Study of Ammonia/Hydrogen as Carbon-free Fuels for Heavy Duty Engines

Author: Leilei Xu, Lund University

Project ID： 21-345, from 2021 to 2022

1. Summary

Thanks to the ÅForsk foundation, I have conducted several large-scale simulations of ammonia combustion processes under various conditions. With the support of the ÅForsk, I also built collocations with different universities and companies in different countries. (a) I have developed, optimized, and validated our in-house simulation code for large-scale parallel simulations of turbulent reactive flows, which can be used to perform large eddy simulation (LES) and reynolds-averaged navier–stokes (RANS) study of turbulent reactive flow in piston engines, spray flames, as well as flame instability studies. I have developed and validated a skeletal chemical kinetic mechanism for ammonia/n-heptane combustion. This mechanism is the first published ammonia/n-heptane mechanism for 3D simulations. The OpenFoam-based LES and RANS solvers have been used to simulate direct injection for dual fuel stratification (DDFS) and reactivity-controlled compression ignition (RCCI) engine combustion concepts in heavy-duty engines and marine engines. In the present project period (one year), the following works have been carried out and published:

- The decoupling methodology and an optimization algorithm were employed to develop a skeletal chemical kinetic mechanism for the combustion of n-heptane/ammonia blend fuels. The newly developed ammonia/n-heptane mechanism was validated against the experimental data of pure ammonia, ammonia/ hydrogen, and ammonia/n-heptane mixtures. The final skeletal mechanism includes 69 species and 389 reactions. This work is referred to the WP1 in the proposal and has been published in the high-impact journal "Fuel" [1];
- Numerical modeling of ammonia spray under GDI and diesel engine conditions was investigated. Several questions are addressed, including whether the widely used Lagrange particle tracking spray models (e.g., breakup, vaporization, etc.) developed for traditional fossil fuels are suitable for ammonia spray and whether certain improvement of the current models should be introduced. This work is referred to the WP2 in the proposal and is revised in the high-impact journal "Applied Energy" [2];
- LES study of the ignition and combustion characteristics of ammonia/diesel dual fuel combustion in a constant volume vessel (CVV). This work is referred in the WP3 in the proposal and will be submitted to a high-impact journal;
- RANS study of direct dual fuel stratification (DDFS) and reactivity-controlled compression ignition (RCCI) combustion in a heavy-duty engine. The engine performance and emission source are investigated. This work is referred to the WP3 in the proposal and will be orally presented in the 12th Mediterranean Combustion Symposium [4].

Below are some highlights of the results obtained in the past year within the ÅForsk project (ID:21-345).

1) The skeletal chemical kinetic mechanism for the combustion of n-heptane/ammonia blends is developed using a technique known as the decoupling methodology. The

basic idea of the decoupling methodology can be described to consist of three steps: development of a complete sub-mechanism for C0–C1 hydrocarbons, development of a reduced sub-mechanism for C2–C3 hydrocarbons, and development of a skeletal fuel specific sub-mechanism. In the present work, the n-heptane skeletal mechanism is taken from the recent work of Chang et al., in which a set of skeletal mechanisms were developed for normal alkanes of C5–C20 by coupling the decoupling methodology, the reaction class-based global sensitivity analysis method, and a genetic algorithm. The ammonia mechanism is adapted from the original work of Stagni et al. that was optimized by Bertolino et al. using a machine-learning method. The H2/O2 and NOx sub-mechanisms are nearly the same as those in the n-heptane skeletal mechanism, except that a few reactions need to be adjusted. For the duplicate reactions of these two mechanisms, the reaction rates in the n-heptane mechanism are considered a high priority. The sub-mechanisms for the ammonia and n-heptane skeletal mechanism are illustrated in Fig.1. It can be found that the initial skeletal mechanism obviously over-predicts the IDT of the mixture (NH3, 9.8 vol.%, C7H16 1.03%, O2 9.37%, and Ar 79.8% at p=15 atm and Φ=2.0.) as compared with the measured data, especially for the data under low-temperature conditions. A sensitivity analysis of the IDT was performed to identify the key reactions. Then, their rate constants are optimized to enhance the performance of the skeletal mechanism using the genetic algorithm. As seen in Fig. 1, the final skeletal mechanism satisfactorily reproduces the ignition behavior of the n-heptane/ammonia blends.

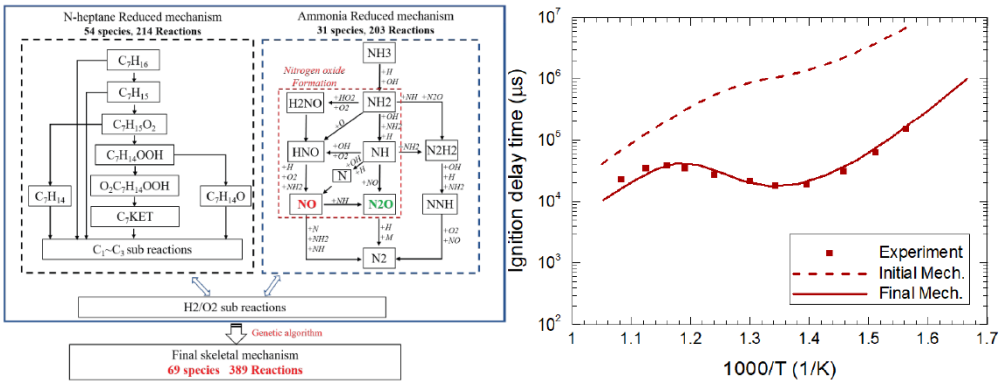


Fig. 1. The sub-mechanisms in the ammonia/heptane mechanism, and comparison of the measured IDTs (symbols) with the calculated results using the initial/final skeletal mechanism (lines) for the mixture of NH3

Experimental studies on the fundamental combustion behavior of NH3/n-heptane blends are rare. Recently, Yu et al. measured the IDTs of ammonia/n-heptane mixtures in a rapid compression machine with a pressure of 10 ~ 15 bar and temperature ranging from 600 ~ 1000 K. The IDTs of four ammonia/n-heptane mixtures with various NH3/n-heptane blending ratios and equivalence ratios studied by Yu et al. are simulated to evaluate the performance of different mechanisms in the literature the present skeletal mechanism. Figure 2 shows the measured and predicted IDTs of various ammonia/n-heptane mixtures at 10 and 15 bar pressures. The simulations are done using the present skeletal mechanism and the detailed mechanisms of Yu et al. (1376 species and 6499 reactions) and Shrestha et al. (402 species and 2543 reactions). The negative temperature coefficient (NTC) ignition behaviors for ammonia/n-heptane mixtures is well predicted by the three chemical kinetic mechanisms. It can be seen that the present skeletal mechanism, specially developed for ammonia/n-heptane blend fuel, predicted the NTC behaviour well. The pressure dependence behavior is clearly captured by the three chemical kinetic mechanisms

with the present skeletal mechanism showing the best agreement with experiments. The Yu mechanism over-predicts the IDTs for mixtures 3 and 4 at 15 bars.

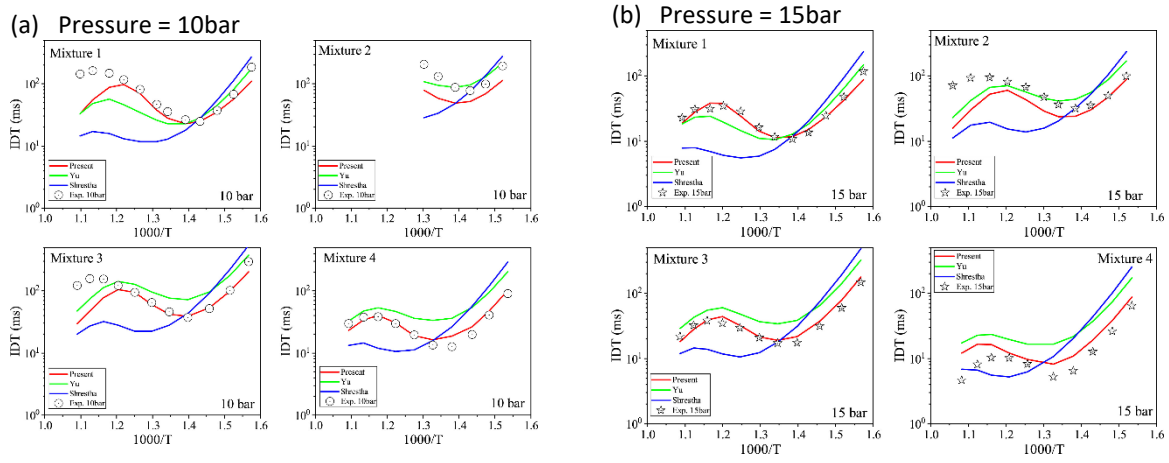


Fig. 2. IDTs of n-heptane/NH3/O2/Ar mixtures at the pressure of 10 bar (a) and 15 bar (b). Symbols are the experimental results and lines are the simulation results using different mechanisms.

The newly developed ammonia/n-heptane mechanism was also validated against the experimental data of pure ammonia and ammonia/ hydrogen, including ignition delay times measured in shock tubes and rapid compression machines, species data measured in jet-stirred reactors, and laminar flame speed in burner-stabilized premixed flames and spherical flame vessels. The present mechanism is shown to be capable of replicating the experimental results under wide conditions. Further results can be referred to the reference paper [1].

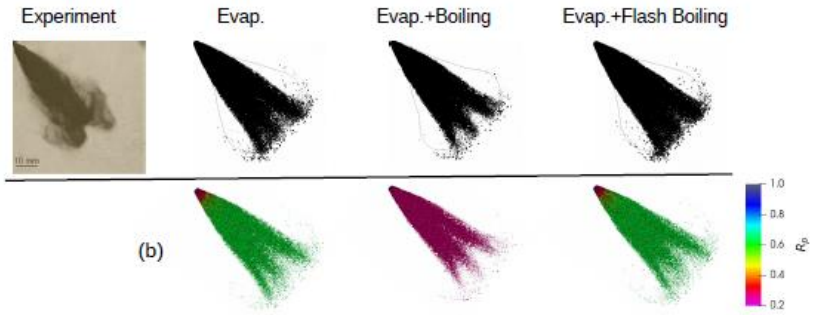
2) CFD modeling of the fuel/air mixing characteristics of liquid ammonia under direct injection engine-relevant conditions are investigated. Several questions are addressed including whether the widely used Lagrange particle tracking spray models (e.g., breakup, vaporization, etc.) developed for traditional fossil fuels are suitable for ammonia spray, whether certain improvements of the current models should be introduced, and under what conditions the improvement of models needs to be considered. It is found that the current Lagrange-based spray models under non-flash boiling conditions can well reproduce liquid ammonia spray characteristics. However, there are obvious gaps between measurements and predictions under strong flash boiling conditions. A control parameter known as the initial superheat degree,

$$R_P = \frac{P}{P_s(T_P)}$$

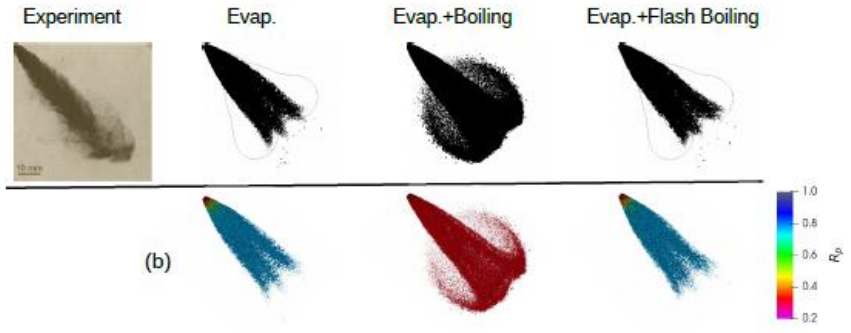
Which is defined as the ratio of ambient pressure (P) to the saturation vapor pressure (P_s) at initial fuel temperature (T_s), can be adapted to determine the boundary of the flash boiling model. When R_P<0.3, the vaporization process is referred to as the flare flash boiling, 0.3<R_P<1 corresponds to the transition flash boiling regime, and R_P>1.0 corresponds to the condition of non-flash boiling. As shown in Fig.3, the flash model considering only the evaporation promotion effect cannot replicate the ammonia spray characteristics, and it does not result in obvious differences compared with the results from the conventional evaporation model. The thermal breakup effect due to flash boiling must be taken into account. Compared with other alternative fuels, ammonia has higher saturation vapor pressure, showing a higher sensitivity to fuel temperature.

Thus, a more accurate and robust flash boiling model that considers the thermal breakup effect on both primary and secondary breakup characteristics should be employed to predict the spray and fuel vapor/air mixing characteristics in engine-relevant conditions.

a. Case 1, the initial superheat degree R_P = 0.26, initially under the flare flash boiling condition



b. Case 2, the initial superheat degree R_P = 0.34, under the transition flash boiling regime



c. Case 3, the initial superheat degree R_P = 1.2, initially under the non-flash boiling condition

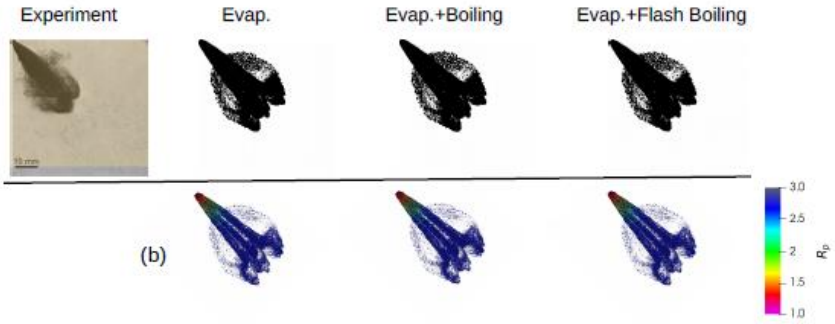


Fig. 3. Morphology of ammonia spray liquid phase from different models and experiments and predicted liquid spray morphology colored with the superheat degree Rp for different conditions.

Flash boiling is a complex process, including bubble nucleation, growth, and breakup, as illustrated in Fig. 4. The so-called thermal breakup effect caused by flash boiling should be taken into account in the current breakup models. Furthermore, flash boiling in the near-nozzle region also significantly alter the structural characteristics of primary spray, resulting in smaller spray angles and then higher probability of spray collapse

especially for multi-plume sprays. The spray cone and included angles for ammonia sprays had to be decreased from those for the ethanol spray to capture the spray characteristics reasonably well. Thus, the effect of flash boiling for primary and secondary breakup characteristics should all be considered simultaneously in the modeling. It is worth noting that although the current Lagrange-based spray models can well simulate the liquid ammonia spray characteristics under direct injection conditions when R_P >1, the saturation vapor pressure of ammonia is significantly larger and more sensitive to temperature than that for other alternative fuels such as ethanol. For high-pressure common rail injection systems, the compression process of ammonia in the common rail systems results in a significant increase in the fuel temperature. Thus, the operating conditions that the flash boiling occurs for ammonia are considerably broadened. Thus, it is necessary to introduce a robust flash boiling model to accurately predict the fuel/air mixing characteristics of ammonia direct injection under wide operating conditions.

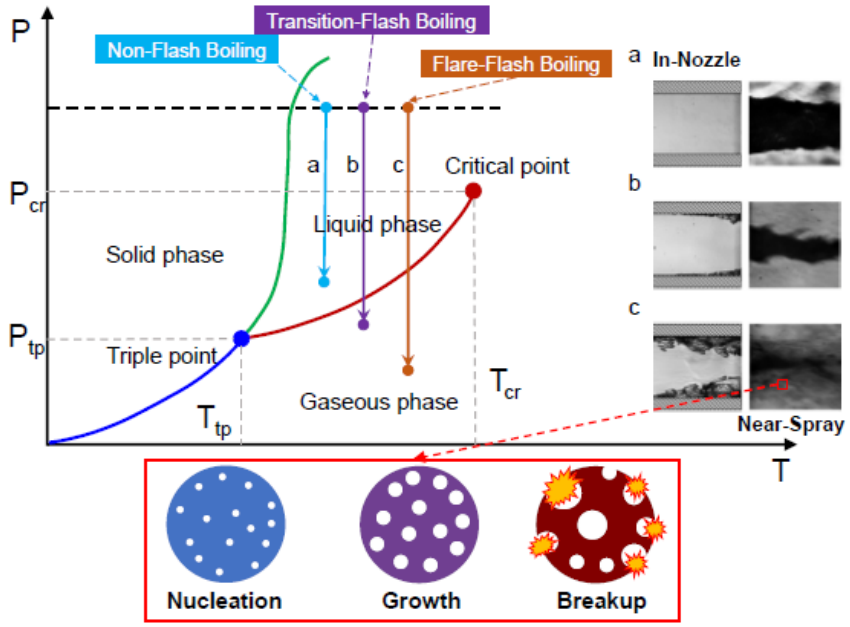
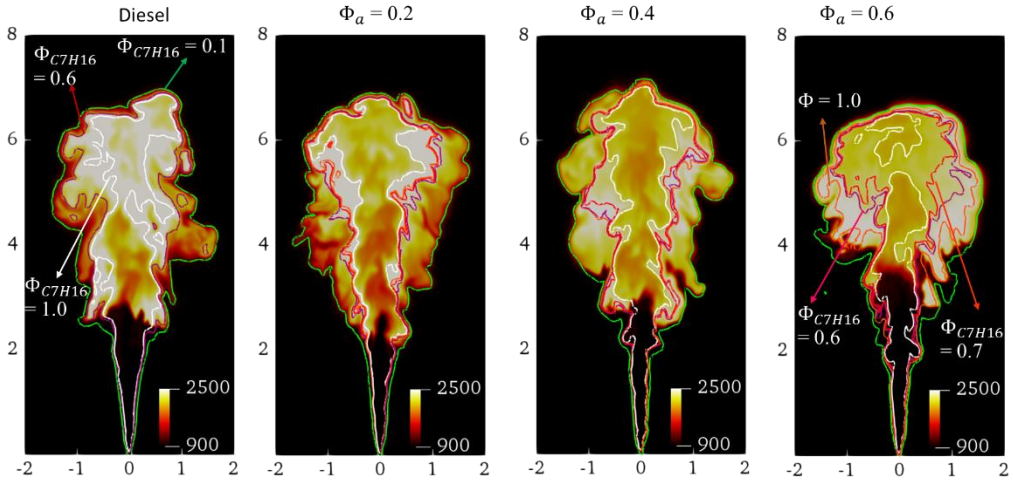
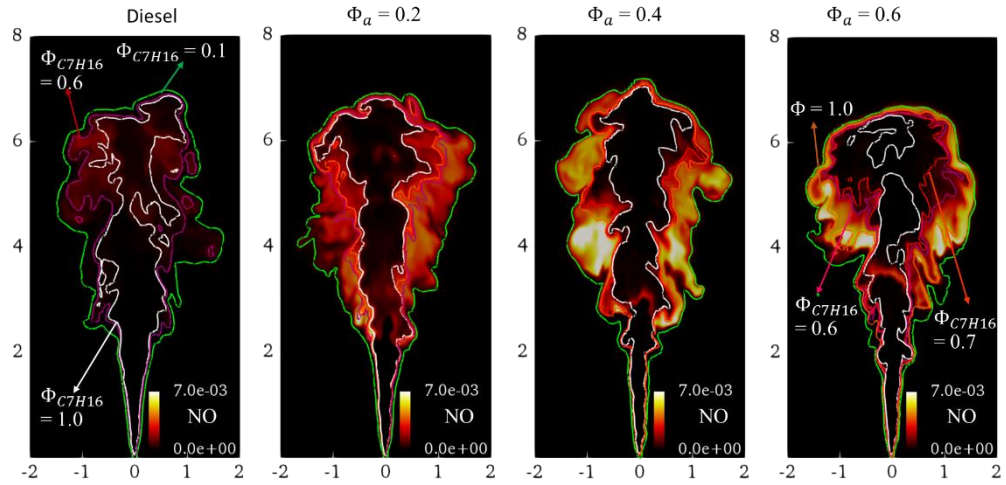


Fig. 4. Schematic illustration of the boiling regimes and spray characteristics.

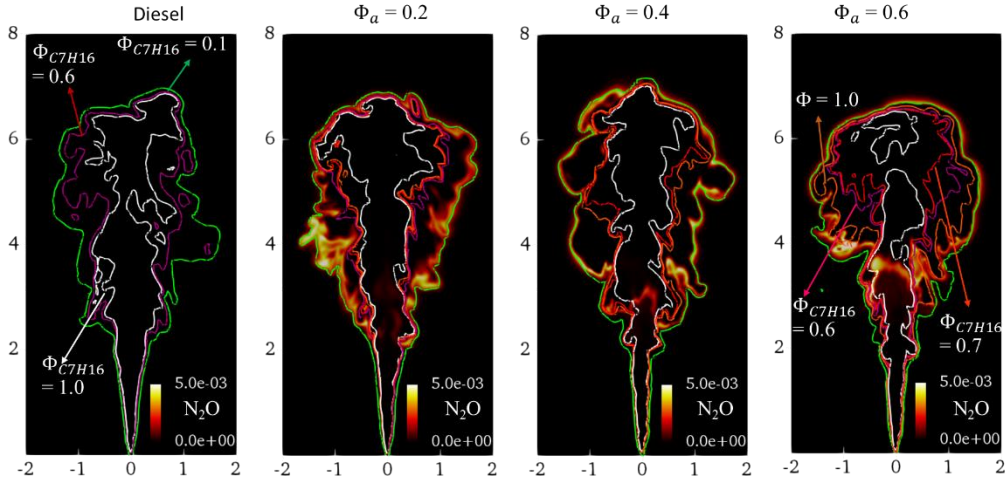
3) *LES study of the effects of ambient ammonia on pollutants formation in dual-fuel spray combustion.* Ammonia (NH_3) is recognized as one of the promising energy vectors for next-generation engineering applications to achieve zero emissions of greenhouse gases (CO_2). However, ammonia suffers from difficult ignition and high nitrogen oxide (NO and N_2O) emissions due to its thermo-chemical characteristics (very low flame speed and fuel-bound nitrogen fuel). The dual-fuel combustion concept, RCCI, is a potential solution to address ignition and emission issues. This study aims to gain a deeper insight into the mechanisms of combustion and pollutant emissions fueled with the NH3 under the RCCI concept. The effect of ambient ammonia mixture on combustion performance and emissions of an RCCI engine is comprehensively investigated in a CVV. The results are prepared to submit to the journal of combustion and flame.



(a) Temporal evolution of local temperature distribution at 2ms



(b) Temporal evolution of NO distribution at 2ms



(c) Temporal evolution of N_2O distribution at 2ms

Figure 5. Temporal evolution of temperature (a), NO (b), and N_2O (c) distribution at 2 ms after the SOI of diesel under the different ambient conditions （ammonia premixed Φ_{NH3}=0,0.2,0.4 and 0.6). Solid green, red and white lines denote the local equivalence ratio Φ_{C7H16}=0.1, 0.6, and 1.0, respectively.

Fig. 5 shows a 2D distribution of the temperature, NO, and N_2O distribution at 2ms after the start of injection of n-heptane for four cases. Case A is a single-fuel baseline reference case in which the ambient gas is pure air (without the use of ammonia). Case B, C, and D are three ammonia-premixed cases in which the ambient gas is a mixture of air and ammonia (Φ_{NH3}=0.2, 0.4 and 0.6). From Fig.5, ammonia can suppress the onset of n-heptane ignition. The more ammonia is premixed, the longer ignition delay time is observed. The ambient ammonia is hardly burned. Compared with Case A and the other three cases, ammonia combustion generates more NO emissions. NO species exist in the region where NH_3 is burned. N_2O is mainly formed in the outer reaction front, where NH_3 is burning.

4) Experimental and numerical investigation of performance and emission characteristics of an ammonia/diesel dual-fuel heavy-duty engine. The experiment work is the collocation with Prof. Xingcai Lyu's group at Shanghai Jiao Tong University in China. The experiments were carried out on a heavy-duty direct-injection engine, modified so that only one cylinder is operating, as shown in Fig. 6. The specification of the diesel engine and operating conditions are given in Fig. 6. The in-cylinder gas pressure was measured by a pressure transducer (Kistler model 6125B). The charge output was converted to an amplified voltage using an amplifier (Kistler model 5015A). The heat release rate and in-cylinder temperature were calculated using the D2T combustion analyzer. The total unburned hydrocarbon (HC) and NOx emissions were measured using a heated flame ionization detector (HFID CAI 600). The simulations were conducted using an in-house solver developed for compressible turbulent flow on the computational fluid dynamics (CFD) platform OpenFOAM-V7. The fuel spray process was modeled based on the well-established Lagrangian-Eulerian approach. The Reynolds-Averaged Navier Stokes (RANS) model was used to predict the turbulence in the cylinder. Spray droplets are subject to several processes from the time of injection until the time of vaporization, cf. Fig.6. The detailed submodel description is referred to our previous work. The ammonia fuel is injected into the intake port and is premixed with the air. The diesel is directly injected into the cylinder near the top death center (TDC) to ignite the premixed ammonia/air mixture. This study studied two engine load, 4 bar IMEP as the low load and 10 bar IMEP as the medium load. Besides, three different diesel injection timings (-20, -15, and -10 CA ATDC) were conducted to investigate the effect of the diesel injection timing on the engine performance. The energy share ratio of the ammonia fuel is around 60% for all the cases. The equivalence ratio of the premixed ammonia/air mixture varies from 0.2 (4 bar cases) to 0.5 (10 bar cases). The injection duration was 6 CA for 10 bar cases and 4 CA for 4 bar cases, with an injection pressure of 1200 bar for all cases. The engine speed is 1500 rpm. In the simulation, the case is modeled from intake valve closing (IVC, −141°CA) to exhaust valve opening (EVO, 137°CA). The charge temperature, pressure, and species density at the IVC are assumed to be uniform in the entire combustion chamber. The initial flow inside the cylinder is assumed to be a solid-body rotational flow with a swirl ratio of 2.1 (in accordance with experiments). The turbulence intensity at the IVO is assumed to be 0.1 of the average piston velocity.

Engine lab: Shanghai Jiao Tong University, China. Prof. Xingcai Lyu

Displacement (cm^3)	1325
Stroke (mm)	130
Bore (mm)	114
Connecting rod (mm)	216
Compression Ratio	18:1
Number of valves	4
Swirl ratio	2.1
IVC (° CA ATDC)	-145
EVO (° CA ATDC)	112
Injector type	Solenoid
Number of nozzles	7
Nozzle hole diameter (mm)	0.175
Spray included angle (°)	155

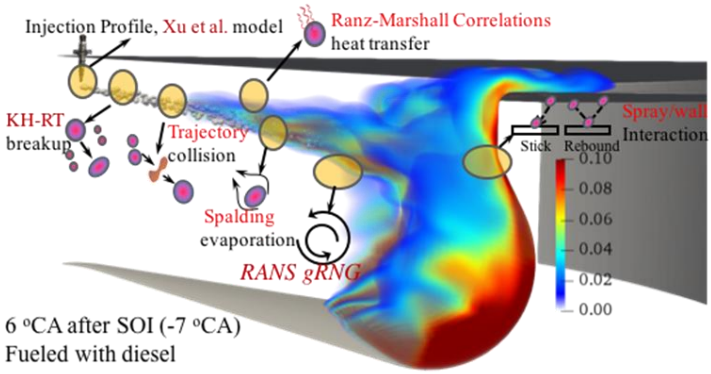
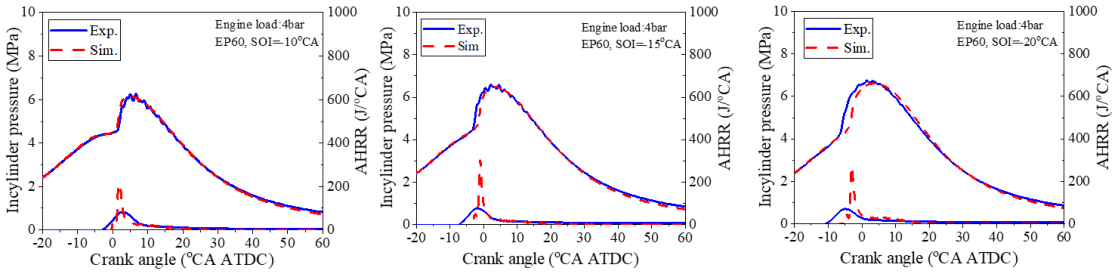


Figure 6. The specification of the diesel engine and the numerical simulation setup

Fig. 7 shows the experiment and simulation results of in-cylinder pressure and heat release rate for the different cases. As shown in Fig. 7, the current model can repeat the experimental results for all the SOIs and engine loads. The heat release rate from the simulation results is higher than that from the experimental measurement. This difference is due to the sector model used in the simulation. In the simulation, the computational domain is a 51.4° sector of the full cylinder, which represents one spray plume. This model means the 7-diesel spray will ignite and burn together, resulting in a higher heat release rate. However, the seven diesel spray has slightly different ignition time in the real engine due to the cycle variation and different wall temperatures. Besides, the simulation models and combustion mechanisms are sources of these differences. In general, the current simulation models are acceptable and reliable.

(a) Low load cases, 4 bar IMEP



(b) Low load cases, 10 bar IMEP

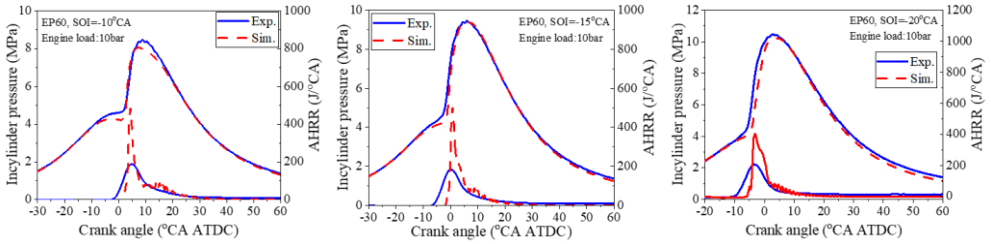
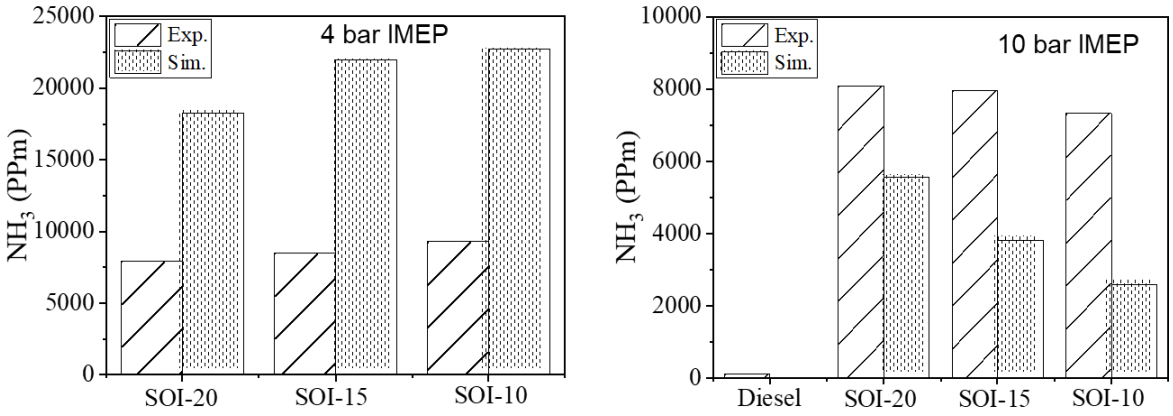


Figure 7. In-cylinder pressure and heat release rate with respect to the crank angle for different SOIs under the two engine loads.

Figure 8 shows ammonia leakage and the N2O emissions for the different cases. As shown in Fig. 8a, the ammonia leakage in the exhaust gas is very high for the load. The ammonia combustion efficiency is only around 50%. Under the low load, the equivalence ratio of the premixed ammonia/air mixture is lower than 0.2, an extremely fuel-lean mixture. The mixture cannot self-ignite, and the flame propagation is also very low under this condition. Thus, the combustion mode in the cylinder is the diesel flame-driven mode. The ammonia only can burn with diesel spray. However, the amount of diesel is also very low. The diesel required is even lower if the higher ammonia energy share is used. While if the lower ammonia energy share is used, the equivalence ratio of the premixed ammonia/air mixture is further low. As shown in Fig.5, the N2O emissions are from the ammonia flame. Incomplete ammonia combustion will lead to high N2O emissions. As shown in Fig.8b, the N2O emissions in the low load are very high. It is noticed that the green gas effect of the N2O is around 300 times of the CO2. For the low load, the RCCI concept is not a good solution for heavy-duty engines. The DDFS concept could be a solution for the usage of ammonia. The ammonia is directly injected into the cylinder to form a stratification mixture before or after the diesel injection. The optimization of the injection timings for diesel and ammonia could improve the engine performance. This concept is not fully investigated in this project. I am looking forward to getting further support from the ÅForsk for further investigation. As shown in Fig.8a, the ammonia leakage is much lower for the medium load. The reason is that the total energy for the high load increase. The equivalence ratio of the premixed ammonia/air mixture significantly increases, and the injected diesel amount also increases. The premixed ammonia can be burned with the support of the diesel flame initially and then self-ignite or flame propagation in the post-flame stage. The ammonia combustion efficiency is much improved. The N2O emissions is also lower for medium load condition.

(a) Ammonia leakage



(b) N2O emissions

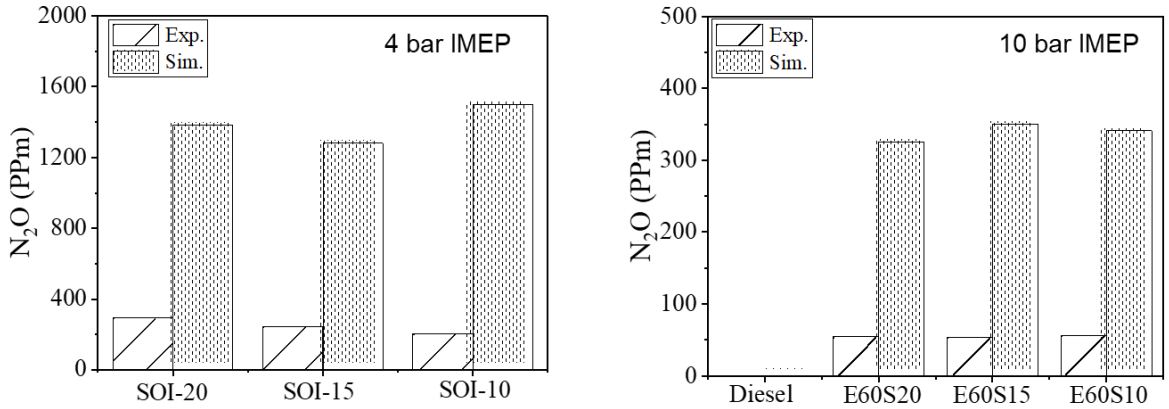


Figure 8. Ammonia leakage and N2O emissions for the different SOIs under two engine loads.

2. International collaboration

In this project, I collaborate closely with the experimental groups at Lund University (LUCC), where a well-equipped experimental facility exists. For the ammonia/n-heptane combustion mechanism development, WP1 in this project, I built the collaboration with Prof. Ming Jia's group at the Dalian University of Technology. For the ammonia spray study, WP2 in this project, I work closely with Tianjin University in China and Alto University in Fenland. They provide me with the optical experimental results for my model validation. This year, Prof. Hu Wang and I apply a China-Sweden mobility project. For the engine study, WP3 in this project, I worked closely with two world-leading marine engine companies (Wärtsilä and MAN Energy) work together to develop ammonia-fueled marine engines. Thanks to the ÅForsk for giving me this chance to build this collocation, which benefits Sweden to develop a zero greenhouse emission energy system by 2045.

3. Publication list

I have published two journal papers and two conference papers within this project. I attended the 1st Symposium on Ammonia Energy in Cardiff, United Kingdom, and gave an oral presentation at this conference. On January 23rd, 2023, I will give a presentation on the ammonia engine at the 12th Mediterranean combustion symposium. Besides, I am preparing another two papers in this project related to WP2

and WP3. Ammonia is a scorching topic worldwide and is a future fuel for marine and heavy-duty engines.
I am looking forward to getting further support from the ÅForsk to investigate the ammonia application deeply.

Journal papers

[1] **L Xu**, Y Chang, M Treacy, Y Zhou, M Jia, XS Bai. A skeletal chemical kinetic mechanism for ammonia/n-heptane combustion. Fuel 331 (2023): 125830.

[2]Y Zhang, **L Xu***, Y Zhu, S Xu, XS Bai. Numerical study on liquid ammonia direct injection spray characteristics under engine-relevant conditions. Applied Energy, Revised (*Corresponding author).

Conference papers

[3]**L Xu**, XS Bai. Numerical investigation of engine performance and emission characteristics of an ammonia engine under RCCI operating conditions. Accepted for oral presentation at the 12th Mediterranean Combustion Symposium.
[4]**L Xu**, Y Chang, M Treacy, XS Bai. Development of a skeletal chemical kinetic mechanism for the combustion of n-heptane/ammonia blends. 1st Symposium on Ammonia Energy, in Cardiff, United Kingdom.