Autoignition characteristics of ethers blended with low cetane distillates

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Abstract

The introduction of high cetane components has enabled the use of low cetane base gasoline in compression ignition engines. This study provides an understanding of the autoignition characteristics of various ethers blended with light distillates. The spontaneous ignition of mixtures was herein studied both experimentally (Ignition Quality Tester) and computationally, allowing to unravel the impacts of distillate composition, ether structure and reaction progress on key ignition pathways. Various multicomponent base fuel surrogates were formulated to closely match actual fuel composition thereby accurately simulating the interplay between distillates and oxygenates. Despite its lower cetane number, di-n-butyl ether (DNBE) was found to promote a more vigorous ignition than diethylether (DEE). However, OH radical scavenging by p-xylene counteracts DNBE effect. Two preignition phases may be distinguished, namely oxidation initiation by ether and subsequent chemical runaway involving simultaneously fuel and ether. According to the present kinetic mechanism, direct cross-reactions between ether radicals and light distillate components have little impact on the ignition delay time under the IQT operating conditions. As ignition progress increases, ether contribution to OH production decreases and oxidation paths related to aliphatic and cyclic alkanes become dominant. In the case of polyoxymethylene methyl ethers, the extra production of formaldehyde during the ignition phase does not impair the overall reactivity. The respective effects of OME₁ and OME₃ on ignition may be explained by the emergence of a new OH production path from OME₃ oxidation products, while methyl formate production from OME₁ acts as an OH radical sink. Even though locally lean zones of the IQT reactor may favor specifically neopentane oxidation at the expense of n-hexane, the new OH production path remains active over a wide range of conditions. Overall, the present detailed model qualitatively captures the non-linear impact of various ethers on autoignition over the 15-30 DCN range, which makes it attractive for optimizing low cetane fuels formulation.

Keywords : Derived Cetane number, IQT, polyoxymethylene dimethyl ethers, gasoline, naphtha, ignition.

1. Introduction and Background

Gasoline fuels are widely used in spark ignition (SI) engines, but research in the past decade has also shown their potential use in compression ignition (CI) engines^{1,2}. For gasoline compression ignition (GCI) application, it has been shown that fuels with lower octane (higher cetane) such as naphtha offer improved combustion characteristics². The introduction of high cetane components such as dialkyl ethers, among others, has opened up the use of lower cetane gasoline fuels in compression ignition engines such as gasoline compression ignition (GCI) engines^{3,4}. Understanding the base gasoline interaction with cetane boosters, specifically gasoline / ether interaction, has thus become vital for fuel / engine co-design.

Despite recent progress in ether combustion chemistry^{5–12} there is a lack of fundamental studies of the interaction of commercial gasolines and ethers. Most of the studies focused on ether addition to diesel fuel blends^{13–15}, n-alkanes^{16–19}, or other oxygenated fuels²⁰. Dialkyl ethers have been put forward as a clean blendstock for compression ignition engines²¹ as their addition to diesel fuel was shown to reduce soot emissions^{22–25}. However, the cetane boosting effect of these ethers on light distillates such as gasoline or naphtha remains poorly understood²⁶.

The autoignition of dimethyl ether (DME) / n-butane blends was found to give rise to competitions between the fuel components for H and methyl radicals²⁷. The increase in DME blending ratio was seen to result in OH radical concentration increase¹⁹, thereby shortening overall ignition delays, which was related to low C-H bonds energies in DME¹⁸. Further, n-butane addition to DME was found to result in the slight promotion of DME low-temperature oxidation paths during the first-stage ignition. Similar to n-butane²⁸, the extent of promotion of n-pentane ignition by DME is equivalence-ratio dependent²⁹. Co-operative effects between the individual components in the Negative Temperature Coefficient (NTC) zone were found³⁰, but these effects were not captured satisfactorily by kinetic modeling, supposedly because of the lack of low-temperature cross-reactions. Conversely, Green et al.³¹ noticed that cross-reactions between propane and DME do not have a significant effect on ignition, suggesting that kinetic models may be assembled from the addition of their subsets.

Interestingly, several authors found that the addition of ethers to fuels with high aromatic content does not necessarily promote ignition^{32,33}, as a result of complex interaction of aromatics with ethers. The interaction between toluene and DME appears to be dominated by the scavenging of DME-generated radicals by toluene, leading to resonantly-stabilized benzyl radicals. Their subsequent recombination to bi-benzyl turns out to be affected by DME through altered HO₂ production³⁴.

Recently, Fikri et al.³⁵ analyzed the ignition of Primary Reference Fuel (PRF95) / DEE mixtures and noticed that low-temperature DEE chemistry contributes to around 30% of OH production for only 10% vol. DEE added, and that DEE addition leads to the shift of NTC zone boundary towards higher temperatures.

Despite several dedicated studies^{36–39}, fundamental knowledge on the ignition of polyoxymethylene dimethyl ethers (OME_x) / petroleum distillate mixtures remains very scarce. It was reported that the addition of dimethoxymethane (DMM, methylal also known as OME₁) to n-heptane results in the decrease of ignition delay times at high temperature as a linear function of DMM content⁴⁰. Wang et al.⁴¹ found that HCCI engine combustion of OME

exhibits multiple-stage ignition with pronounced low temperature heat release. The heat release profile may result from the separate oxidation of accumulated formaldehyde ⁶.

To our knowledge, no study on the impact of ethers addition on the ignition of olefinic / naphthenic compounds was reported in the literature. However, Bogin et al. ⁴² showed that an IQT is a suitable tool for investigating ignition kinetic mechanisms. Relying on a detailed kinetic analysis approach, the present study aims to meet the challenge of interpreting observed synergies between various light-distillates and several ether additives. For this purpose, we base our analysis exclusively on IQT experiments to decipher the mechanisms involved in autoignition enhancement as a function of ether alkylic chain length and number of ether groups in the additive.

2. Methodology

2.1 Ignition Quality Tester (IQT) experiments

Two low-cetane gasoline fuels (obtained from a refinery in Saudia Arabia) and four cetane improvers were considered in the present study. Table 1 sums up the ether added to base fuels. DEE (di-ethyl ether), DMM (dimethoxy methane) and DNBE (di-n-butyl ether) were used as high cetane additives (>99% purity). In addition to these pure components, a mixture of polyoxymethylene dimethyl ethers (OME_x) exhibiting a Schulz-Flory distribution in the 100-250 amu range was considered (1% wt OME₂ + 47% OME₃ + 29% OME₄ + 17% OME₅ + 6% OME₆). Table 2 presents the characteristics of fuels investigated. For each fuel, two surrogates were formulated to fit RON, MON, DCN and PIONA using Chemkin surrogate blend optimizer ⁴³ (surrogate #1 and #3) and KAUST surrogate formulation tools ⁴⁴ (surrogate #2 and #4). While surrogates #2 and #4 focus on a limited set of well-studied palette components, surrogates #1 and #3 aim at matching the actual composition of the base fuel, thereby involving less well-studied species but with higher chemical relevance ⁴⁵. Comparison of the PIONA and target properties such as RON, MON DCN, density, H/C ratio and average molecular weight of the fuels, surrogates are shown in Figs. S1 and S2 in the supporting information.

Name	Most stable conformer (Avogadro ⁴⁶ MMFF94 force field ⁴⁷ optimization)	Cetane number ^{48,49}
Di-ethyl ether		125
Di-n-butyl ether		90
Dimethoxy methane		29
OME _x mixture		74 ^{PW}

Table 1 – Cetane boosters considered in the present study. ^{PW} : present work.

	Light Naphtha	Surrogate 1	Surrogate 2	Commercial gasoline	Surrogate 3	Surrogate 4
DCN	27.6 (IQT)	25.7	28.4	19.2 (IQT)	18.8	18.5
Paraffins (% vol liq)	17% n-pentane	20% n-pentane	29.3 % n- heptane	3% n-butane 7% n-pentane 6% n-hexane 2% n-heptane	13.8% n- pentane 5.0% n-hexane	12.6 % n-butane 16.4 % n-heptane
	19% n-hexane	10.9% n-hexane				
	<i>Subtotal : 36%</i>			<i>Subtotal : 18%</i>		
iso- Paraffins (% vol)	7% i-pentane	14.2% i-pentane	44.8 % i-pentane	9% i-pentane	26.2% i-pentane	27.5 % i-octane
	12% 3-methyl pentane	18.3% 2-methyl hexane		6% 2-methyl pentane	9.3% 2-methyl hexane	
	18% 2-methyl pentane	7.9% neo-pentane		4% 3-methyl pentane		
				3% 2-methyl hexane		
	3% 2,3- dimethyl butane			3% 3-methyl hexane		
	<i>Subtotal : 41%</i>			<i>Subtotal : 34%</i>		
Olefins (% vol)	NA	NA	NA	2% 1,3 pentadiene	2.6% 1-pentene	2.2 % 1- hexene
				<i>Subtotal : 5%</i>		
Naphth- enes (% vol)	16% methyl cyclopentane	21.3% cyclopentane	17.9 % cyclopentane	3% methyl cyclopentane	5.4% cyclopentane	2.0 % cyclopentane
	2% cyclopentane					
	<i>Subtotal : 19%</i>			<i>Subtotal : 5%</i>		
Aromatics (% vol)	4% Benzene	7.4% benzene	8.0 % 1,2,4 trimethyl benzene	18% toluene 3% 3- ethyl toluene 5% 1,2,4 trimethyl benzene	18.3% toluene 19.4% p-xylene	39.4 % toluene
	<i>Subtotal : 4%</i>			<i>Subtotal : 37%</i>		

Table 2 – Specification of the fuels tested. The PIONA analysis was put together using the Detailed Hydrocarbon Analysis method outlined in ASTM D6730 and D6733. Detailed volumetric liquid composition is given for species with concentration higher than 2% volume liquid. Surrogates 1 and 2 correspond to light naphtha. Surrogates 3 and 4 correspond to commercial gasoline. DCN of surrogates are evaluated by linear-by-volume rule ⁴³.

The ignition quality tester (IQT) was herein used to characterize CI engine fuels according to the ASTM standard D6890. The CN obtained from the IQT is referred to as the derived cetane number (DCN) as the CN measurements are obtained from a constant volume combustion chamber.

The experimental setup has been already described in previous publications^{50–52}, therefore only essential details will be provided in the following. The IQT has a chamber volume of 0.21 L filled with pressurized zero air that has an O₂ concentration of 20.9 vol%, remaining N₂ and trace amount (< 0.1 ppm) of hydrocarbons. The prefilled zero air is at a pressure of 21.3 bar that is heated to the required standard temperature with electric heaters. The exact chamber temperature is determined with a calibration procedure as prescribed in the ASTM D6890 standard. The fuel stored in the reservoir⁵² is injected into the combustion chamber with an inward opening single hole S-type nozzle, which typically has a nozzle tip temperature of 325 K. The injected liquid fuel atomizes, evaporates and mixes with air at an overall equivalence ratio of 0.58, close to IQT standard value⁵³. This gradually initiates chemical reactions eventually leading to chain branching that results in a sharp rise in pressure. This sharp rise in pressure is defined as the start of ignition. The opening of the nozzle is measured with a proximity sensor, which defines the start of injection⁵². The time difference between the start of ignition and injection is defined as the ignition delay time (IDT) of the measured fuel at the respective condition.

The IQT is designed to measure the ignition delay time of highly reactive fuels for which the presence of low temperature heat release (LTHR) may not be apparent if it exists. However, for long ignition delay time fuels such as gasoline, LTHR may be apparent if it exists, as a result the start of ignition definition in the IQT provided system software might not provide the exact start of ignition. To account for LTHR for such fuels, the gradient method was proposed by Naser et al.^{51,52}, which is used in the present study to measure the ignition delay times.

The IQT fuel injection system is designed for diesel fuels that have high boiling points. A series of studies^{42,54–57} have adopted the IQT to measure fuel ignition quality of full boiling-range gasolines and other fuels that have comparatively lower boiling points than diesel. For fuels with boiling points in the gasoline range fuel boiling issues have been reported^{42,54}. To avoid fuel boiling issues in the present study, the pressure in the fuel line for the present experiments were maintained at 6–7 bar using N₂, thereby increasing the boiling point of all the components than that defined at atmospheric conditions. This was to an extent helpful in reducing the fuel boiling issues for gasoline-like fuels. For the highly volatile fuels used in the present study, i.e., light naphtha, to minimize the exposure time of the fuel to the hot injector tip to prevent fuel boiling in the delivery lines the bleed valve⁶² was opened to bleed vaporized fuel just before injection. This enabled fresh fuel to fill the lines prior to injection. The higher fuel line pressure and the timely operation of the bleed valve prevents long exposure of the fuel to the injector tip, which reduces compositional variations in the injected fuel resulting from boiling issues.

Each DCN measurement involves 15 pre-injections whose data are not logged followed by 32 main injection events with the data logged. The data obtained is then processed to calculate the ignition delay time with the gradient method and the average of the 32 injections is used in the present study. As mentioned above the standard temperature is obtained by performing a calibration procedure that involves the IDT measurement of *n*-heptane. The chamber

temperature is adjusted such that the average of three runs (i.e., 15 pre-injections and 32 main injections for each run) is 3.78 ± 0.01 ms. This temperature is then fixed for IDT measurement of all other fuels. The DCN is then calculated with the average IDT (τ_{id}) using Eq. (E1). The standard deviation of 32 main injection for all the measurements are also provided in the present study. For IDT in the range of 3.1 – 6.5 ms Eq. (E1a) is used, whereas for all IDT outside the range of 3.1 – 6.5 ms, Eq. (E1b) is used.

$$DCN = 4.46 + \left(\frac{186.6}{\tau_{id}}\right) \quad (E1a)$$

$$DCN = 83.99 (\tau_{id} - 1.512)^{-0.658} + 3.547 \quad (E1b)$$

Excellent correlation between CN and DCN for IDT in the range of 3.1-6.5 ms is given by Eq. (E1a). Equation (E1b) is less precise than (E1a) but many recent publications^{57–60} have used this correlation for DCN evaluation.

2.2 Chemical kinetic modeling

The present kinetic mechanism (10601 reactions and 2444 species) was obtained by adding DEE, DNBE and OME_x subsets to multicomponent KAUST-LLNL-NUIG FACE gasoline mechanism⁶¹. The DEE subset was extracted from the mechanism of Tran et al.⁶³ which includes new primary low-temperature reaction paths leading to acetic acid and acetic anhydride and was coupled to the previously developed high-temperature model⁶⁴. The DNBE subset was taken from a recent stirred reactor study performed by Thion et al.⁶⁵ over an extended range of residence times and equivalence ratios. The authors refined the rates constants for ketohydroperoxide decomposition initially proposed by Cai et al.⁶⁶ and calculated the rate constants of the β -scissions of DNBE radicals using TST/RRKM modeling. Both DEE and DNBE subsets are able to account for the two-NTC-zone occurrence reported for these ethers. The OME₂₋₃ subset from Tsinghua group⁶⁷ includes both low and high temperature chemistry. It was complemented with the DMM subset generated in a recent collaboration between Tsinghua, Orleans and Sandia⁶⁸. Figure 1 shows a validation of the full mechanism against available experimental measurements. In the present study, the OME_x mixture (DCN of 74) was represented by OME₃ due to its reported cetane number of 78⁴¹.

Figure 1 – Present model (lines) validation against shock tube IDT (symbols) of Fikri et al.³⁵ and He et al.⁶. The modeled ignition delay corresponds to the time required to reach the maximum heat release rate (main inflection point).

2.3 IQT modeling

A multizone model using the Chemkin Pro software package⁶⁹ was employed to model the IQT. The IQT zones are modeled as closed gas-phase homogeneous reactors which interact with each other exclusively through pressure work (physical expansion due to combustion), the total volume being held constant⁷⁰. The present model does not take into account spray formation and evaporation. However, recent calculations carried out at KAUST⁷¹ demonstrate that for volatile low-reactivity fuels such as iso-octane, the evaporation time of these species under IQT conditions is significantly shorter than chemical ignition time. Complementary calculations presented in the supporting information indicate that the physical delay time associated to the spray breakup and subsequent droplets evaporation may represent typically 23% of the overall ignition delay time for a gasoline with a DCN of 20. The physical/ overall ignition delay ratio becomes higher than 50% for $DCN > 35$ due to the shortening of the gas-phase chemical ignition delay. This provides an upper DCN value of 35 for the present model validity. The addition of DNBE was previously seen to impact sprays atomization⁷². According to the Sauter Mean Diameter (SMD) expression presented in the supporting information, the use of DNBE (resp. DEE) instead of gasoline is expected to result in an increase (resp. a decrease) of the SMD by 20% for DNBE (resp. 12% for DEE) due to the higher (resp. lower) viscosities⁷³ and surface tensions⁷⁴ of these ethers than those of gasoline. As moderate amounts ($< 25\%$) of ethers are herein blended to the base fuel, our calculations indicate that the atomization-related effect of ethers on DCN should remain limited (< 1).

The computed IDT was defined as the time required for the all zones of the system to reach $T_{init} + 400$ K, which coincides well with the occurrence of the average temperature inflection point (relative deviation $< 5\%$). The DCN is then deduced from computed IDT using the same correlation as the one used experimentally (E1). The zone volume fractions of the 20-zone model obtained by Osecky et al.⁷⁵ at 20 ms contact time were normalized to the present overall equivalence ratio (0.58). The same temperature distribution accounting for the evaporating

cooling of iso-octane was used for all fuels blends. Osecky et al. showed that this distribution is relevant to reproduce ignition delays and that relying on a late macromixing state (i.e. 20 ms instead of typically 7-15 ms for the fuels investigated) would not significantly affect the predicted ignition delay times. Additional calculations presented in Figure 2 demonstrate that the present multizone model is indeed able to predict the measured DCN of a variety of Toluene Primary Reference Fuels (TPRFs) within a reasonable error range ($\text{DCN} \pm 4$) over the range 20-35, taking implicitly the physical delay into account through Osecky's initial gas-phase mixing state. In all calculations, the pressure was 21 bar. The adopted 20-zone reactor parameters are provided in table S3 (supporting information). In the kinetic analysis, normalized rate-of-production (ROP) of a given reaction was obtained by dividing its species production rate by the sum of the rate-of-progress variables over all reactions producing the targeted species⁷⁶.

Figure 2 – Parity plot for a wide range of TPRFs⁵². The DCN was computed using Osecky's 20-zone model and equation (E1). The dotted lines correspond to $y = x \pm 4$.

3. Results and Discussion

3.1 Phenomenological description of cetane enhancement

For the two investigated base fuels, the promoting effects of ethers were found to follow the order $\text{DNBE} > \text{DEE} > \text{OME}_x$ (Figure 3). Hence, the intuitive order $\text{DNBE} < \text{DEE}$ that would come out of linear blending rules is actually reversed. This might be due to a synergetic chemical behavior at low ether concentrations or to higher DEE volatility which influences temperature and concentration stratification⁷⁷.

Prior to proceeding to detailed kinetic modeling, the impact of additives on IDT (and hence DCN) may be first rationalized by the a simple ignition time scale analysis⁷⁸ accounting for the sequencing of fuel/additive interaction with ignition progress.

$$\tau_{id} = \tau_{initiation} + \tau_{runaway} \quad (E2)$$

During initiation phase, it can be assumed that ether and fuel oxidation are occurring almost sequentially, as will be demonstrated by the chemical kinetic analysis below (section 3.3). Therefore, the corresponding delay may be estimated as a volume-weighted sum of individual reaction times (derived from table 1 properties and (E1)).

$$2\tau_{initiation} = v_{additive}\tau_{additive} + (1 - v_{additive})\tau_{fuel} \quad (E3)$$

After initiation, chemical branching leads to simultaneous runaways of fuel and additive. Thus, the corresponding delay involves an harmonic mean of individual reaction times.

$$\frac{2}{\tau_{runaway}} = \frac{v_{additive}}{\tau_{additive}} + \frac{1-v_{additive}}{\tau_{fuel}} + \alpha v_{additive}(1 - v_{additive}) \quad (E4)$$

The third term of the right-hand side of (E4) accounts for the interaction⁷⁹ between fuel and additive. While this term was found to be negligible for DEE and OME_x, a value of $\alpha = 0.75$ (i.e. nearly 3 times Lorentz's average of reciprocal times⁸⁰) was required to reproduce the concavity of DNBE plot displayed in Figure 3. Note that the present volume-weighted hybrid mixing rule performs better than its molar counterpart (Figure 3 inset) at low ether content (< 10% vol.). At higher ether contents (>10 % vol.), the present phenomenological mixing rule fails to capture cetane boost accurately, calling for detailed chemical kinetic modeling.

Figure 3 – Comparison of cetane boosts of different ethers for the two base fuels considered. Symbols represent experimental measurements and lines represent phenomenological mixing rule (equations (E2)-(E4) with $\alpha = 0.75$ for DNBE). Inset on the top left presents a comparison of the present volume-based hybrid mixing rule (green continuous line) with the volume-based linear mixing rule (black continuous line) using base fuel DCN derived by IQT in the present work. Corresponding molar mixing rules are depicted by dashed lines.

3.2 Effect of the dialkyl ether chain length on ignition kinetics

Figure 4 shows a comparison between experimental and modeled DCN in the case of dialkyl ether addition. Measured IDT and relative experimental errors are presented in the supplementary material (Figure S6). Uncertainty calculations using polynomial chaos expansion⁸¹ (MUM-PCE) reveal that 30% represents a lower boundary of error estimate of IDT prediction associated with the present set of Arrhenius prefactors, let alone the additional uncertainty on thermochemical properties⁸². It is important to notice that owing to the strong non linearity of equation (E1), a relatively modest error on IDT can induce a large error on DCN.

Figure 4 – Measured (symbols) and predicted (lines, surrogates 1 and 2) DCN boost effect of dialkyl ethers on light naphtha (first row) and commercial gasoline (second row). Continuous and dashed lines stand respectively for surrogates 1 and 2 (top row) and respectively for surrogates 3 and 4 (bottom row). Experimental error bars correspond to the value estimated in figure S5 (supporting information). Shaded areas are related to surrogate 2 (top row) and 4 (bottom row) and corresponds to 30% uncertainty on IDT (see text).

For all surrogates, the modeled impact of various ethers on DCN is in reasonably good agreement with measurements for ether concentrations lower than 20% given the respective uncertainties (Figure 3). However, surrogates tend to slightly overpredict the slope of cetane boost with respect to dialkyl ether concentration. This might be partly due to specific termination reactions not included in the present kinetic scheme and to the behavior of the 20-zone model as illustrated on Figure 2 by the migration of the points of the parity plot towards its upper half-plane with increasing DCN.

Under the present conditions, bringing the surrogate formulation a step closer to the actual fuel composition (i.e choosing surrogates 1 / 3 over 2 / 4) does not appear to be beneficial for predicting the increase of global reactivity induced by ethers addition. Nevertheless, it can be expected that the use of surrogates 1 and 3 would allow a more instructive view of the coupling of dialkyl ethers and naphtha oxidations as a result of their more detailed compositions. As an illustration, a reversal of importance of relative OH ROP of straight-chain and branched-chain alkanes oxidation paths can be noticed (respectively 21 and 25% for surrogate 3 but 32 and 20% for surrogate 4) for commercial gasoline / 10% DNBE mixture at 10% τ_{id} (ignition delay). The same trend can be noted for OH consumption paths as well. The reason for this is that the iso-alkanes considered in surrogate 3 are much less branched than iso-octane (used in surrogate 4) and hence more reactive over the temperature range of interest.

Our rate-of-production analyses performed with surrogate 1 reveal that at 1% τ_{id} , the first O₂ addition on alkyl ether radicals and the second O₂ addition on QOOH radicals are proceeding respectively 21% and 10% faster in presence of 10% DNBE than with 10% DEE. This may be due to the higher methylene / methyl ratio in DNBE, which favors peroxidation. As a consequence, DNBE addition results in prompt ether alkyl peroxides formation (mole fractions of respectively 530 and 25 ppbv for 10% DEE and 10 % DNBE at 25% τ_{id}) throughout the degenerate chain branching process which in turn results in the shortening of ignition delay.

As can be noticed on figure 5, the normalized sensitivity of ignition delay with respect to kinetic preexponential factors

$$S_j = \frac{A_j}{\tau_{id}} \frac{\partial \tau_{id}}{\partial A_j} \approx \frac{\tau_{id}(1.1 A_j) - \tau_{id}(A_j)}{0.1 \tau_{id}(A_j)} \quad (E5)$$

This comes hand in hand with the involvement of HO₂ in H-abstraction on DEE (accounting for 16% of DEE consumption at 10% τ_{id}), whereas OH is herein the only fast H-abstractor for DNBE. At low ignition progress, DEE dissociates readily to ethylene (7% of DEE consumption at 0.01 τ_{id}), while C-O scission in DNBE does not happen readily at low temperature⁶⁵, making H-abstraction a prerequisite of unimolecular decomposition to reactive 1-butyl radical. The different reactivities of the abovementioned C₂-C₄ decompositions products with the base fuel components give rise to very distinct synergetic effects. Also, the increase of ignition delay through decomposition of alkoxyalkyl radicals (by subtracting carbon from the ether peroxidation path) appears to be less significant for DNBE than for DEE. Note that the sign of sensitivity of production of n-pentyl radical depends on its class due to differing propensities to peroxidation. Finally, adding H-Abstraction reaction by ether radicals on aliphatic alkanes and cyclopentane (with kinetic parameters evaluated by RMG 3⁸³ and provided in supporting material) to the kinetic scheme was found to have negligible impact on ignition delay time (< 0.1%) over the range of ether concentrations investigated. This tends to indicate that naphtha and ether are mainly interacting through the C₀-C₄ radical pool.

Figure 5 – Main reactions affecting IDT for light naphtha + 10% ether mixtures (Surrogate 1 was used in the calculations). Formula were generated by OpenBabel⁸⁴ software.

3.3 Effect of the base fuel composition on ignition kinetics

From the experimental findings displayed in section 3.1, we may notice (Figure 3) that both base fuels give rise to similar additive rankings in term of cetane boost (i.e. DNBE>DEE>OME_x), although the interaction with DNBE shifts from synergetic to anti-synergetic as naphtha is replaced by gasoline. In fact, an increase of 7.6 and 6.1 in DCN is respectively measured for naphtha and gasoline at 10% DNBE, whereas the linear-by-volume mixing rule provides increases of 6.2 and 7.1, respectively. This illuminates the primordial role of base fuel composition, notably the aromatic content³⁴, in counteracting the promoting effect of ethers. Figure 6 further shows that replacing naphtha by gasoline does in fact result in the dramatic increase of the importance of the following OH radical scavenging reaction

The emergence of this inhibitory path may be attributed to the lower cycloalkanes and higher p-xylene and toluene contents in gasoline. Despite their similar concentrations in surrogate 3, toluene and p-xylene exhibit differing propensities to scavenge OH radicals as they account respectively for 5% and 8% of OH consumption at 10% τ_{id} for gasoline / 10% DNBE mixtures.

Figure 6 – Normalized sensitivities of OH concentration with respect to kinetic preexponential factors in zone #10 of the IQT chamber (corresponding to volume-averaged thermochemical conditions in IQT) for the ignition of fuel + 10%v. DNBE mixtures. Green and red curves stand respectively for naphtha and gasoline. Surrogates 1 and 3 were used in the calculations. Sensitivities of monoaromatics + OH reactions are not displayed for naphtha ignition as they are lower than 0.1.

Figure 7 – Predicted contributions of chemical families to OH average rate-of-production (ROP) inside the IQT chamber for the ignition of fuel + 10% DEE mixtures (Left : Surrogate 1. Right : Surrogate 3). Dash-dotted lines denote the results obtained by a single-zone model at 756 K and $\phi=0.58$ (volume-averaged conditions).

The base fuel composition may not only impact OH consumption paths but also the relative contributions of chemical families to OH production during pre-ignition phase. Figure 7 illustrates the sharp decrease of ether contribution to OH production with ignition progress (t / τ_{id}), substantiating the fuel-ether interaction phenomenology previously put forward in section 3.1. Mixture stratification (continuous vs. dash-dotted lines) contributes to increase ether

promoting effect at the expense of iso-paraffins contribution to OH production. Utilizing the single-zone modeling neglects the contribution of temperature and mixture/equivalence-ratio stratification, which have significant effect on ignition kinetics.

While ether contribution to OH dominates up to 1% τ_{id} for light naphtha, its dominance is extended to times as high as 10% τ_{id} for commercial gasoline, due to a lower reactivity of base fuel. This compensation effect explains why cetane boosts of 20% DEE addition in quite similar for naphtha and gasoline (respectively +9 and +8 on experimental DCN).

According to our rate-of-production analyses for fuel +10% DEE blends, OH early production ($t < 1\% \tau_{id}$) by ether involves mainly hydroperoxyl radical decomposition

and subsequent peroxyhydroperoxy radical decomposition to keto species. As time increases, aliphatic iso-alkanes are increasingly competing with ether through the production of cyclic ethers and ketohydroperoxides.

Then, for $t > 0.1\% \tau_{id}$, the oxidation of straight-chain alkanes takes over for OH production through degenerate chain branching.

Interestingly, cycloalkane oxidation starts releasing significant amounts of OH much later than aliphatic alkanes, proceeding mainly through the following reaction (E11)

The significant contribution of cycloalkanes to reactivity in the NTC region confirms previous findings on FACE gasolines⁶¹. However, in the case of commercial gasoline, which contains six times less cycloalkanes than light naphtha, OH production by cyclopentane oxidation encounters competition from 1-pentene oxidation through Waddington reaction (E12).

Similar pathways can be identified for fuel + 10% OME_x mixtures, with the formation of trioxane derivatives (E13).

3.4 Effect of the polyoxymethylene ether chain length on ignition kinetics

Similar to the case of alkyl ethers, all proposed fuel surrogates were found to correctly reproduce the experimental observations. Figure 8 shows that dimethoxymethane (methylal, DMM or OME₁) addition to either of the two base fuels does not result in a significant cetane boosting effect. Unlike in the case of dimethoxymethane, OME_x addition exhibits a strong and non-linear effect on DCN. Hence, increasing the level of polymerization of OME_x is beneficial to cetane boosting effect. Although OME_x mixture is herein represented by OME₃ due to the lack of validated oxidation mechanisms for OME₄₊, the present model is able to capture correctly this effect at low OME concentrations (< 20% vol. liq.).

Figure 8 – Measured (symbols) and predicted (lines) cetane number boost effect of polyoxymethylene dimethyl ethers. Green and red colors denote respectively light naphtha (first row) and commercial gasoline (second row). Continuous and dashed

lines stand respectively for surrogates #1/#3 and #2/#4. Error bars correspond to the value determined in figure S6 (supporting information).

While methyl formate formed from methylal oxidation does not readily oxidize (Figure 9), according to the present model, the production of hydroperoxy-methylformate ($\text{HO}_2\text{CH}_2\text{OCHO}$) from OME_3 contributes to accelerate chain branching. Indeed, $\text{HO}_2\text{CH}_2\text{OCHO}$ decomposition rate through

is found to be nearly 4 times higher for OME_3 than for OME_x . This effect is in line with previous evidence of the key role of $\text{HO}_2\text{CH}_2\text{OCHO}$ in cool flame DME chemistry^{85,86}. Although methyl formate oxidation is known to be quite slow⁸⁷, in presence of OME_3 $\text{HO}_2\text{CH}_2\text{OCHO}$ production proceeds via DMM3B (SMILES $\text{COCOCO}[\text{CH}]\text{OC}$) and DMM3C (SMILES $\text{COCO}[\text{CH}]\text{OCOC}$) paths, whereas DMM3A (SMILES $\text{COCOCOCO}[\text{CH}_2]$) path leads essentially to C_5 hydroperoxy-polyoxymethylene ether formation. As a result, OME_3 oxidation relies on multiple OH production paths involving C_2 , C_3 and C_5 ethers peroxidation.

Figure 9 – Impact of OME chain length on main OH formation pathways in zone #10 ($\phi = 0.57$, 756 K) of IQT reactor at $t = 10\% \tau_{id}$ for light naphtha + 10% OME mixtures. Left : methylal. Right : OME_3 . Continuous and dashed lines correspond respectively to fluxes higher than $5 \text{ mmol.m}^{-3}.\text{s}^{-1}$ and fluxes ranging from 1 to $5 \text{ mmol.m}^{-3}.\text{s}^{-1}$. Red and green lines correspond respectively to OH consuming and OH producing pathways. The shaded area depicts the ether-related paths.

Previous studies put forward that the formaldehyde released by polyoxymethylene ethers could potentially inhibit ignition at initial temperatures lower than 900 K⁸⁸. In fact, Yamada et al.⁸⁹ mentioned a radical scavenging effect involving formaldehyde through reaction (E15)

thereby removing OH radicals for base fuel oxidation. The present model confirms that this reaction corresponds in fact to the main consumption channel of formaldehyde under the present conditions at 10% τ_{id} (representing around 60% of total consumption rate). However, even if the addition of 10% dimethoxymethane (respectively OME₃) to light naphtha results in an enhancement of the rate of (E8) by a factor of 22 (respectively a factor of 5) at 10% τ_{id} , the OH removal rate by CH₂O (0.029 $\mu\text{mol.m}^{-3}.\text{s}^{-1}$ in zone #10 at 10% τ_{id}) lies still five orders of magnitude below the overall OH consumption rate (Figure 9). The contribution of (E15) to overall OH consumption increases to roughly 0.1% at 30% τ_{id} , therefore remaining insignificant during the preignition phase. Hence, the inhibition of light naphtha ignition by dimethoxymethane does not result from supplementary CH₂O production but is rather a consequence of the balance between OH consumption by methylal and OH production from hydroperoxy ether radicals formed during its oxidation (Figure 9).

The impact of local equivalence ratio on OH formation pathways is displayed on Figure 10. As can be seen, under very lean conditions neopentane supersedes n-hexane as a major contributor to OH consumption paths. Complementary calculations of neopentane / air and n-hexane / air constant volume autoignition at 21 bar and 750 K indicate higher reactivities of neopentane at $\phi < 0.1$. This confirms the trend observed and highlights the need for further investigation of fuel oxidation chemistry in ultra-lean conditions. DMM3C (COCO[CH]OCOC) oxidation route runs through C₃ instead of C₂ ethers. However, in all IQT zones, HO₂CH₂OCHO remains a hub for OH production paths.

Figure 10 – Impact of local thermochemical state in the IQT reactor on main OH formation pathways at 10% τ_{id} for light naphtha + 10% OME₃. Left : zone #1, $\phi = 0.016$, 817 K. Right : zone #15, $\phi = 1.10$, 718 K. Continuous and dashed lines correspond respectively to fluxes higher than 0.1 and fluxes ranging from 0.05 to 0.1 $\text{mmol.m}^{-3}.\text{s}^{-1}$. Red and green lines correspond respectively to OH consuming and OH producing pathways. The shaded area depicts the ether-related paths.

4 Conclusions

The spontaneous ignition of mixtures of commercial distillates and a variety of ethers was studied both experimentally and computationally, allowing to unravel the impact of distillate composition, ether structure and reaction progress on key ignition pathways. The synergy between fuel and DNBE leads to the reversal of the expected order of promoting effects (DNBE < DEE) from linear blending rules. The synergy is less pronounced in presence of p-xylene, partly due to vigorous OH radical scavenging. Ether and naphtha components interact mainly through the C₀-C₄ radical pool : direct cross-reactions have a negligible impact on ignition delay time under the present IQT conditions. Phenomenologically, two preignition phases may be distinguished, namely oxidation initiation by ether and subsequent chemical runaway involving simultaneous oxidations of fuel and ether. Regardless of distillate composition, ether contribution to OH production decreases with time, whereas oxidation paths related to aliphatic and cyclic alkanes become dominant for times higher than 1% τ_{id} . In the case of polyoxymethylene methyl ethers, the extra production of formaldehyde during ignition phase does not significantly impact the overall reactivity. The respective effects of dimethoxymethane and OME_x on ignition delay times may be attributed to the emergence of a new OH production path from hydroperoxy-methyl formate (HO₂CH₂OCHO), while methyl formate production from OME₁ acts as an OH radical sink. Considering different OME_x blends and associated surrogates would be useful in further unravelling these complex structure-dependent effects on reactivity. While locally lean zones of IQT reactor may favor neopentane oxidation at the expense of n-hexane, HO₂CH₂OCHO path for OH production remains active over a wide range of local equivalence ratios. Overall, the present detailed model qualitatively captures the non-linear impact of various ethers on autoignition over the 15-30 DCN range, which makes it attractive for optimizing low cetane fuels formulation. The very stringent accuracy requirements for quantitative DCN predictions over an extended reactivity range (i.e. error on ignition delay time < 10%) highlight the importance of more accurate ignition kinetics for a much wider spectrum of species than just conventional n-heptane / isooctane / toluene mixtures as well as advanced multicomponent multiphase turbulent reactive flows models.

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