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**EXPERIMENTAL STUDY OF THE IMPACT OF BIOALCOHOL STRUCTURE ON
THE OXIDATION STABILITY OF A SURROGATE JET-FUEL**

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ABSTRACT

The addition of biofuel in jet fuels can be seen as a promising answer to reduce the carbon footprint of the aviation transport sector. In this work, we investigated the impact of the addition of alcohol on the oxidation stability of a jet fuel surrogate. Different chemical structures of bioalcohols were considered and blended with *n*-decane used as the jet-fuel surrogate. The thermal oxidation stability of the mixtures was measured in a standard PetroOxy apparatus, which gives an induction period (IP). In addition to this global indicator of the fuel thermal stability, we quantified the total hydroperoxide concentration at the end of the test by iodometric titration. The influence of the length of the carbon chain in alcohols (*n*-butanol to *n*-decanol) and the isomeric structure of butanol on the IPs of pure *n*-decane have been quantified. We show that the addition of a low percentage by volume of alcohols in the fuel increases its oxidation stability. This effect is non-linear, and the IP value increases with the volume percentage of alcohol in the fuel up to 15%. Beyond this value, a rapid decrease in the stability of the mixture is observed. The influence of the length of the carbon chain is shown to be negligible. In contrast, the structure of butanol isomers strongly impacts the stabilization efficiency of the alcohol in the fuel. Conclusions on the fundamental chemical mechanism are drawn from these experiments and highlight the central role of aldehyde formation in alcohol oxidation kinetics.

KEYWORDS: autoxidation, bioalcohols, jet fuel

INTRODUCTION

New environmental regulations for the reduction of the carbon footprint of the transportation sector encourage the use of biofuels in this sector and especially in the aviation field since aircraft propulsion systems are known to be almost impossible to electrify.^{1,2} However, blending oxygenated biofuels with a jet fuel is difficult since in aircrafts, the fuel is also used as a thermal sink and is submitted to high temperatures. Therefore, thermal and oxidation stability of jet fuels are crucial parameters.³⁻⁵ The present paper focuses on the oxidation stability of a conventional fuel surrogate, *n*-decane, which has been selected as a surrogate to represent a real jet fuels. It is well established that *n*-decane is among the major components of petroleum-derived fuels (jet fuels) and it has been shown that this hydrocarbon suitably represents the reactivity of jet fuels.⁶⁻⁹ The first part of this study is dedicated to the oxidation of *n*-decane and to the impact on its stability of the addition of different types of oxygenated biofuels, at different proportions (0.2 – 20 %). The measurement of the induction period (IP) as a function of additive percentage will quantify the oxidation stability of these blends. IP is defined as the time necessary to observe a 10 % pressure decrease from the maximum pressure recorded in the PetroOxy during the auto-oxidation of a fuel.³ Several molecules of the next-generation biofuel additives (bioalcohol) have been studied at a temperature of 413 K and oxygen pressure of 700 kPa. Several parameters in the bioalcohol chemical structures such as the size of the chain (C₄, C₆, C₈, C₁₀) in linear alcohols, position of the –OH group (butan-1-ol, butan-2-ol), and level of branching in the hydrocarbon chain (*n*-butanol, iso-butanol, tert-butanol) were studied.

EXPERIMENTAL SECTION

Oxidation stability of fuel blends was tested in a PetroOxy from Anton Paar, one of the references of the Rapid Small Scale Oxidation Test of the ASTM 7545 methods. This method involves the introduction of a small amount, 5ml, of liquid fuel in a gold-plated cell, which is pressurized with pure O₂ under 7 bar at room temperature. The fuel blends inside the cell are then heated to the test temperature (413 K in this case) and the evolution of the pressure is recorded as a function of time at a constant temperature. The induction period (IP), which corresponds to the time required to reach a 10 % pressure decrease (O₂ consumption in the liquid fuel) is measured and characterizes the oxidation stability of the fuel. Figure 1 represents the IP result obtained for a pure *n*-decane sample tested at 413 K.

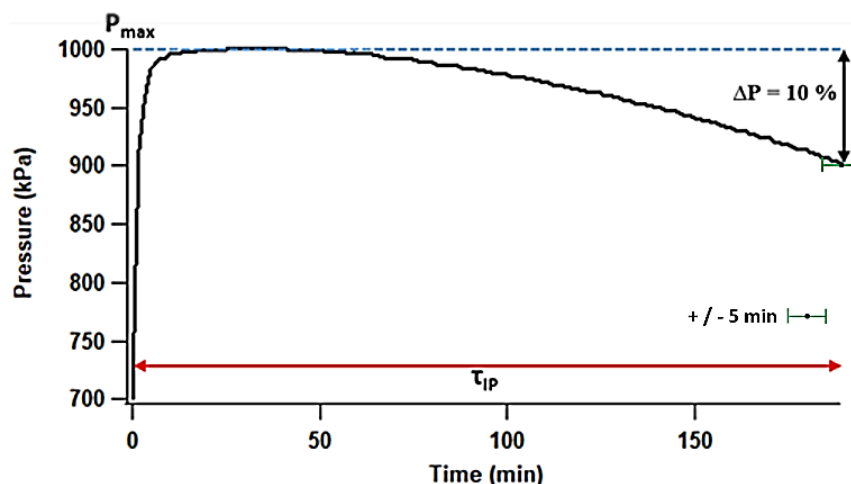


Figure 1: Typical induction period measurement with the PetroOxy device for *n*-decane at 413 K and 700 kPa of molecular oxygen

The PetroOxy measurements present a high reproducibility. The absolute average deviation of results, measured on fuel samples at the same temperature and pressure, can be expressed as a function of the relative standard uncertainty of IP determined which is $\pm 2.5\%$ IP in this case. For each test, the volume of the sample is the the same and equal to 5 mL. The joint (viton) of the cell was changed between each test.

Reactants

n-Decane ($\geq 99\%$), 1-butanol (99.8 %), 1-decanol ($\geq 99\%$), tert-butanol ($\geq 99.5\%$), 2-butanol (99.5 %) and isobutanol (99.5 %) were all anhydrous and purchased from Sigma Aldrich. 1-hexanol (99 %) comes from Alfa Aesar and 1-octanol (99 %) was provided by Fisher Scientific.

RESULTS AND DISCUSSION

Influence of the length of alcohol's carbonated chains

The impact of the various alcohols was studied on the auto-oxidation of *n*-decane. Pure alcohols were studied first in the PetroOxy to compare their behavior and results are given in Figure 2.

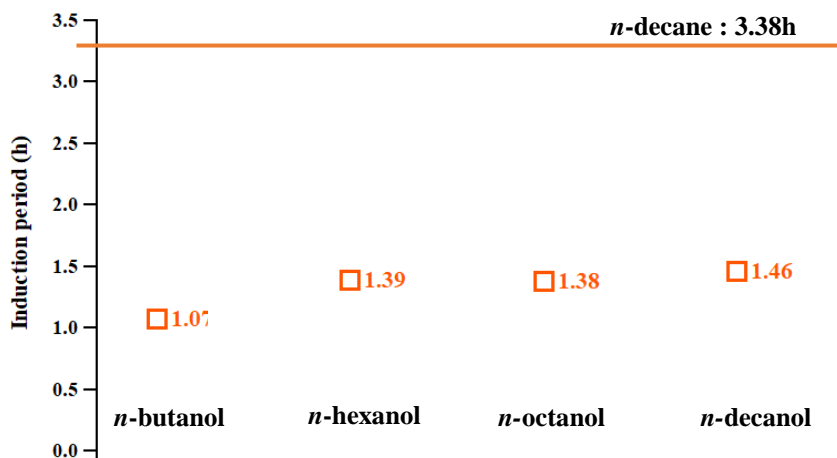


Figure 2: Influence of length of carbonated chain of primary alcohols, 140 °C / 7 bar

The length of the carbon chain of the alcohols is shown to lightly increase the induction period but the IP of each alcohol is much shorter than that of the neat surrogate fuel. As a first guess, one can predict that the blending of *n*-decane with the alcohols should then decrease its oxidation stability.

The evolution of the measured IPs of all these linear alcohols (*n*-butanol, 1-hexanol, 1-octanol, 1-decanol) blended with *n*-decane (5% alcohol / 95% *n*-decane), as a function of their size is presented in Figure 3

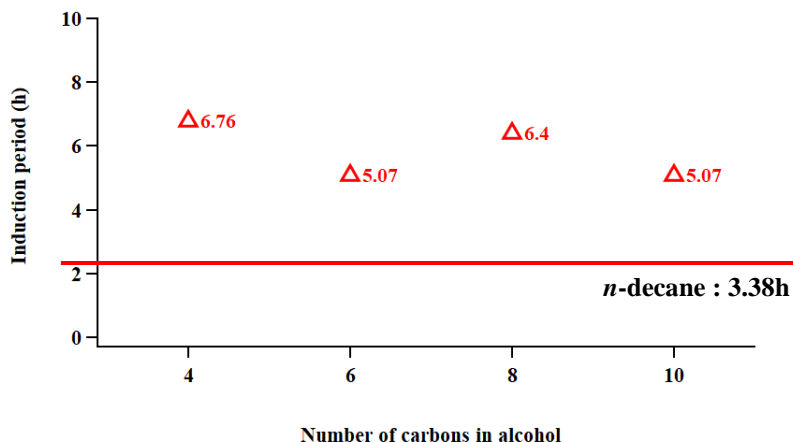
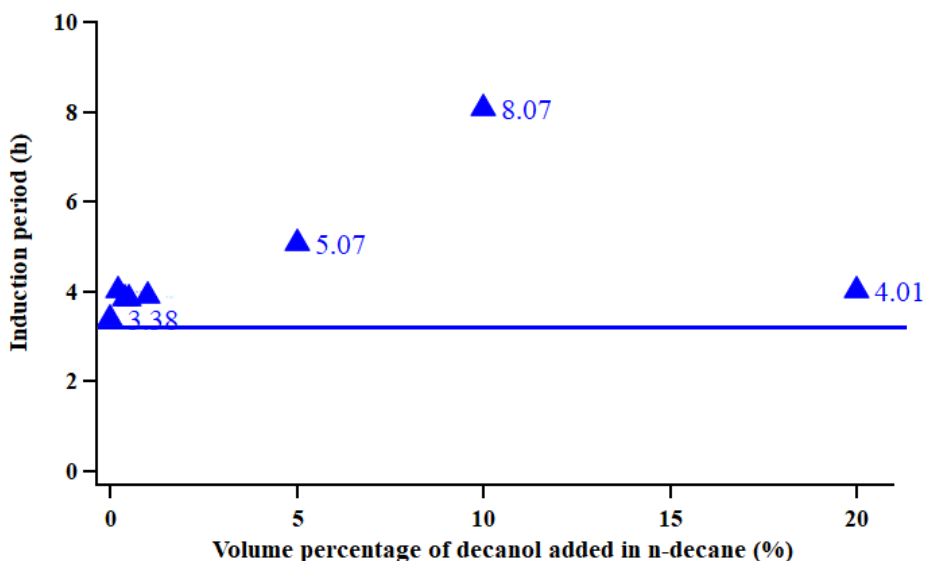


Figure 3: IP for 5% volume of alcohol added to *n*-decane 140 °C / 7 bar

The addition of alcohols is shown to strongly increase the stability of the jet fuel surrogate, for all alcohols. However, the evolution of the IP with the length of the carbonated chain show that this parameter has a little impact on the oxidation stability. The results observed for all the linear alcohols studied in this work highlight the importance and efficiency of these alcohols as additives with *n*-decane to improve the oxidation stability of the fuel surrogate. In the following section, we explore the effect of the proportion of linear alcohol on the IP of *n*-decane, using *n*-decanol.

Influence of the quantity of *n*-decanol in the blend

IP variation of blended *n*-decane was measured with different proportions of *n*-decanol. Results given in **Erreur ! Source du renvoi introuvable.** show important variations in the IP of *n*-decane / *n*-decanol blends with the proportion of *n*-decanol. The upper plot in Figure 4 show % vol. of *n*-decanol between 0 and 20%, while the lower plot zooms in on a % vol. range from 0 to 1%. The IP increases from 3.38 h for pure *n*-decane to 8.07 h when 10 % *n*-decanol is added.



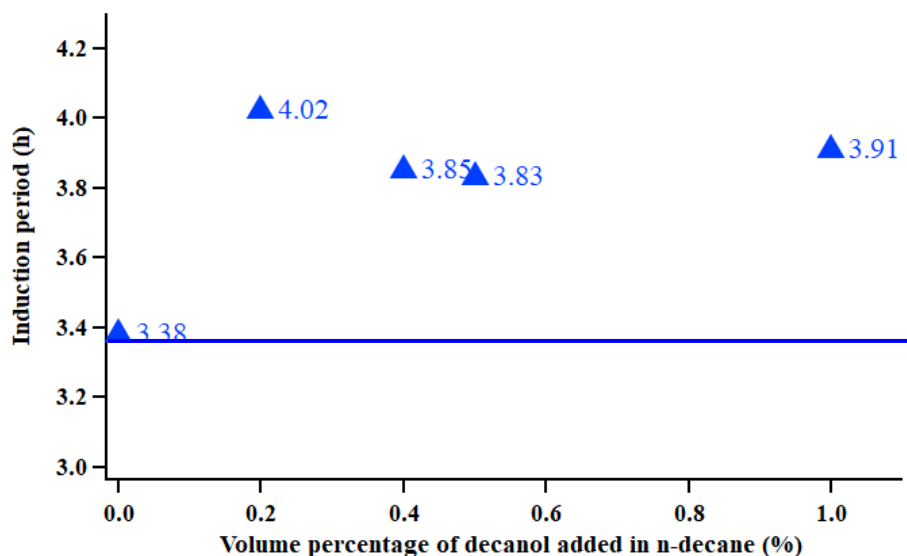


Figure 4: Effect of the addition of *n*-decanol on induction period of *n*-decane, 140 °C | 7 bar. Lower plot is for %vol. < 1

We show that the addition of a low percentage by volume of alcohols in the fuel increases its oxidation stability. This effect is non-linear and the IP value increases with the volume percentage of alcohol in the fuel up to 10%. Beyond this value, a decrease in the stability of the mixture is observed. This result is shown with other alcohols which have been blended. Indeed, above 10% added, the induction period and so the oxidation stability of the fuel decreases.

Stability of butanol's isomers

The previous paragraph showed that all alcohols have the same behavior regarding the oxidation stability, either pure or added to the *n*-decane fuel, independently of their sizes. Another structural parameter that can be explored is the influence of the branching and the position of the OH group in alcohols. Butanol isomers represent an adequate test set to probe these effects. The induction periods of pure butanol isomers are represented in Figure 5.

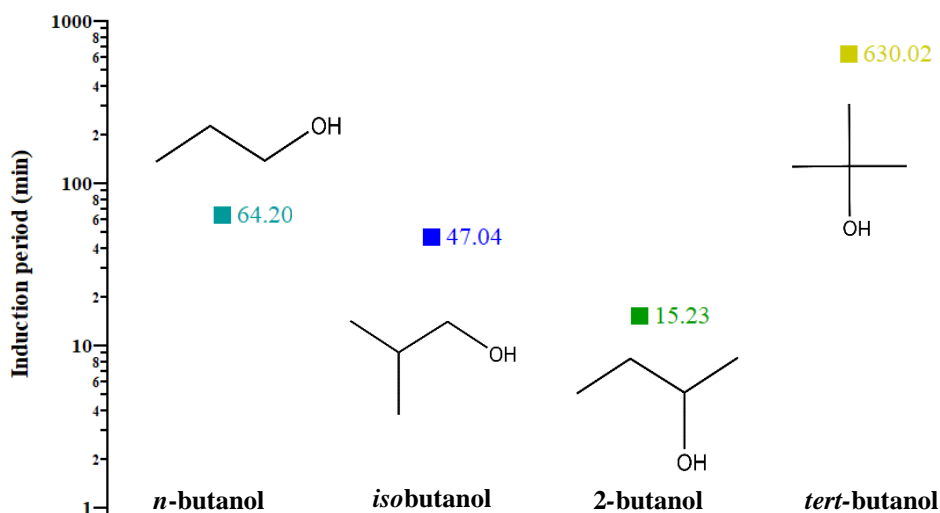


Figure 5: Induction periods of the isomers of butanol, 140 °C / 7 bar

The structure of butanol isomers strongly impacts the induction period the alcohol. *Tert*-butanol is shown to be the most stable butanol isomer, while 2-butanol is the least stable. The addition of butanol isomers in *n*-decane was also studied and the results are shown in Figure 6

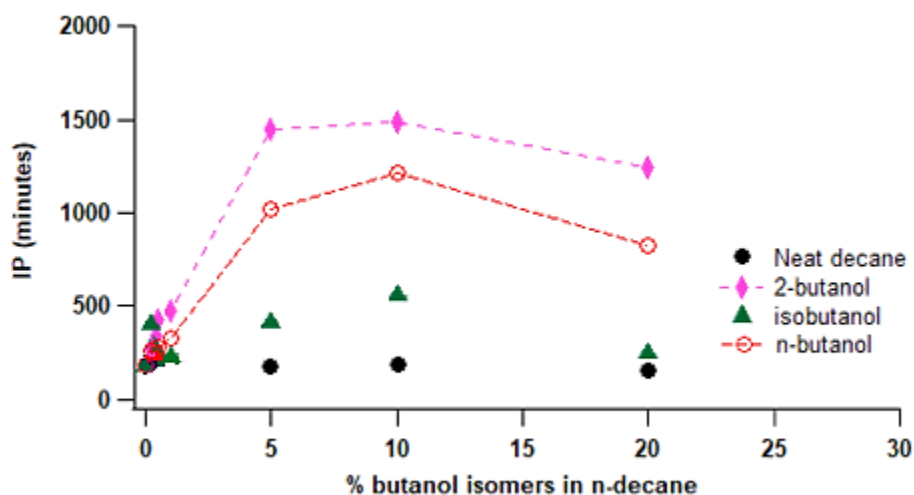


Figure 6: Induction periods of blends of *n*-decane and butanols as a function of the %vol. added in *n*-decane, 140 °C / 7 bar.

The addition of these butanol isomers to the fuel surrogate leads to a strong increase in oxidation stability, for all proportions added, except for *tert*-butanol. The largest impact is observed at 10% of butanol blended which is similar to 1-decanol results.

The increase in oxidation stability (higher IPs) non-linearly depends on the proportions of butanols blended with the fuel surrogate. The position of the alcohol group and the level of substitution of the alcohol (*n*-butanol isomers) are shown to affect the oxidation stability of the fuel surrogate, in a non-linear way.

CONCLUSIONS

The oxidation stability of a fuel surrogate, *n*-decane, doped with different alcohols has been investigated. The induction period of *n*-decane at 413 K and an initial pressure of pure oxygen of 700 kPa is 3.38 h. The IP of all pure alcohols (*n*-butanol to *n*-decanol, *i*- and 2-butanol) are shown to be lower than the IP of *n*-decane, by at least a factor of 2. Pure alcohols are therefore less stable than *n*-decane regarding oxidation stability. However, when added to *n*-decane, alcohol fuels are demonstrated to strongly enhance its oxidation stability with a maximum enhancement of stability at 10% volume percentage. Oxidation stability of the biofuel/fuel blends is impacted to different extents by the variations in the alcohol chemical structures. In linear alcohols (C₄, C₆, C₈, C₁₀), an increase of the chain length seems to have a little effect on the induction period. The position of the alcohol group and the level of substitution of the alcohol showed a greater impact in the oxidation stability of the fuel surrogate.

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