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# Antioxidant Effect of 2-4 Xylenol on Fuel Oxidation in Liquid and Gas Phase over a Wide Temperature Range

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## Abstract

The inhibiting effect on fuel ageing of 2,4-xylenol, a phenolic antioxidant that can be produced from biomass, was investigated experimentally in the liquid phase, while its impact on combustion was studied in the gas phase. The antioxidant effect of 2,4-xylenol in liquid phase has been examined in *n*-decane and in a surrogate, containing 65%vol. toluene and 35%vol. *n*-heptane. Experiments were performed in a PetroOxy at initial oxygen pressure 7 bar and temperature held at 180°C. The impact of 2,4-xylenol on the gas-phase reactivity of the surrogate fuel was investigated on ignition delay times and laminar flame velocities. Ignition delay times were measured in the rapid compression machine at 10 bar, from 675 to 1000 K at two equivalence ratios, 0.5 and 1. Laminar flame velocity measurements were conducted in a heat flux burner at atmospheric pressure and an initial temperature of 398 K. For all experiments considered in this work, the doping level of 2,4-xylenol was kept below 1%mol. Results are compared to effect of other usual additives, EHN and ferrocene. Results show that 2,4-xylenol exhibits a remarkable antioxidant effect in liquid phase, without affecting the main combustion characteristics of the fuel.

## 1. Introduction

The improvement of engine performance and the reduction of harmful or greenhouse-gases emissions, in particular through the implementation of new combustion modes, relies to a large extent on the optimization of the adequation between fuel and engine. Fuel reformulation remains a crucial issue for increasingly sophisticated and demanding energy systems, and in particular for the control of the reactivity of the gas mixture in the combustion chamber [1–3]. Before combustion in the engine, liquid fuels are stored in tankers and then spend some time in the vehicle tank, and the stability over time of the liquid fuel must therefore be guaranteed [4,5]. Fuels are however reactive in the liquid phase and subject to autooxidation and ageing. Liquid fuels can oxidize in the tank, fuel system, or injectors [6,7]. The autooxidation of fuels results in the formation of undesirable products and gums [8]. Gums form solid deposits and can reduce engine performance by affecting several mechanical components such as the pump, the injector filter system, etc. [6]. In addition, autooxidation products can affect the combustion. Deposits can cause pre-ignition in highly-boosted SI engine under low-speed and high-load operating conditions [9]. Furthermore, the increasing incorporation of oxygenated biofuels in commercial fuels can reduce the oxidative stability of liquid fuels [10,11].

Internal combustion engines require strict control of reactivity. A compression ignition (CI) engine requires easy auto-ignition, i.e. a reactive fuel at low temperatures [12], whereas a spark ignited (SI) engines requires low gas-phase reactivity to avoid knocking or pre-ignition [13]. This control of reactivity is achieved through the formulation of the fuel and the use of additives. Additives allow at a low concentration the control of a characteristic, e.g. stability improvers, octane/cetane boosters, corrosion inhibitors, anti-static, anti-foam, lubricity, deposit-control

additives, etc. Cetane and octane improvers increase or reduce the tendency to auto-ignition of diesel fuels and gasolines, respectively [14,15]. Antioxidants are added to limit liquid fuel and engine lubricant autooxidation [16]. Among the many classes of antioxidants, hindered phenols are commonly used and can be produced renewably from biomass [17,18]. These free radical scavengers allow to quench peroxy free radicals  $ROO\bullet$  responsible for the autoxidation reaction by reacting via a H-atom abstraction to yields less reactive phenoxy radicals. This step limits the reaction of  $ROO\bullet$  with the parent fuel and slows down the liquid-phase oxidation [19].

A common hindered phenol used as antioxidant is 2,6-di-tert-butyl-4-methylphenol (BHT) which has been shown to be very effective in fuels [20]. However, lighter molecules that can be produced in renewable ways are desirable. McCormick et al. [21] studied some phenolic antioxidants that can be produced from fast pyrolysis of lignocellulosic-biomass, possibly after an upgrade of the pyrolysis oils by hydroprocessing to reduce the oxygen content. Potential hindered phenol additives were 4-methylanisole, phenol, p-cresol, 2,4-xylenol, guaiacol, 4-methylguaiacol, and 4-propylguaiacol. 2,4-Xylenol was found to be the most effective antioxidant in the liquid phase when added to petroleum base diesel fuels by dramatically increasing the induction time measured by the ASTM D7545 method. In addition, this compound, which has a RON of 140 and a MON of 113, slightly improved the RON of a base gasoline from 85.8 to 89 at a doping level of 2% vol. The addition of a higher amount in a gasoline blendstock designed for blending with ethanol showed that 10% vol. of 2,4-xylenol led to MON and RON values close to that obtained with the addition of 25% vol. of ethanol (E25) [22]. An increase of the final distillation temperature and more particulate matter emission in engine were however observed due to the low volatility and high boiling point of 2,4-xylenol.

Liquid phase oxidation of organic molecules [23] and gas phase oxidation in the low temperature range [24] involve the same radical mechanisms. An additive in one phase could therefore modify the oxidation kinetics in the other as well. These synergetic effects have been little investigated. The development of new additives must take care of the effect of the additives in both phases: an antioxidant must not degrade combustion performance, while an octane or cetane booster must not promote the ageing of the liquid fuel. This study aims at experimentally investigate the effect of low levels of 2,4-xylenol as autoxidation inhibitor additive in the liquid phase and on the main combustion parameters in the gas phase. The autooxidation of doped fuels was studied in the liquid phase in a standard petroOxy device. To examine the effect low levels of 2,4-xylenol on combustion, auto-ignition delay times and laminar flame velocities were measured in a rapid compression machine (RCM) and in a heat flux burner (HFB) respectively.

## 2. Experimental methods

### 2.1. PetroOxy Oxidation Stability Tester

The oxidation stability measurements in liquid phase were performed in a PetroOxy from Anton Paar. This device is used as a reference instrument to test fuel oxidation stability in ASTM D7525 [25], ASTM D7545 [26]. It allows a fast oxidation test, which has shown to agree very well with other normalized test in Rancimat [27]. A detailed description of the petroOxy and of the experimental procedure can be accessed elsewhere [28]. The core part is a gold-plated test cell, whose volume is 25 ml and which be considered as a closed batch reactor. The test consists of the introduction of 5 ml of fuel into the cell, which is then pressurized with 7 bar of oxygen. The reactor is heated quickly, in about 3 minutes, from the ambient to the desired temperature, set

to 180 °C in this work and kept constant until the end of the test. The oxidation reaction then consumes slowly the oxygen. The pressure history in the reactor is recorded and the induction period (IP) is defined as the time corresponding to a 10% pressure decrease from the maximum pressure reached at the beginning of the test; the longer the PI, the more stable the fuel.

High purity reactants including *n*-decane ( $\geq 99\%$ ), *n*-heptane (99%), toluene (99.8 %), and 2,4-xylenol ( $\geq 98\%$ ) from Sigma-Aldrich were employed. The antioxidant effect of 2,4-xylenol was examined in two fuels: (1) *n*-decane considered as a diesel surrogate fuel, with a cetane number of 76 [29] and (2) a blend of toluene (65% vol.) and *n*-heptane (35% vol.) as a surrogate of a low RON gasoline (RON=84) [30]. These two types of fuel allow the study of the interaction of 2,4-xylenol with different chemical structures. The doping level of the additive was kept below 1% molar basis. Each PetroOxy experiment was repeated at least twice. The IP uncertainty is about  $\pm 4\%$ , which was characterized by conducting PetroOxy experiments on 12 samples of *n*-decane at 140°C and 7 bar of initial pressure of oxygen.

## 2.2. Rapid Compression Machine

The effect of the addition of 2,4-xylenol on the auto-ignition characteristics of the surrogate fuel was investigated in the Rapid Compression Machine (RCM) developed at the University of Orleans. The RCM allows to study the ignition at low and intermediate temperature regimes in engine relevant conditions [31]. This single-piston RCM involves a creviced piston, which permits to avoid the formation of vortex during the compression and maintains the homogeneity of the post-compression charge. Further details of the RCM of the University of Orleans can be accessed elsewhere [32]. Only a brief description of this machine is presented here. The intake pressure was measured by a Keller PAA-33X/80794 piezoresistive transducer.

The in-cylinder pressure history was recorded by an AVL QH32C piezoresistive transducer, which is protected from thermal shock by a silicone coating. The temperature in the preparation reservoir and the intake temperature of the combustion chamber and the piston were measured with K thermocouples. The gas mass flow rates were controlled by a Bronkhorst Cori-flow M13. The uncertainties of in-cylinder pressure, intake pressure, intake temperatures, and mass flow rate are  $\pm 1\%$ ,  $\pm 1$  mbar,  $\pm 2$  K and  $\pm 1\%$  respectively.

The piston is pneumatically driven and braked close to the top dead center by a hydraulic system. The total duration of the compression is about 33 ms. The pressure at top dead center ( $P_c$ ) rises from  $P_c/2$  to  $P_c$  within 3.5 ms ( $t_{50}$ ). The compression ratio is varied from 8.9 to 20.7 to achieve the desired experimental conditions. For this set of experiments in RCM, the pressure at top dead center was set to 10 bar. The temperatures at top dead center ( $T_c$ ) were investigated from 675 to 995 K. These experimental conditions were obtained by adjusting the intake pressure ( $227 \text{ mbar} < P_0 < 600 \text{ mbar}$ ) and the piston initial temperature ( $55 \text{ }^\circ\text{C} < T_0 < 120 \text{ }^\circ\text{C}$ ). The temperatures  $T_c$  are calculated by considering an isentropic compression as represented by Eq. (1), where  $\gamma$  is the ratio of specific heats of gas mixture:

$$\int_{T_0}^{T_c} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \left( \frac{P_c}{P_0} \right) \quad (1)$$

The main IDT is defined as the duration between the end of compression and the combustion Maximum Pressure Rise Rate (MPRR). The last value corresponds to the peak of  $dP/dt$  profile. In the case of two-stage ignitions, the 1st-stage IDT is measured as the time between the end of compression and the first distinguishable peak of  $dP/dt$ . The standard deviation of 1st-stage IDT and main IDT in this work are  $\pm 10\%$  and  $\pm 5\%$  respectively.



The impact of 2,4-xyleneol on the gas-phase oxidation of the toluene/*n*-heptane surrogate fuel was examined for two doping levels, 0.1 % and 1% mol. respectively.

### 2.3. Heat flux burner

Laminar burning velocity of fuels in air was measured in a heat flux burner (HFB) at Laboratoire Réaction et Génie des Procédés (LRGP) in Nancy, France. To measure the adiabatic burning velocity of a laminar flame stabilized on a burner, this type of setup compensates for thermal losses from the flame toward the burner surface by a convective heat flow from the burner surface to the flame front. The global heat exchange is thus zero and it can be proved that the velocity of gases corresponds to the adiabatic laminar burning velocity [33–35].

The burner is composed of a circular perforated plate at the top of the mixing chamber. The perforated plate, made of brass, has a diameter of 30 mm and a thickness of 2 mm. The diameter of each hole is 0.5 mm and the pitch between the holes is 0.7 mm as suggested by Van Maaren et al. [33]. Eight K-type thermocouples with a diameter of 0.5 mm are stuck in some holes on the surface of the plate. These thermocouples are positioned on the radial axis of the plate surface in the form of a diverging spiral. The temperature of the plate is kept about 50 K higher than that of the combustion chamber to compensate thermal losses of the flame.

The liquid fuel mixture is put in a stainless-steel tank pressurized by nitrogen. The mass flow rate of the liquid fuel is regulated by a Bronkhorst Coriflow meter. The liquid fuel is mixed to air and vaporized into the Evaporation and Mixing Control (EMC) system to form the reactive gas mixture. Temperature regulators are placed in the tubes connecting the flow meters with the burner to avoid condensation. Temperatures of the mixing chamber and burner plate are

controlled by thermostatic baths. A computer controls mass flow meters and track the temperature of thermocouples placed on the burner plate. The velocity of the adiabatic flame is determined by adjusting the gas flow to obtain a uniform temperature profile at any point on the burner plate. Thus, the velocity of adiabatic flame  $S_L$  (cm/s) is calculated by the Eq.2, where  $Q_v$  (cm<sup>3</sup>/s) corresponds to the volumetric flow of fresh gas and  $S$  (cm<sup>2</sup>) is the surface of the perforated plate of the burner

$$S_L = \frac{Q_v}{S} \quad (2)$$

The main uncertainty in the burning velocity is that of the mass flow measurements (around 0.5% for the liquid and the air mass flow controller, respectively), which can lead to a global uncertainty of 1% in the gas flow rate and thus in the burning velocity. The error in the temperature measurement can be estimated to induce an uncertainty of 0.4 cm s<sup>-1</sup> in the burning velocity. Flame distortions such as edge effects account for 0.2 cm s<sup>-1</sup>, and become more important for rich mixtures. The total uncertainty on the flame speed is thus of the order of 1 cm s<sup>-1</sup>. The uncertainty on the temperature of the fresh gas is around 3 K for the high temperature of 398 K used here. Concerning the determination of equivalence ratios, the main uncertainty is due to the error in the mass flow regulation, which leads to an uncertainty around 1%.

In this work, the effect of 2,4-xylenol on the laminar burning velocity of the gasoline surrogate fuel in air was examined. HFB experiments were conducted at atmospheric pressure. The temperature of the fresh gases was set to 398 K to insure the complete vaporization of the fuel

over a wide range of equivalence ratios. The additive was introduced into fuels at a level of 1% weight basis.

### 3. Results and Discussions

The effects of 2,4-xylenol in both gas and liquid phases are presented in this section. In the liquid phase, the relationship between the chemical structure of pure fuels and the antioxidant effect of the additive is discussed. In the gas phase, the effect of 2,4-xylenol on reactivity is compared with ones of ferrocene and 2-ethyl hexyl nitrate (EHN), which are conventional octane booster and cetane booster, respectively.

#### 3.1. Antioxidant effect of 2,4-xylenol in liquid fuels

Induction periods (IP) were measured in the PetroOxy with an initial oxygen pressure of 700 kPa and a vessel temperature at 180°C. Under the investigated conditions, the *n*-heptane/toluene gasoline surrogate is much less reactive than *n*-decane. The measured IP of the surrogate is about 255 min while the one of neat *n*-decane is about 15 min. Figure 1 presents the measured IP of fuels doped with 2,4-xylenol. The doping level of 2,4-xylenol in *n*-decane was set at 0.1 and 0.5 % mol. while the concentration of this additive in the gasoline surrogate was kept as low as 0.08 % mol to limit the duration of the experiment. Indeed, for very long durations, beyond 15 hours, the precision of the experiment deteriorates because of the leakage rate (about 3 kPa/hour) of the cell which becomes non-negligible on the decrease of the oxygen pressure. 2,4-Xylenol enhances the IP of both considered fuels. The antioxidant effect of this additive increases with its doping level as shown in figure 1.a. Besides, the antioxidant effect of 2,4-xylenol depends on the chemical structure of the fuel. Figure 2 presents the relative antioxidant

effect of 2,4-xylenol on *n*-decane and the gasoline surrogate. The inhibiting effect of the additive is remarkably higher for the pure *n*-decane than for the surrogate containing a large amount of aromatic at comparable doping levels.

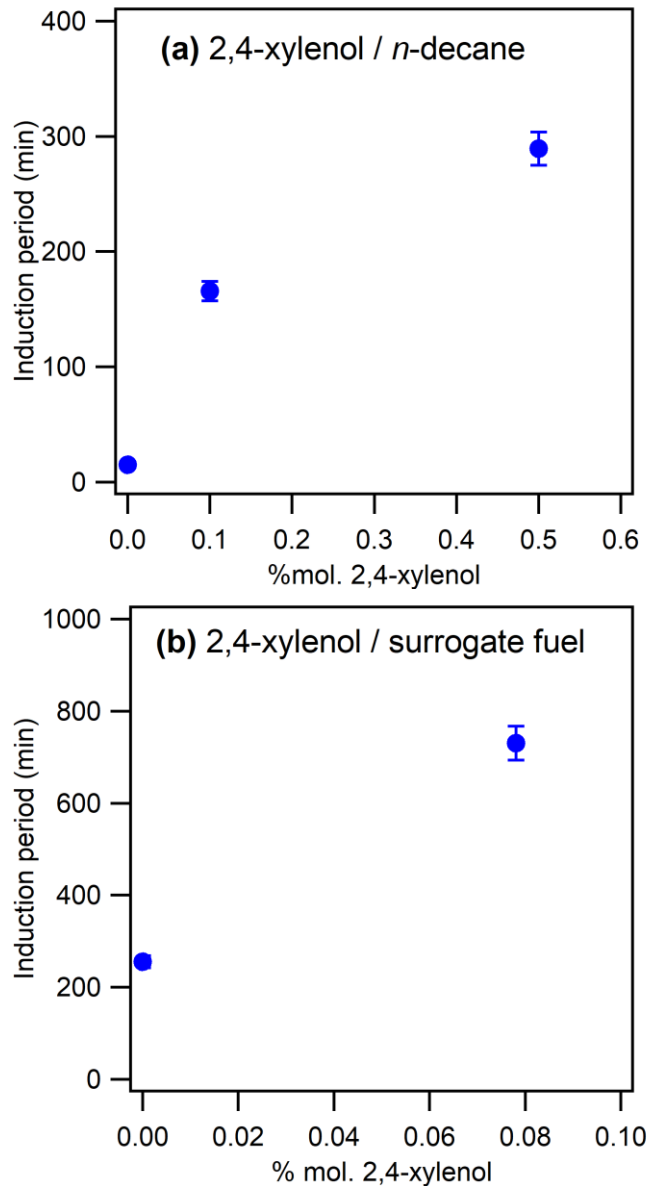


Figure 1. Effect of 2,4-xylenol on the measured induction period of *n*-decane and the *n*-heptane/toluene surrogate fuel at experimental conditions: initial oxygen pressure of 700 kPa, reactor temperature of 180 °C.

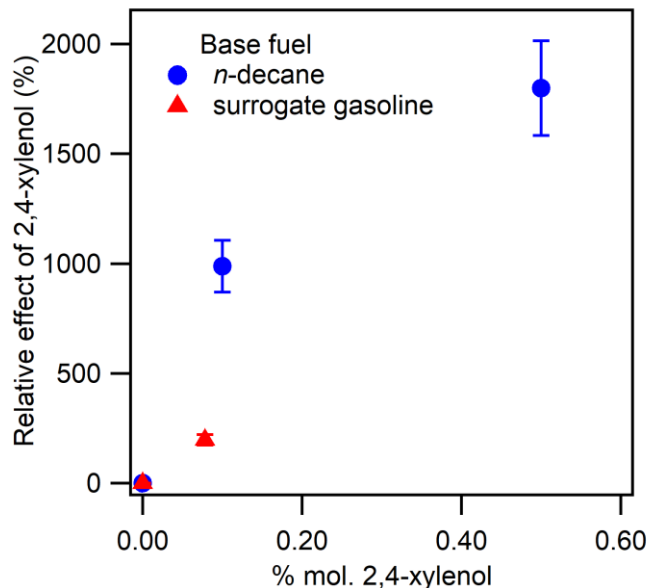


Figure 2. Relative antioxidant effect of 2,4-xyleneol on the measured induction period of *n*-decane (circles) and the gasoline surrogate (triangles) at the experimental conditions: initial oxygen pressure of 700 kPa, reactor temperature of 180 °C.

The chemical mechanism of fuel autooxidation in the liquid phase provides insight into inhibiting effect of 2,4-xyleneol. The oxidation of hydrocarbons in the liquid phase involves a mechanism of formation of hydroperoxides [36,37] and is summarized in figure 3. The main consumption channels of an alkane (RH) are H-atom abstractions by peroxy radical (ROO•) and alkoxy radical (RO•), all yielding the main alkyl radical R•. This latter radical reacts by addition on dissolved O<sub>2</sub> and produces the corresponding peroxy radical ROO•. One of the main reactions of peroxy radical ROO• yields the peroxide ROOH via H-atom abstractions from the reactant. The remaining consumption route of this radical involves the self-reactions (ROO• + ROO•) that produce an alcohol (ROH) and a ketone (or aldehyde) (R(C=O)) in a termination step by the Russell mechanism [38], or two alkoxy radical RO• and O<sub>2</sub>. Hydroperoxide ROOH entirely decomposes into an alkoxy radical RO• and a hydroxyl radical OH. This degenerate branching reaction is the most important reaction governing the liquid-phase reactivity of alkanes as it transforms a molecule into two reactive radicals. Alcohol ROH is produced by both self-

termination reactions of peroxide radical  $\text{ROO}\cdot$  and H-atom abstraction from the reactant  $\text{RH}$  by the alkoxy radical  $\text{RO}\cdot$ . This alcohol  $\text{ROH}$  is then oxidized into ketone (or aldehyde)  $\text{R}(\text{C}=\text{O})$  by some successive reactions, which follow the similar scheme as the alkanes.

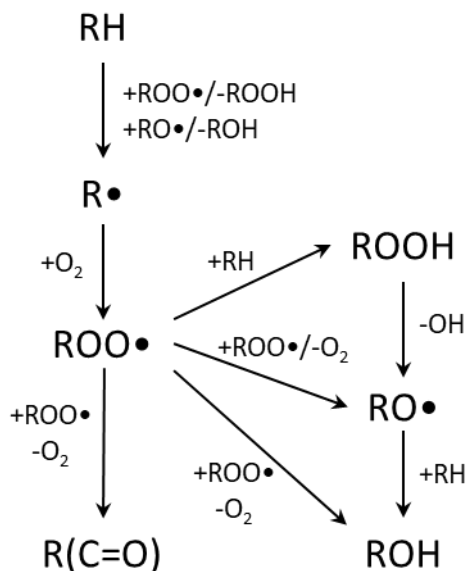


Figure 3. Simplified reaction pathway of an alkane  $\text{RH}$  in the liquid phase.  $\text{R}$  is an alkyl radical,  $\text{ROO}$  a peroxy radical,  $\text{RO}$  an alkoxy radical,  $\text{ROOH}$  a hydroperoxide,  $\text{ROH}$  an alcohol, and  $\text{R}(\text{C}=\text{O})$  an aldehyde or a ketone.

The central role of the peroxy radical  $\text{ROO}\cdot$  and the hydroperoxide  $\text{ROOH}$  in the autooxidation of liquids is shown in figure 3. In this work, it was experimentally observed that  $n$ -decane is much more reactive than the toluene/ $n$ -heptane blend in the considered condition. This is consistent with the decrease of the thermal stability of linear alkanes when the chain length increases [39], which makes  $n$ -heptane more stable than  $n$ -decane. Furthermore, toluene, the main component of the surrogate fuel, is much less reactive in liquid phase than  $n$ -decane, as experimentally observed [40]. This reduced reactivity is due to the greater stability of the resonance-stabilized benzyl radical, which reduces the rate of  $\text{O}_2$  addition, and leads to slower

abstractions of hydrogen atoms by the ROO• radicals produced compared to the corresponding alkylperoxy radicals [41].

The antioxidant effect of 2,4-xyleneol and other similar hindered phenols, for example the conventional antioxidant BHT (butylated hydroxytoluene), has been qualitatively described in the literature [42,43]. These compounds interrupt the chain propagation of the fuel auto-oxidation by reacting with peroxy radicals via H-atom abstraction reactions by the hydrogen atom of phenolic group. These reactions are favored as the radicals produced from hindered phenols are relatively stable thanks to the electron delocalization due to the resonance effect. These reactions are in competition with H-atom abstractions from parent fuel and then slows down the liquid-phase reactivity. 2,4-xyleneol is a phenolic compound with a low O-H bond dissociation energy (BDE). Figure 4 presents the BDE O-H and C-H bonds of the methyl groups, calculated theoretically at the CBS-QB3 level of theory. The low frequency vibration modes, corresponding to internal rotations, were treated as hindered rotors rather than harmonic oscillators, using the software THERMROT [44]. This in-house code performs a one-dimensional hindered rotor treatment (1D-HR) of internal rotations and avoids the coupling of torsional modes met in the frequency analysis. The torsional potentials were obtained from relaxed scans computed at the B3LYP/6-311G(2d,p) level of theory.

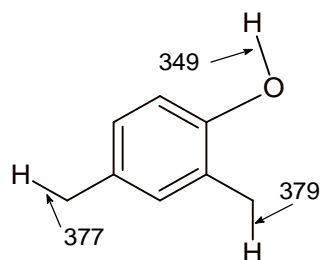


Figure 4. Bond dissociation energy of O-H and C-H bonds in methyl groups in 2,4-xylene calculated at the CBS-QB3 level of theory ( $\text{kJ mol}^{-1}$ ).

The weakest bond is the phenolic one with a BDE as low as  $349 \text{ kJ mol}^{-1}$ , compared to  $364 \text{ kJ mol}^{-1}$  in phenol calculated at the same level of theory. Note that this latter value agrees well with experimental value of BDE in phenol of  $362.8 \pm 2.9 \text{ kJ mol}^{-1}$  [45]. 2,4-Xylene acts then as a radical scavenger by reacting with chain carriers  $\text{ROO}\bullet$  radicals to produce a low reactivity resonance stabilized  $\text{RO}\bullet$  radical. This latter reacts mostly in terminations, which lead to non-radical and non-peroxide products [43].

It could be deduced that the antioxidant effect of 2,4-xylene depends on the concentration of peroxy radicals [ $\text{ROO}\bullet$ ]. The experimental results show that *n*-decane is more reactive than the toluene/*n*-heptane mixture, which induces a higher concentration of  $\text{ROO}\bullet$  radicals in the case of *n*-decane autoxidation than in the case of the toluene-based surrogate. The antioxidant effect of 2,4-xylene is thus proportionally higher for *n*-decane than for the alternative fuel, as it appears in figure 2.

### 3.2. Effect of 2,4-xylene in gas-phase combustion

If an anti-oxidant additive has to be effective in the liquid phase, it is desirable that its effect be as weak as possible in the gas phase so as not to degrade the combustion properties of the fuel. In order to check the effect of 2,4-xylene on the auto-ignition of the surrogate fuel at low and



intermediate temperatures, ignition delay times were recorded in the Rapid Compression Machine for neat and doped fuel in air. Results are presented in figure 5 for the pure toluene/*n*-heptane surrogate, and with addition of 0.1% and 1% of 2,4-xylenol. Experiments were performed for stoichiometric mixtures and in lean conditions at  $\phi=0.5$ . Note that each experimental point is the average of at least 3 shots, with an excellent repeatability. The average deviation is less than 0.4 ms, and the maximum absolute deviation is 1.8 ms for the longest delay times obtained at the lowest temperatures. A negative coefficient temperature (NTC) behavior, well known in the case of alkanes and especially *n*-heptane [46,47], can be observed between 750 K and 890 K in stoichiometric mixture. The NTC is weaker in lean conditions, between approximately 750 K and 810 K. The ignition delay times are up to a factor of 4 longer in the lean mixtures than at the stoichiometry. In both conditions, cool flames are observed at low temperatures ( $T_c < 750$  K), but disappear in the NTC area. In all cases, it appears that the addition of 2,4-xylenol has no kinetic effect on the auto-ignition characteristic of the surrogate fuel. The behavior of the doped mixtures is identical to that of pure fuel, both for cool flame ignition and for main auto-ignition delay times, and for both equivalence ratios.

For comparison, Figure 6 compares the effect of 2,4-xylenol to that of usual additives: EHN and ferrocene, which are respectively conventional cetane booster and octane boosters. The chemical effect of these additives, used to control the gas-phase reactivity during fuel combustion, has been thoroughly analyzed and modelled in previous studies [14,15]. In the experimental conditions  $P_c=10$  bar and  $\Phi = 1$ , EHN strongly promotes the reactivity over the whole range of temperature studied. The addition of 0.1% of EHN induces a strong reduction of delay times of cool flames and main ignitions of the fuel. The temperature range of the NTC is

reduced, as well as the magnitude of the decrease of the reactivity in this temperature domain. Ferrocene, which is an octane booster inhibiting the low temperature oxidation chemistry [15], has almost no effect on the cool-flame delay time of the fuel, but inhibits dramatically the second-stage ignition with an increasing effect with temperature. In contrast to EHN, ferrocene enhance the magnitude of the NTC and expands its temperature range. In contrast to EHN and ferrocene, 2,4-xylenol has no effect on the reactivity of the fuel over the whole temperature range studied and even at concentrations ten times higher (1% mol.) than the other additives.

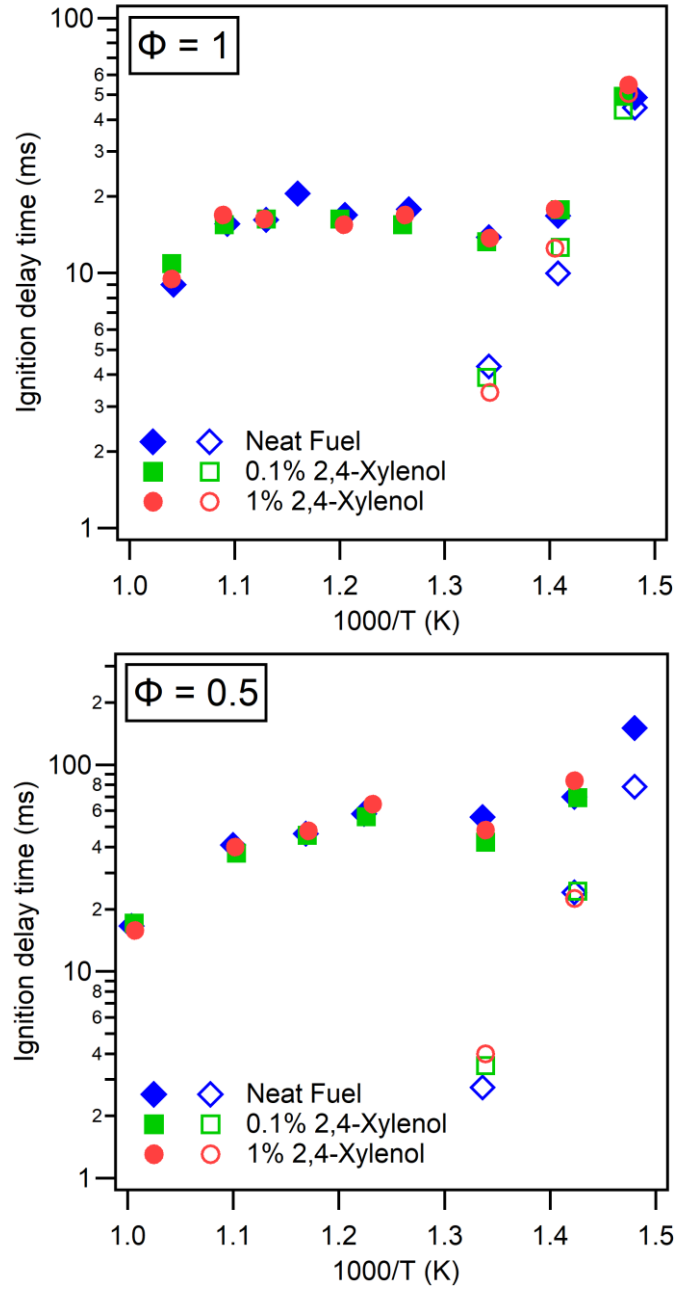


Figure 5. Experimental ignition delay times in RCM of the neat fuel and doped with 0.1%mol. and 1%mol. of 2,4-xylenol, in stoichiometric and lean conditions under  $P_c = 10$  bar. Filled symbols refer to the main ignition and open symbol to the 1<sup>st</sup>-stage ignition.

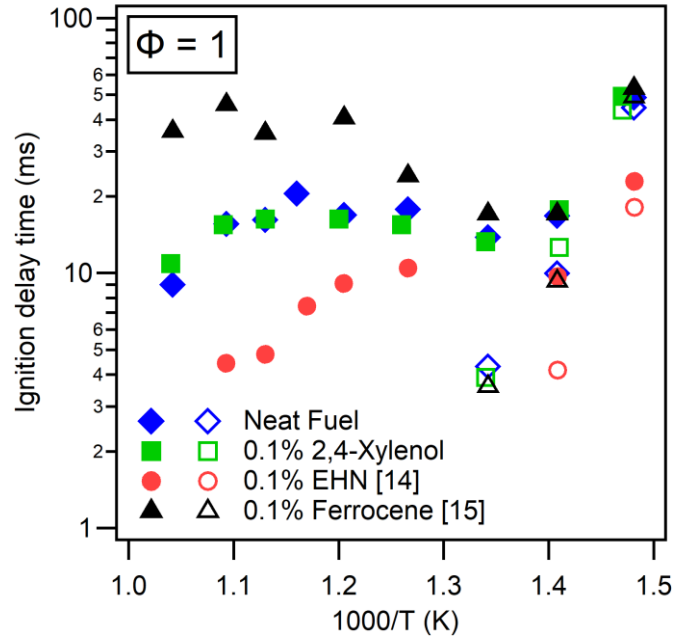


Figure 6. Experimental ignition delay times in RCM of the neat fuel and doped with 0.1%mol. of 2,4-xylenol, EHN [14], and ferrocene [15] in stoichiometric conditions under  $P_c = 10$  bar. Filled symbols refer to the main ignition and open symbol to the 1<sup>st</sup>-stage ignition.

Figure 7 presents the adiabatic flame speed of the pure and doped toluene/*n*-heptane surrogate fuel as a function of the equivalence ratio. Pressure is 1 atm and the fresh gas temperature is set to 398 K. The doping level of additives is 1% for 2,4-xylenol and EHN, and 0.1% for ferrocene, weight basis. The flame speeds vary in the range 30 to 60 cm s<sup>-1</sup>; the maximum is reached for the equivalence ratio  $\Phi = 1.1$ , as in the case of other hydrocarbons in air [34,35]. The results show that the additives, 2,4-xylenol, EHN, and ferrocene, do not change the burning velocity of the fuel in the studied conditions. The small variations observed between the experimental series remain within the uncertainty and the repeatability of the measurements and do not show an effect of the additives.

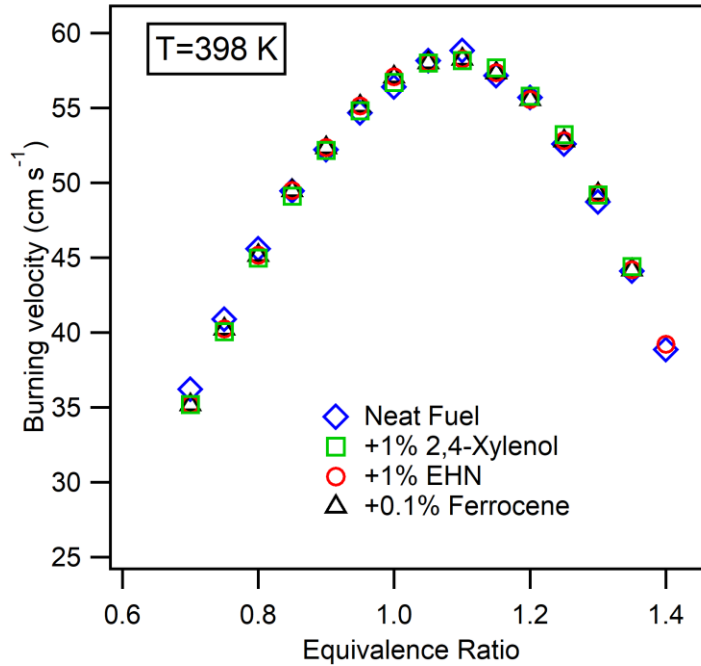


Figure 7. Experimental laminar burning velocity of the pure fuel in air and doped with 1 wt% of 2,4-xyleneol, 1 wt% EHN, and 0.1 wt% ferrocene, at a fresh-gas temperature of 398 K and one atmosphere.

2,4-xyleneol does not show any effect on the gas-phase reactivity of the toluene/*n*-heptane surrogate. Auto-ignition in the low and intermediate temperature range and flame speeds, which are key parameters of engine combustion, are not affected even by an amount of additive of 1%. This amount is much higher than that required to have an antioxidant effect in the liquid phase, since a marked increase of the induction time was found with a doping level as low as 0.08 and 0.1 %mol. McCormick et al. [21] found that 2,4-xyleneol increased the octane number (RON) of a target fuel for a higher doping level of 2% vol, and a RON increase of 1.7 was experimentally observed by incorporating 2% mol. of 2,4-xyleneol into pure *n*-butane by Zhang et al. [48]. The negligible effect of 2,4-xyleneol observed in this work in the gas phase should be due to the lower doping level considered, efficient in liquid phase but not in combustion.

#### 4. Conclusions

The multi-effects of 2,4-xylenol on fuel reactivity in both liquid and gas phases was investigated experimentally. In the liquid phase, autooxidation was quantified by the measurement of induction periods in a PetroOxy. Pure *n*-decane and a toluene/*n*-heptane blends were used as surrogate gasolines. 2,4-Xylenol was found to increase dramatically the oxidation stability of both fuels. The antioxidant effect is stronger in *n*-decane than in the toluene/*n*-heptane blend because the action as radical scavenger is more efficient with reactive decylperoxy radical from *n*-decane than with resonance stabilized benzyl radicals from toluene. In combustion, ignition delay time measured in gas-phase in a RCM at high pressure between 675 K and 1000 K did not show any effect of the additive in stoichiometric and lean conditions, contrary to EHN and ferrocene, cetane and octane boosters added at lower levels. Adiabatic laminar burning velocities of the *n*-heptane/toluene blend at atmospheric pressure and a temperature of the fresh gas of 398 K were not affected by the addition of 1% 2,4-xylenol. These experimental results confirm the potential of 2,4-xylenol as a biomass-based antioxidant at low doping levels for liquid fuel without any additional effects on the gas-phase reactivity of the formulated fuel.

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