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## 2<sup>nd</sup> Symposium on Ammonia Energy

# Effect of hydrogen and ammonia combustions on the ageing of the lubricant

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### Topics: Combustion Applications

### Introduction

With 8,24 GtCO<sub>2</sub> emitted in 2019 (pre-COVID), the transport sector is responsible for around 25% of total CO<sub>2</sub> emissions worldwide [1] and more than 31% in France (2021) [2]. Moreover, this sector contributes to NO<sub>x</sub> and particles emissions which are harmful both for the environment and human health [2]. In this context, research on electrification and alternative fuels rallies scientists and industries. While batteries and electrical engines seem a promising solution for individual vehicles, thermal engines with carbon-free fuels seem to be better suited for certain applications, such as trucks, trains, or ships [3]. As a versatile energy carrier and carbon free fuel, hydrogen is considered one key element for decarbonization, but it faces important challenges, such as storage and transportation [3]. Ammonia, another form of the hydrogen, is more and more considered as an efficient hydrogen carrier [4]. Hydrogen and ammonia can be directly used as fuel but with several differences compared to conventional hydrocarbon fuels [4]. To be efficient, existing thermal engines must be adapted to these new fuels. While an increasing number of studies focus on the optimisation of engine design [5–7], some compatibilities must be assessed for these molecules with a particular reactivity, as with the lubricant.

In thermal engines, lubrication is a key challenge to ensure moderate fuel consumption, high energetic yield, and engine durability. The lifetime of lubricants is usually determined by their consumption rate, and resistance to oxidation. Oxidation engenders impurities, degradation of the lubricants' integrity and modification of their friction reducing ability [8]. These new alternative fuels impose new constraints, the effect of which regarding lubricants' integrity and properties must be studied to guarantee proper functioning and reasonable drain intervals. The effect of ammonia, hydrogen and their blends on lubricants in thermal engines is a relatively new topic in the literature [9–11]. Yet, lubricants degradation processes have been studied in other contexts, with hydrocarbon fuels [8,12], or in compressors using ammonia as a refrigerant for example [10]. This work presents a synthesis of phenomena observed in the literature which could take part in the ageing of lubricants in ammonia and/or hydrogen engines, with a special focus on ammonia. The methodology chosen to perform lubricant study is described here.

### Results and Discussions

As previously shown in [5], high NO<sub>x</sub> levels and unburned ammonia can be emitted at the exhaust, in addition to the important water presence. Hence, lubricants are likely to be in contact with these fluids on the cylinder walls or in the crankcase due to blow-by mechanism. These are all elements which can be expected to degrade the lubricant [9,13–15].

Indeed, similarly to oxygen causing oxidation, NO<sub>x</sub> can solubilize in oils and react with hydrocarbon generating radicals [13]. This is called nitro-oxidation process and leads to functionalization of hydrocarbon chains with ester nitrate ends (RONO<sub>2</sub>) [16]. The overall effect on the viscosity of the lubricant depends on the operating conditions which can product opposite tendencies as in [16] and [17]. This can result in sludge and

deposits. Even though this phenomenon is well-known from lubricants manufacturers, it is yet not fully understood and deserves to be further studied as NO<sub>x</sub> emissions could be high in ammonia and hydrogen engines.

Nitro-oxidation could be reduced by choosing conditions where NO<sub>x</sub> emissions are the lowest. Unfortunately, several studies show that limiting NO<sub>x</sub> and unburned ammonia levels at the exhaust is a trade-off [5,18]. The interaction between oil and ammonia was mainly studied in the context of ammonia compressors in refrigeration systems [19]. It appears that ammonia, as a polar molecule, can be solubilized in oils according to their polarity, causing a viscosity decrease [19]. Furthermore, dissolved ammonia could react, as a base, with acidic compounds in the oil - acidic functions of the base oil itself, acidic additives, or oxidation products - and form sludge and deposits, as it was reported by manufacturers [10,14]. The potential reactivity between engine oil and ammonia must now be studied under typical conditions of an internal combustion engine.

Finally, water produced during the combustion can travel to the crankcase and condensate on cold surfaces. Emulsification issues were reported in the first prototypes, but the consequences on the lubricant's integrity and friction properties remain unclear [20]. In the marine sector, water contamination is a well-known topic. It can be very damaging for the lubricant and the engine, promoting oxidation and corrosion, bacterial growth, and cavitation [21]. If water droplets are drawn into the oil circulation flow, it can destabilize the oil film and decrease the friction reduction ability of the lubricant [21]. Like ammonia, water uptake seems to depend on the polarity of the base oil and its additives [22].

All these elements are likely to affect the lubricants' properties, reducing their lifetime. In addition, as lubricants are partially burned and contribute to particles emissions [23], changes in their properties could have an impact on pollutant emissions which is a key point for the development of new engines.

## Material and Methods

To study these effects, several types of oils usually used in engine lubricants were selected, base oils only without any additive. The test matrix is composed of mineral oils, polyalphaolefins, alkylbenzenes and complex polyesters, obtained directly from suppliers. Conventional degradation mechanisms are currently being studied using two complementary techniques: in-situ oxidation in a headspace sampler associated to gas chromatography (Agilent 7890B), and Rancimat test (Metrohm 893). GC-headspace principle and results are presented in Fig.1. 0,5mL of oil are heated in a sealed vial. In-situ oxidation occurs, with oxygen from the air contained in the vial, leading to light products which are vaporized in the gas phase. 1mL of this gas phase is collected after different heating times and transferred to a HP-5 column which elutes oxidation products according to their molecular weight.

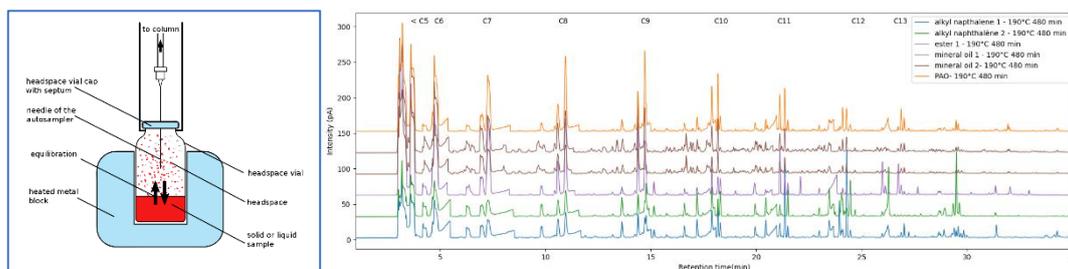


Figure 1. Scheme the headspace sampler (copyright Andi Schmitt) and chromatograms obtained for different oils after 8h heated at 190°C.

Rancimat method consists in heating 3g of oil in a glass tube, with air bubbling at a specified flow. After a stability time, volatile oxidation products are formed and entrained to a beaker containing 50 mL of Milli-Q water. Acidic products solubilize in water as ions, increasing the conductivity of the water. Stability time is measured by the inflexion point of the conductivity curve (Fig. 2).

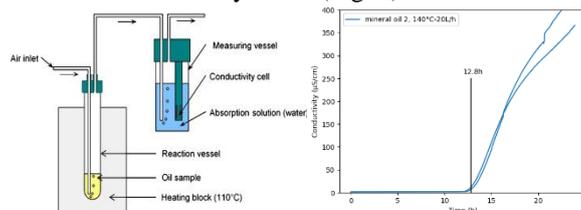


Figure 2. Scheme of the Rancimat method and evolution of the conductivity for sample mineral oil 2 at 140°C-20L/h

## Conclusions

Several distinctive characteristics of ammonia and hydrogen could be associated to different degradation mechanisms according to the current knowledge on lubricants, as important production of water during the combustion, high levels of nitrogen oxides and residues of unburned gas. This first step of this study shows the methodology chosen to evaluate the impact of these new fuels on lubricant aging.

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