Ammonia as carbon free fuel for internal CombusTion engIne driVen AgriculTural vEhicle

Work Package 5
Deliverable Report
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Topic: D5.5

DEMONSTRATION OF PERFORMANCE OF ALTERNATIVE LIQUID FUELS POSSIBLY USED IN THE FUTURE

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1   Introduction

This deliverable outlines the investigation conducted on alternative pilot fuels for the dual-fuel operation of ammonia engines. In previous stages of the ACTIVATE project, both biodiesel and diesel were employed as pilot fuels, offering the ACTIVATE team valuable insights into dual-fuel combustion. Past observations underscore the importance of precise temporal and spatial alignment between pilot and liquid ammonia injections. To achieve this, the ignition properties of the pilot fuel must resemble those of conventional diesel fuel, displaying high reactivity and efficient evaporation in the thermodynamic conditions of a compression ignition engine. Utilizing a fuel with low reactivity, characterized by a prolonged ignition delay time and extended flame lift-off length, is anticipated to complicate the optimization of the combustion process for ammonia dual-fuel operation. Consequently, this report entails an assessment of an alternative fuel in a controlled setting, comparing its performance with a reference diesel fuel. The study encompasses the measurement, analysis, and evaluation of combustion and emission characteristics, accompanied by a discussion on the feasibility of its application in dual-fuel combustion with ammonia.

1.1   HTL fuels

The fuel selected for evaluation is derived from hydrothermal liquefaction (HTL), a process that transforms a biobased waste feedstock into fuel. The carbon in this fuel is sourced from biological materials, rendering the combustion products carbon-neutral. The HTL production method utilizes water under sub-/supercritical conditions as a solvent, as detailed in [1]. This process breaks down hydrocarbons in the feedstock, yielding a high-energy-density crude oil with a high H/C ratio. This crude oil can be further refined downstream, with the production process also involving the removal of oxygen from the feedstock through dehydration and decarboxylation. Depending on the extent of upgrading, the resulting products can range from high-quality diesel to gasoline-type fuel, achieved through hydrotreatment or distillation.

A key advantage of HTL fuels lies in their versatility, as the feedstock can encompass various hydrocarbon-containing materials such as woody residue, solid municipal waste, or sewage sludge. Notably, the preparation of the feedstock before introduction to the HTL reactor does not necessitate drying, leading to significant energy savings in the production process. It is important to emphasize that water is an integral part of the HTL process and is essential for its success.

1.2   Objective

The objective of this work is to develop a kinetic mechanism for an HTL surrogate fuel and test the performance of the model by comparing numerical simulation results with experimental data retrieved in Report D5.5. The targeted contribution from ACTIVATE is a mechanism enabling researchers to investigate the chemical interaction of a novel biofuel with ammonia in a dual-fuel engine mode.

2   Numerical representation for HTL fuels

The above-presented results showed that HTL fuel performance was satisfactory when it comes to the ignition process yet, led to increased level of NO_x emissions. This can be attributed to

the presence of nitrogen component in the HTL fuel. The origin of NO_x emissions is fuel-bouned nitrogen, similar to the case of ammonia but at much lower extent. Additionally, tested HTL fuel blends were in limited quantities, therefore it is worth implementing numerical tools in order to assess the increase in the amount of HTL fuel and proportions with ammonia. For that purpose, an HTL fuel surrogate composition is needed and the relevant chemical kinetic mechanism capable of handling all the components.

2.1   HTL Surrogate

A linear least-squares fit method [2] was employed to replicate the elemental composition of each HTL distillate fraction with targets for C:H:O:N:S ratio, aromatic content, alcohol content, cyclic content and density. The ten distillate fractions were gathered into four groups: gasoline, jet fuel, light diesel and heavy diesel fuels types. Different surrogate species candidates have been considered to represent various functional groups such as alkanes (n-heptane, n-decane, dodecane, iso-octane), alcohols (ethanol, butanol, methanol), ethers (Methyl-tert-butylether (MTBE), Ethyl tertiary-butyl ether (ETBE), Dimethylether (DME) Methyl decanoate (MD)), cyclo-alcanes (cyclo-hexane), aromatics (alpha-methyl-napthalene, Tri-methyl-benzene, toluene) and nitrogen components (nitromethane, ammonia, pyride, pyrolle). Similar method has been adopted previosly by Hossain et al. [3]. However, the composed HTL fuel blends used in the present work consisted mainly of the heavy diesel fraction which in a major part consists of alkanes and the nitrogen component. Since n-heptane (C_7H_{16}) and n-decane ($C_{10}H_{22}$) are widely used surrogates for diesel-type fuels the main task remains to select proper nitrogen containing specie. Nitromethane (CH_3NO_2), although consisting of nitrogen, turned out to not have good overall nitrogen content, keeping other targets within the fuel composition at satisfactory levels, and was also problematic due to the presence of oxygen atoms. Ammonia (NH_3) is known to reduce NO and might lead to underestimation of NO, and also, its presence within the surrogate would be undistinguishable when ammonia is a primary fuel in a dual fuel mode as in the course of the present project. Therefore we have decided on testing pyridine (C_5H_5N) as a representative of nitrogen content in the diesel HTL fuels surrogate.

2.2   HTL Chemical Kinetic Mechanism

In order to make use of numerical models capable of handling detailed chemical kinetic to investigate in-depth pollutant emissions process, we decided to employ comprehensive chemical kinetics schemes. The chemical mechanism used in the present study is based on the detailed CRECK mechanism (Version 2003, March 2020) consisting of 413 species and 14922 reactions, including the majority of the components required for HTL fuel representation mentioned above. This opens a possibility to use this scheme in the future if different HTL distillate fractions are blended to compose another final fuel with different properties. Although this mechanism is well validated for multiple fuels it does not consist of pyridine, which had to be incorporated from a different scheme. Therefore, relevant 29 new species and 139 reactions were added from the mechanism of Wu et al. [4] to include the pyridine and other associated components and chemical pathways. The newly composed mechanism consists of 440 species and 15061 reactions.

The new mechanism has been validated with a focus on the proper representation of pyridine decomposition as well as HCN production, which can contribute to the NO_x formation process. The data from the two experiments in a flow reactor [5] and in the jest stirred reactor [4] have been

used for that purpose. LOGEresearch software well described in the WP3 of the ACTIVATE project has been used utilizing the Perfectly Stirred Reactor (PSR) simulations module. Experimental and numerical conditions for the two cases are presented in Table 2.1 and Table 2.2. The experimental data of Alzueta et al. [5] consists of data series from lean conditions ($\phi = 0.16$) to rich ($\phi = 2.5$) and a broad range of temperatures from 900 K to 1400 K, while the experiment of Wu et al. [4] consists of only rich conditions ($\phi = 2.5$) and lower temperatures (800 K to 100 K). The second column in the table contains reactor residence time, which in the case of Alzueta et al. [5] experiment is a function of temperature, while in the second experiment of Wu et al. [4], it was kept constant.

The data presented in Fig. 2.1 and Fig. 2.2 show the comparison of PSR simulations and experimental results for pyridine consumption and HCN formation. The pyridine profiles are very well predicted by the newly developed mechanism for both experiments and all four conditions. The shape of the HCN profile is also well captured. However, in the case of stoichiometric and rich conditions in Alzueta et al. [5] experiment, HCN stops to increase at lower temperatures and is underestimated beyond its peak. Otherwise, lean conditions are predicted well, and the rich conditions HCN profile in Wu et al. [4] provide a satisfactory agreement.

Table 2.1: Conditions for the PSR simulations of Alzueta experiment [5] in the flow reactor diluted in nitrogen at atmospheric pressure in the temperature range of 800-1500 K..

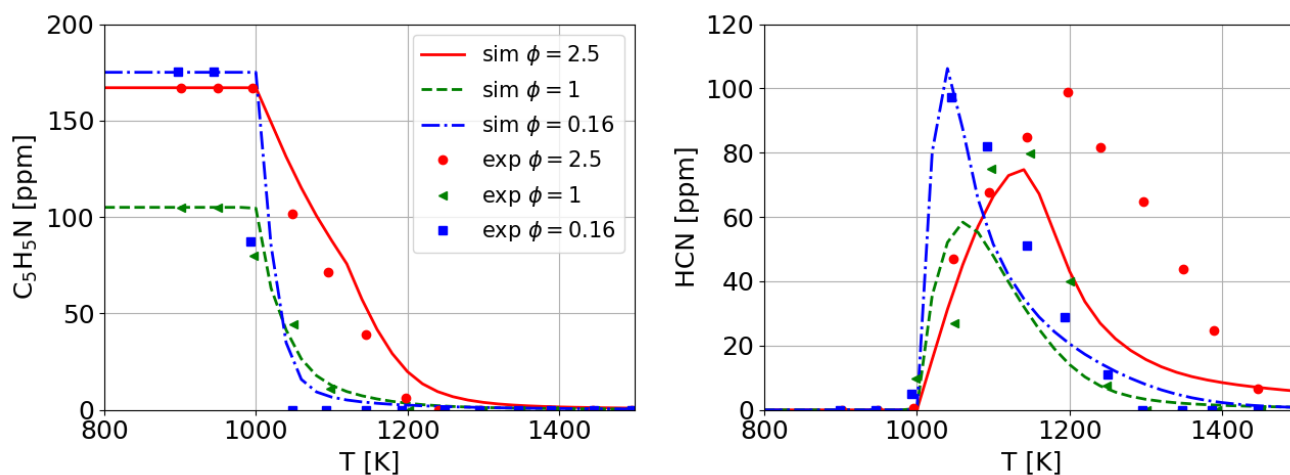| ϕ	τ [s]	C_5H_5N [ppm]	O_2 [ppm]
2.5	206/T[K]	167	906
1.0	200/T[K]	105	1 450
0.16	205/T[K]	175	14 500

Figure 2.1: Comparison of pyridine consuption and HCN formation in a flow reactor experiment [5] for three equivalence ratios 0.16, 1.0 and 2.5 with the composed chemical kinetic mechanism.

Table 2.2: Conditions for the PSR simulations of Wu experiment [4] in the jest stirred reactor diluted in argone at atmospheric pressure in the temperature range of 700-1000 K.

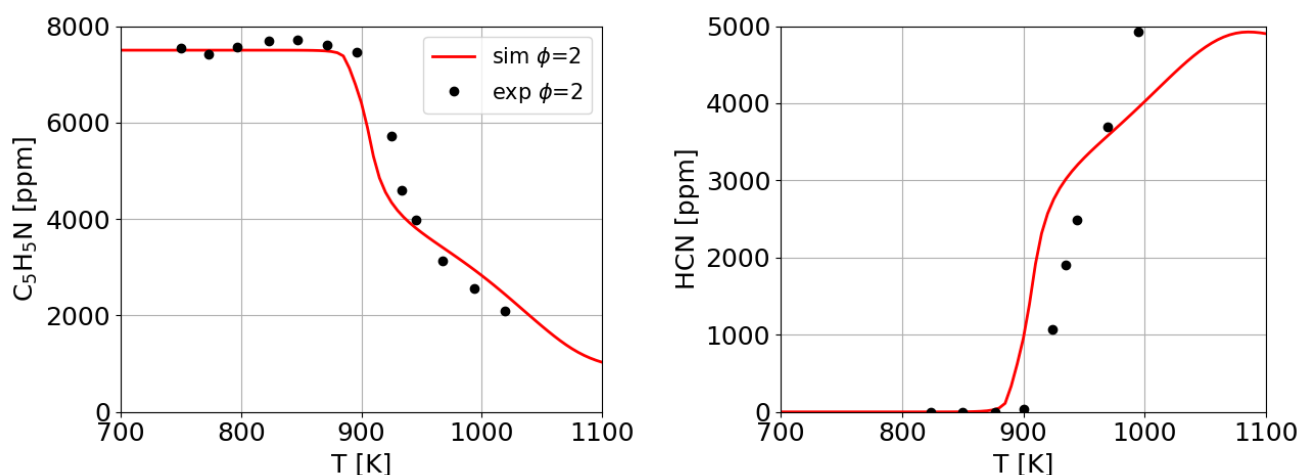| ϕ	τ [s]	C_5H_5N [ppm]	O_2 [ppm]
2.0	2	7 500	25 300

Figure 2.2: Comparison of pyridine consumption and HCN formation in a jet stirred reactor experiment [4] for the equivalence ratio of 2.0 with the composed chemical kinetic mechanism.

2.3 Stochastic Reactor Model simulations

The performance of the presented above HTL fuel surrogate and the chemical kinetic mechanism is now assessed using the Stochastic Reactor Model simulation. This numerical tool has been extensively described in WP3 of the ACTIVATE project and respective reports. Here it has been employed to demonstrate the effect of an increased fraction of HTL in the pilot fuel blend to 60%, 80% and 100% of the renewable fuel on the NO_x emissions, which have not been measured experimentally. In the future, this method can be applied to dual fuel mode to assess the interference of the alternative pilot fuel containing nitrogen, thus producing HCN, with the ammonia combustion chemistry.

In the first stage, the model was calibrated against the experimental data using pure reference diesel with dodecane as its surrogate. Initial thermodynamic conditions were adjusted to match the compression phase and further parametric mixing time scale profile has been determined. The characteristic mixing time scale is required as an input parameter to provide the measure of mixing or turbulence intensity. Its evaluation is challenging in the 0D space but recognizing the temporal variability and dependency on engine geometry and speed in turbulence levels, simplified approaches can be devised to characterize it for DI strategies [6]. For that purpose, the three-parameter mixing model by Pasternak et al. [7] has been applied by adjusting the parameters to match the pressure trace. Next, with the same setup fuel composition was changed by including HTL fuel represented by n-decane and pyridine with the proportions given in Table 2.3. Figure 2.3 shows the comparison of numerical and experimental pressure trace together with heat release rate for the RD and HTDM40 cases. Figure 2.4 shows NO_x emissions for the experimentally measured cases compared to the

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numerical values obtained with SRM simulations with additional numerical results for cases with increased amounts of HTL fuel. There is a trend of increasing NO_x emissions with increased amounts of renewable fuel. The shift from pure reference diesel to pure HTL fuel results in the increase of NO_x by around 80 ppm, which is quite large compared. With different injection strategies and in conjunction with dual fuel modes with ammonia this effect can vanish or become less important if we account for a substantial increase of NO_x due to the ammonia combustion. Nevertheless, more detailed investigations into that matter are needed to be taken in the future.

Table 2.3: Composition of surrogate formulation for diesel and HTL fuel in mass fractions.

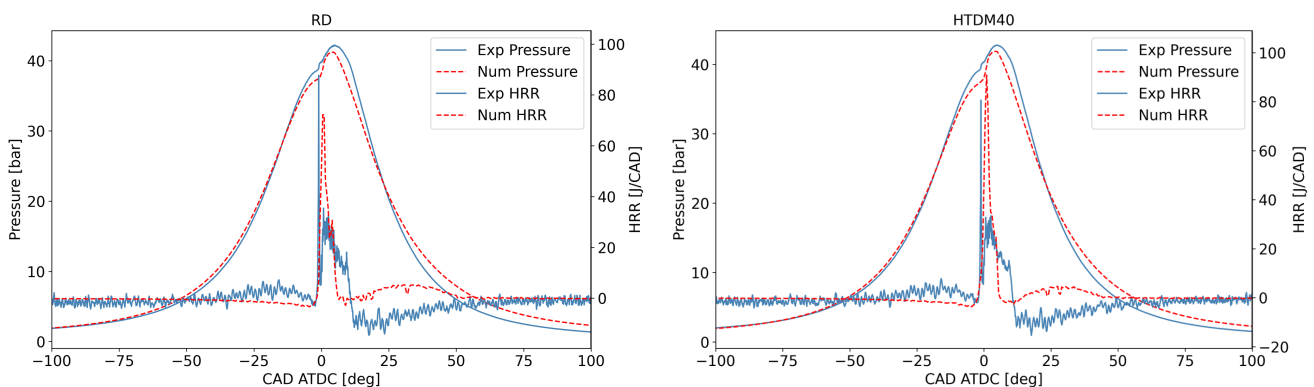| Fuels	N-Dodecane	N-Decane	Pyridine
RD	1	-	-
HTDM5	0.95	0.045	0.005
HTDM10	0.90	0.09	0.01
HTDM40	0.6	0.36	0.04
HTDM60	0.4	0.54	0.06
HTDM80	0.2	0.72	0.08
HTDM100	-	0.9	0.1

Figure 2.3: Comparison of experimental and numerical pressure traces and heat release rate for the case fuelled with the reference diesel and the blend with 40% HTL fuel.
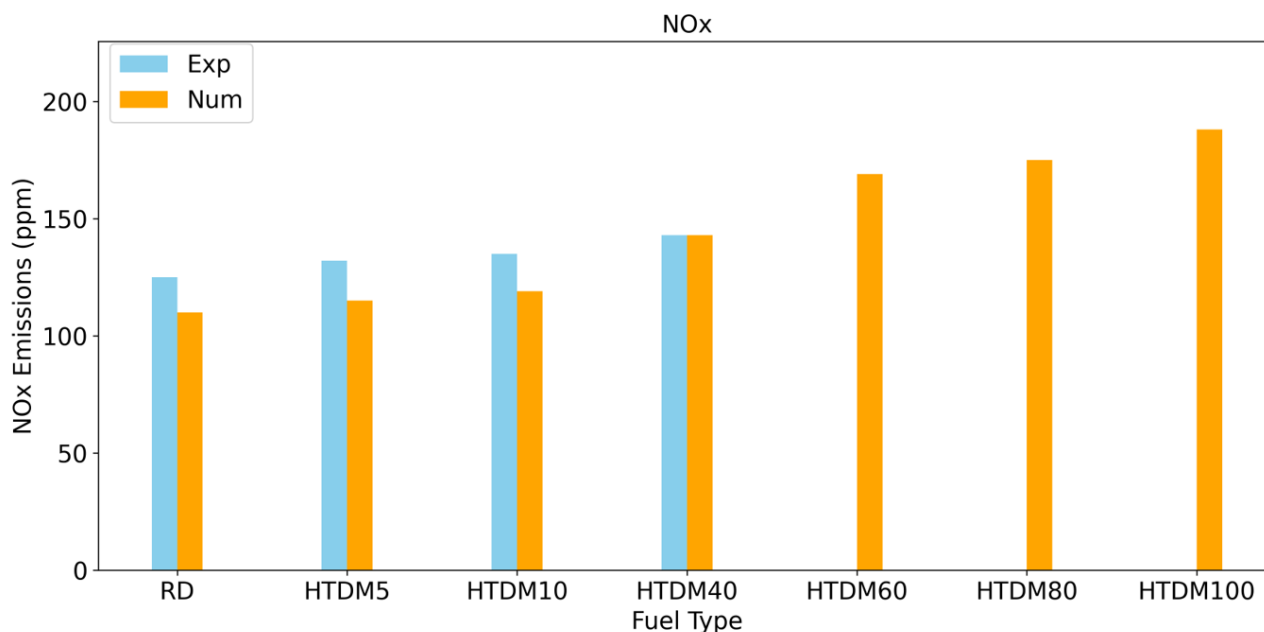
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Figure 2.4: Emissions of NO_x obtained experimentally for cases with up to 40% HTL (blue, left-side bars) and a complete spectrum of blends obtained numerically (yellow, right-side bars).

3   Discussion of the influence of HTL fuel as pilot fuel

As shown in the experimental (in Report D5.2) and numerical results presented in this report, HTL fuel is suitable as a substitute for diesel fuel in compression ignition engines. Blend ratios up to 40 w% show similar combustion and emission characteristics as with diesel fuel. In particular, the ignition delay times and flame lift-off length are similar to diesel fuel, which is considered positive with regard to ammonia dual fuel operation. Diesel fuel and biodiesel have previously been shown to work well as pilot fuel for high-pressure ammonia dual-fuel engine mode. The substitution of HTL fuel is therefore considered technically sound in terms of stable operation. In terms of emissions, especially for the BCDM HTL fuel, there might be some interaction between fuel-bound nitrogen compounds with ammonia, affecting the chemical reactions during combustion. These could, for instance, affect the pathways leading to N2O formation and consumption, potentially altering the N2O emissions. N2O is a very important emission from ammonia-fired engines due to its very high global warming potential, and this effect must therefore be researched further. With a surrogate fuel developed for the HTL fuel, chemical kinetic calculations could reveal the impact of fuel-bound nitrogen on the formation/consumption of N2O in the engine. However, this is outside the scope of this work. Additionally, when using HTL fuels as pilot, the ammonia dual-fuel operation is considered carbon-neutral if considering that the production process of the HTL is carbon-free.

4   Conclusions

This report presents the findings achieved numerical work on HTL fuel as a potential pilot fuel for ammonia dual-fuel engines. A surrogate fuel was developed and validated enabling future work

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to study the chemical interaction between a nitrogen-containing biofuel and ammonia, which would be important to understand. The This work is ongoing in the NTNU team.

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