. References

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