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Ethanolic gasoline, a lignocellulosic advanced biofuel†

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In line with society's growing need for a more sustainable fuel economy, various biofuels and alternative fuel formulations are being proposed. In this work, the ignition quality of a novel tricomponent advanced biofuel is examined. Ethyl levulinate, diethyl ether and ethanol (EL/DEE/EtOH) result from the acid hydrolysis of lignocellulosic biomass in ethanol. In this paper, derived cetane numbers are established for a wide variety of blend fractions, using Ignition Quality Tester measurements. EL/DEE/EtOH mixtures of ignition quality equivalent to market diesel and gasoline are identified. One mixture of Motor Octane Number (MON) 88.3 and Research Octane Number (RON) 95 is selected for detailed analysis in comparison to a FACE (Fuels for Advanced Combustion Engines) gasoline, as a representative of petroleum-derived gasoline, with a similar MON of 88.8 and RON of 94.4. Ignition delay times for the EL/DEE/EtOH gasoline fuel are measured using a rapid compression machine at equivalence ratios of 0.5 and 1.0, at 20 and 40 bar over a temperature range of 600–900 K. The data shows that at temperatures >800 K, the EL/DEE/EtOH fuel behaves quite similar to the petroleum derived gasoline, FACE-F. However, the tri-component biofuel shows a dramatically truncated extent of ignition reactivity at lower temperatures, with a total absence of low-temperature chemistry or negative temperature coefficient (NTC) region; in this respect this biofuel blend is very different to conventional gasoline. To understand this differing behaviour, a detailed chemical kinetic model is developed. Analysis of this model shows that ignition of the EL/DEE/EtOH blend is inhibited by the dominance of alkyl radical elimination pathways, which leads to a heightened rate of production of HO_2 radicals. At high temperatures, while both fuels maintain a similar ignition delay time, the sensitivity analysis and the radical pool population shows that a different combustion mechanism is occurring for the EL/DEE/EtOH fuel, where ethyl and methyl radicals play a much more prominent role in the ignition process.

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Introduction

Growing concern about the consequences of society's reliance on petroleum derived fuels has led to looming regulatory commitments for the uptake of sustainable energy sources. As a result, several routes for the production of liquid transportation fuels from lignocellulosic biomass (advanced biofuels) are currently being explored. In this regard, a definitive factual techno-economic state of art is currently not easily apparent. However, the basic options are summarized in various literature contributions.[1–3] In each, it is clear that the task of producing sellable liquid fuels produced from non-food, non-vegetable oil biomass is technically challenging and under development, with cost-competitiveness with petroleum fuels extremely challenging and to be regarded as more of a future hope. But, according to the cost analysis estimates of Dimitriou *et al.*, the current state of the art processes to produce an advanced biofuel diesel and petrol are optimistically 7.7%/MJ and 17.6%/MJ more expensive than that for petroleum derived equivalents.[4] Upcoming EU regulations, as part of the Revised Renewable Energy Directive (RED II), will require fuels to be composed of a minimum 6% advanced biofuels with the established "1st generation" (from food) biofuels limited to only 4%.[5] Presently technological and economic gaps prevent the filling of this requirement. It is well identified that advanced biofuels face extremely challenging technical circumstances to be cost competitive with petroleum and even 1st generation biofuels, due to the technically inferior nature of the lignocellulose feedstock. But, in the context of RED II, it is important to evaluate the techno-economics of any advanced biofuel production technology relative to the other competitive advanced biofuel production technologies, and not relative to the cost of 1st generation biofuels or to petroleum.

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For the production of advanced biofuels, an important aspect highlighted by Dimitriou *et al.* is that processes with fewer synthesis steps are more cost competitive over other production processes.[4] Thus, simple processes with few synthesis steps and purification steps, have a greater potential for cost effective production. One such route is the acid hydrolysis of carbohydrates, such as cellulose, that can be derived from waste lignocellulosic plant matter. Here, a solvent is required to mediate the conversion of biomass into lower molecular weight components. The solvent is usually water, resulting in the production of levulinic acid. However, if the solvent is an alcohol, alkyl levulinates result, and these have received suggestion as viable drop-in biofuels.[6] Thus far, the collective approach has primarily focused on synthesising and isolating the individual biofuel component (alkyl levulinate) for use as an individual fuel "additive". However, alongside the formation of the alkyl levulinate, Xu *et al.* have noted that the alcohol is simultaneously converted to the corresponding ether. Such processes therefore readily result in mixtures of alkyl levulinate, alcohol and ether.[7] Given the diverse range of physical and combustion qualities of these three components, mixtures of alkyl levulinate, alcohol and ether may be very compatible with existing liquid fuel engine combustion technologies. This is especially true in terms of autoignition propensity, but perhaps equally with other fuel properties as the availability of three biofuel components allows for more extensive degrees of freedom in fuel formulation, by blending the fractions of each biofuel, but also in their combination with the often disparate properties of petroleum derived fuels. The fractions of each component can be tailored in synthesis through adjustment of the reaction engineering parameters (temperature, time, [acid]), allowing for the possibility of tailoring the final fuel composition to be of desired fuel properties.[8] Most importantly though, this approach does not incur the significant cost and process performance penalties involved in purifying one single fuel component from a mixture.

This paper therefore focuses on the properties of fuel mixtures of ethyl levulinate (EL), diethyl ether (DEE) and ethanol (EtOH), that result from the acid hydrolysis of lignocellulosic wastes in ethanol.

There are several legal fuel specifications that sellable fuels must be compliant with, 98/70/EC (gasoline)[9] and 2008/68/EC (diesel),[10] in order for successful integration with current infrastructures, either blended with petroleum derived gasoline or diesel, or even someday as standalone fuels. Miscibility, flash point, vapour pressure, viscosity and of course autoignition propensity are all crucially important parameters. In this initial paper on ternary mixtures, of ethyl levulinate, diethyl ether and ethanol, the autoignition propensity is examined. The combustion kinetics of ternary blends of these three biofuel components are determined and analyzed to understand what ignition quality their blending will produce and what important differences, if any, they may present relative to conventional petroleum-derived fuels.

Each of the alkyl levulinate, ether, and alcohol fuel components have distinctive fuel properties, notably, disparate ignition qualities. Ethyl levulinate (EL) has been considered as an oxygenated blending component for diesel fuel due to its high boiling point, flash point and energy density. Modest blending of ethyl levulinate with petroleum diesel, up to 10 vol%, has been shown to have negligible effect on volatility,[11] and cetane number.[12] However, Christiansen *et al.* highlighted that miscibility can be a limiting issue when blending ethyl levulinate with diesel. They found that for 10% ethyl levulinate blends in diesel, ethyl levulinate would separate from a tested set of diesel fuels at temperatures <5 °C.[13] An appropriate co-solvent would be required in order to improve the solubility of ethyl levulinate in diesel fuels. Others espouse that ethyl levulinate would be more suited as a gasoline additive due to its anti-knock tendency. In a detailed kinetic model study, Ghosh *et al.*[14] estimate ethyl levulinate to have a research octane number (RON) of >97.7 and motor octane number (MON) of >93. Tian *et al.* agree with this hypothesis and attribute the anti-knock propensity of ethyl levulinate to its ability to decompose to stable intermediates such as levulinic acid during auto-ignition;[15] this is further supported by the combustion kinetic model developed by Ghosh *et al.*[14]

Obviously, ethanol (EtOH) is well-established as an octane booster in gasolines.[16] However, the high octane of ethanol makes it a poor diesel additive, and the blending with diesel would drastically reduce the cetane number of the resultant mixture. The blending of ethanol with diesel is further limited due to the polarity mismatch of each substance, which limits the solubility of ethanol in diesel to ethanol fractions of <15 vol%.[17] However, the largest concern of blending ethanol with diesel is its propensity to lower the flashpoint of the resultant diesel fuel. McCormick *et al.* have shown that for diesel fuels containing as little as 10% ethanol, the resultant flashpoint falls well below the legal requirements.[18]

Diethyl ether (DEE) is much better suited to blending with diesel in terms of autoignition behaviour, as it has a much higher cetane number (139)[19] and is long known as an ignition enhancer to improve the reactivity of several other fuels, such as biodiesel.[20] Diethyl ether is also highly miscible with diesel fuel. Bailey *et al.* observed no phase separation when blending diethyl ether with a reference diesel at room temperature; thus it has potential for use as a co-solvent for other less miscible biofuels, such as ethanol, with diesel.[21] Alike ethanol, diethyl ether also has a very low flashpoint; thus its use as a standalone fuel additive is limited.[22]

The blending of ethanol and diethyl ether to formulate fuels of particular combustion properties has been extensively studied.[19,23] The inclusion of alkyl levulinates in this biofuel mix is, therefore, of obvious technical potential. Given, the ease of production for this triumvirate, and considering the impending EU legislative requirements there may be a real commercial potential. This paper studies the autoignition behaviour of the ethanol-derived levulinate, EL, in this context, to begin the assessment of the compatibility of tricomponent biofuel blends of EL/DEE/EtOH with existing engines, fuels and fuel legal metrics [Euro VI]. This understanding is achieved by global ignition quality measurements in an Ignition Quality Tester (IQT) and fundamental ignition delay measurements with a Rapid Compression Machine (RCM). Fundamental meaning of these observations is provided by the development and analysis of a detailed chemical kinetic combustion model for the oxidation reaction of the full fuel blend and that of petroleum derived gasoline, specifically FACE (Fuels for Advanced Combustion Engines)-F gasoline.[24,25]

Experimental and numerical methods

Materials

Fuels were purchased from a commercial chemical shop (Sigma-Aldrich Chemie GmbH) and purities were as follows: ethyl levulinate 99%, diethyl ether 99.7%, ethanol 99.8%.

Derived cetane number measurements

Derived cetane number (DCN) measurements were performed using an ignition quality tester (IQT) as per ASTM D6890. The IQT determines an experimental ignition delay of a fuel spray in a pressurized (21.37 ± 0.07 bar) and heated constant volume chamber of air (0.21 L). As the fuel delivery relies on liquid fuel injection,[26] the ignition delay time obtained with an IQT is a combination of overlapping physical and chemical processes[27,28] but believed to be principally chemical. The ignition delay measurements reported here are the average of thirty-two individual experimental measurements and the derived cetane number is obtained using a correlation provided by ASTM D6890 and by Naser *et al.*[29] and Yang *et al.*[30]

Rapid compression machine measurements

The fundamental chemical reactivity of an EL/DEE/EtOH mixture was measured using the KAUST rapid compression machine (RCM) facility. The KAUST RCM has dual opposed piston design similar to the NUI Galway RCM which was described previously.[31] This dual piston arrangement is advantageous when comparing with a single piston RCM in terms of mechanical stability and faster compression times. The combustion chamber diameter is 50.8 mm and with a total stroke length of 238 mm. The compression ratio applied was 13 : 1, which can be varied by changing the piston stroke. The pistons are driven pneumatically and arrested at the end of compression position by the hydraulic locking system. Moreover, the pistons are designed with crevices to supress the vortex roll-up.[32] Pressure profiles were recorded by a Kistler 6045A pressure transducer.

The homogenous mixtures of fuel and diluent gas were realized in two heated mixing vessels which are equipped with magnetic stirrers. The mixture was prepared manometrically by monitoring the partial pressures.

The definition of ignition delay time is the time from the end-of-compression to the maximum rate of pressure increase, with the compressed gas temperature (T_c) calculated from the isentropic relation:

$$\ln\left(\frac{P_c}{P_i}\right) = \int_{T_i}^{T_c} \frac{\gamma}{\gamma - 1} \frac{dT}{T} \qquad (1)$$

where T_i and P_i are the initial temperature and pressure of the mixture, T_c and P_c are the compressed gas temperature and pressure and γ is the ratio of specific heats. Experiments were performed at 20 bar and 40 bar, at equivalence ratios of $\Phi = 1$ and $\Phi = 0.5$, and over a temperature range of 600–900 K. Exemplar experimental pressure histories can be seen in Fig. S1,† with non-reactive volume profiles available on request. The uncertainty in RCM ignition delay time measurements is ±15%. For each reactive case, non-reactive experiments were performed by replacing oxygen with nitrogen in the reactive mixture. Pressure profiles from non-reactive experiments are converted to volume profiles and used in chemical kinetic simulations to account for heat loss in the RCM.

EL/DEE/EtOH kinetic model development

To interpret the combustion behaviours of EL/DEE/EtOH mixtures, a detailed chemical kinetic model was developed. The model is hierarchical, and as previously reported for ethyl levulinate,[33] based on the gasoline surrogate model of Mehl *et al.*,[34] which also includes combustion chemistry for ethanol. However, this structure does not contain chemistry for diethyl ether.

There has been recent iterative activity toward a diethyl ether combustion model, which has been carefully reviewed here. Yasunaga *et al.*[35] and Tran *et al.*[36] have both constructed kinetic models for the high-temperature combustion of diethyl ether, which were validated using shock tube measurements of diethyl ether combustion at 900–1900 K and 1–4 bar, also using species profiles from laminar premixed flames. Sakai *et al.* calculated potential energy surfaces for the unimolecular reactions of both peroxy radicals (RO_2),[37] and peroxy alkylhydroperoxide radicals,[38] with CBS-QB3. Using this, they constructed a low-temperature kinetic model for diethyl ether combustion, which they validated using ignition data measured with a high-pressure shock tube (900–1300 K and 10–40 bar) and a rapid compression machine (500–1060 K and 2.5–13 bar) from Werler *et al.*[39] However, some important oxidation pathways were not included in the mechanism, including the decomposition pathways of alkylhydroperoxide radical species. Hu *et al.* modified the Sakai *et al.* model with calculated rate constants for hydrogen abstractions by H, $\dot{O}H$, HO_2, $\dot{O}$ and $CH_3\dot{O}$, and also for the decomposition and isomerization of diethyl ether and its radicals using TST-RRKM theory with G3-MP4.[40] These adjustments offered some minor improvement to the Sakai *et al.* model. At the same time, Eble *et al.*[41] also developed a simplified low-temperature kinetic model for diethyl ether combustion, considering just 25 reactions, including hydrogen abstraction only from the methylene group of diethyl ether but not from the methyl group. More recently, Serinyel *et al.* studied the combustion of diethyl ether in a jet stirred reactor connected with an online analytic suite to analyse the formation of combustion intermediates and products over a temperature range of 450–1250 K and low pressures of 1–10 bar at residence times of 70 and 700 ms.[42] To interrogate the experimental observations, they developed another kinetic model for diethyl ether, using the base thermochemistry developed by Sakai *et al.*, and validated the model using their recorded experimental measurements. They also attempted to validate their model using the RCM measurements of Werler *et al.*;[39] however, the experimental effect of heat loss was not considered in their validation simulations. Thus, the applicability of their model is limited to the narrow range of conditions employed in the jet stirred reactor experiments used to validate the model. Having analysed this state of art, it is clear that the model of Sakai *et al.* is the most complete diethyl ether mechanism. Hence, it was adopted in the present study.

Analysis of this multi-fuel model necessitated the following modifications to ensure that each fuel component was treated in a consistent scientific fashion and that the model was fit for purpose, (the effect of these modifications can be seen in Fig. S2†):

(1) The hydrogen abstraction reactions are assigned to describe abstraction by the same set of species from each fuel component, *i.e.*, H, $\dot{O}H$, $C\dot{O}H_3$, $CH_3\dot{O}$, $CH_3O\dot{O}$, HO_2, $\dot{O}$, O_2 and C_2H_5 were considered by Ghosh *et al.*,[33] but $C_2H_5O\dot{O}$, $CH_3C(O)O\dot{O}$, $\dot{O}OCHO$ and diethyl ether peroxy radicals were considered by Sakai *et al.* Reaction rate constants for these combinations with ethyl levulinate, diethyl ether and ethanol were prescribed at the recommendations of Li *et al.*,[43] or in the case of diethyl ether peroxy radicals, where no recommendation is available, the rate constant prescription was adopted from Sakai *et al.*[38]

(2) The formation enthalpy of the diethyl ether peroxy alkylhydroperoxide radicals were previously arbitrarily reduced in the Sakai model by 10 kJ mol^{-1} from the values computed with CBS-QB3 atomization. These were returned to the calculated formation enthalpies as they are important in accurately defining important equilibrium constants.

(3) The original combustion model for ethyl levulinate developed by Ghosh *et al.*[14] only contained high-temperature chemistry. Low-temperature oxidation pathways for ethyl levulinate radicals were not considered because when combusted as a pure fuel component, ethyl levulinate has negligible reactivity at low temperatures. In this work, with the addition of diethyl ether, the range of reactivity at lower temperatures is possible due to the radical generating propensity of diethyl ether. Therefore, the chemical kinetic model of ethyl levulinate must be expanded to include low-temperature oxidation pathways of alkyl radicals that dominate at such temperatures. Reaction pathways for the oxidation and subsequent decomposition of the ethyl levulinate radicals are prescribed by analogy to the known process of alkanes.[34] The thermochemistry for each species were calculated using Benson's group additivity method,[44] implemented using the THERM software. A full list of reactions and assigned rate parameters can be seen in Table S1.† In most cases, reaction rate constants were adopted from literature for similar chemical processes,[14,34] with the exception of:

(a) H-abstraction reaction rate constants were prescribed at the recommendations of Li *et al.*[43]

(b) As no reliable thermodynamic data was available for the description of RO_2 and alkylhydroperoxide radical species to describe the important equilibrium of elimination pathways, the recommended rate constants and equilibrium constants of Villano *et al.* were used.[45–47]

The fundamental modelling assumptions used in comparing the purely chemical kinetic calculations with experiments are as follows: homogeneous adiabatic conditions were assumed; non-reactive volume history approach was used to describe the heat losses in the post-compression period of the RCM; the simulated ignition delay time was defined as per the experiment. These simulations were executed in the closed homogeneous batch reactor subroutine of ChemkinPro.

Results and discussion

EL/DEE/EtOH fuel formulation

A series of EL/DEE/EtOH mixtures were measured with an IQT to assess the dependence of the combustion reactivity on the fraction of each component in the mixture. To use this information to formulate EL/DEE/EtOH mixtures of specified ignition quality, the measured DCNs were fitted to the following equation:

$$\mathrm{DCN} = \sum_{\mathrm{i}} \mathrm{DCN}_{\mathrm{i}} \left(a_{\mathrm{i}} x_{\mathrm{i}} + b_{\mathrm{i}} (x_{\mathrm{i}})^2 + c_{\mathrm{i}} (x_{\mathrm{i}})^3 \right) \qquad (2)$$

where $\mathrm{DCN_i}$ is the DCN of the pure component i, x_{i} is the mole fraction of component i, and a_{i}, b_{i} and c_{i} are constants for component i, obtained through linear regression using the lsqnonlin minimization function of MATLAB. Table 1 contains the values for a_{i}, b_{i} and c_{i}, and results in an R^2 of 0.977.

The experimental data is summarized in Fig. 1, and tabulated as ESI (Table S2†). As expected, mixtures with a high fraction of diethyl ether have a high DCN, whereas mixtures with high fractions of ethanol or ethyl levulinate have low DCNs. In fact, the DCN is much more strongly dependent on the diethyl ether concentration, varying the ratio of ethanol and ethyl levulinate at a constant diethyl ether fraction had very little effect on the mixture DCN. This is due to the similarly low DCNs of ethanol (DCN = 11) and ethyl levulinate (DCN = 5).[48] Eqn (2) is proposed as a tool for the formulation of EL/DEE/EtOH diesel compatible mixtures where DCN is a defining metric.

To assess the use of EL/DEE/EtOH mixtures as a blending component or replacement for gasoline, octane number is a required parameter. Haas *et al.*[49] and Naser *et al.*[28] show that the Research Octane Number (RON) can be estimated from DCN measurements using measured RONs and DCNs of toluene/iso-octane/*n*-heptane reference fuels. Haas *et al.* derived a RON to DCN relation as:

$$\begin{aligned}\mathrm{RON} = {} & 116.609 - 0.784(\mathrm{DCN}) \\ & - (0.00662(\mathrm{DCN}^2)) - (3.401 \times 10^{-4}(\mathrm{DCN}^3))\end{aligned} \qquad (3)$$

Table 1 DCNs and parameters for eqn (2)

Component (i)	DCN	*a*	*b*	*c*
Ethyl levulinate	5	7.931	−10.254	2.985
Diethyl ether	139	0.394	0.277	0.301
Ethanol	11	−0.871	−1.300	2.801

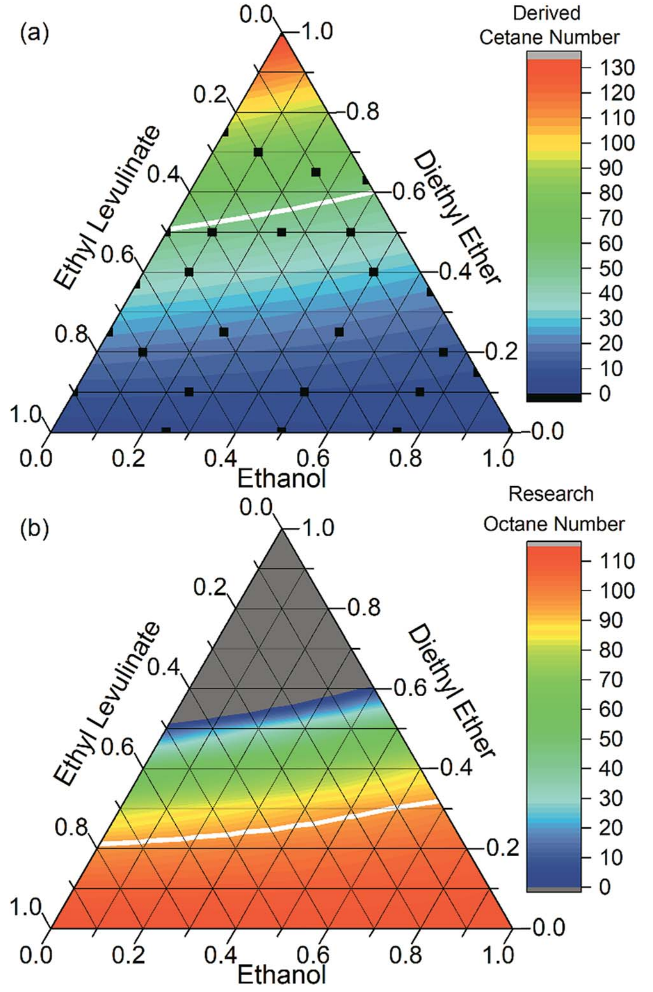

Fig. 1 DCN (a) and RON (b) of EL/DEE/EtOH blends. Symbols are measured DCNs. The white lines correspond to a DCN of 54 in (a) and RON of 95 in (b).

From these relations, it can be seen that 50–60% diethyl ether is required to produce a EURO VI "diesel" with DCN of 54, and mixtures with diethyl ether in the range of ∼20–30% can produce a EURO VI "gasoline" of RON >95.

EL/DEE/EtOH gasoline

To understand how the gas phase combustion reactivity of an EL/DEE/EtOH mixture formulated to have a RON of 95 compares to that of a conventional gasoline of the same octane number, one mixture is selected for detailed study. Considering that ethyl levulinate is to be derived from lignocellulosic waste, and is, therefore, the value-added component, the fraction of ethyl levulinate was specified to be at a minimum of 33%. With this imposition, and utilising the relations above, a mixture of 35/27/38 mol% EL/DEE/EtOH is estimated to have a RON of 95. Henceforth, this mixture is referred to as "EL/DEE/EtOH gasoline". To confirm the accuracy of the octane number estimation, attempts were made to measure both the RON and the MON of the EL/DEE/EtOH gasoline in a CFR (Cooperative Fuel Research) engine according to ASTM D2699-18 [50] and ASTM D2700-18.[51] While the MON was measured to be 88.3, the RON could not be measured due to flow rate limitations in the specific fuel handling system utilized. Based on the measured MON and estimated RON, FACE-F gasoline was selected as an example of a conventional gasoline with similar RON (94.4) and MON (88.8) to the EL/DEE/EtOH gasoline.[25] A number of fundamental and applied studies have been performed on this FACE gasoline,[25,52] making it a suitable fuel for the comparison purposes in this work. The ignition properties of both fuels are summarized in Table 2.

Fig. 2, shows the ignition delay data of the EL/DEE/EtOH gasoline measured in a rapid compression machine, also tabulated as ESI (Table S3†). It is contrasted to FACE-F data also obtained in an RCM at the same conditions.[25] The EL/DEE/EtOH gasoline blend shows reactivity increasing with equivalence ratio as would also be expected for conventional gasoline at both 20 and 40 bar. However, it shows severely truncated Arrhenius reactivity, where the low-temperature reactivity and negative temperature coefficient (NTC) reactivity is totally absent at both pressures. Ignition delay times for the EL/DEE/EtOH gasoline mixture were greater than 500 ms at temperatures below ∼750 K. This is strikingly different to that observed for FACE-F, where measurable ignition delays were obtained at temperatures as low as 645 K. Both fuels have the same measured MON of 88 (and speculated to have a very similar RON). The disparity in gas phase ignition delay times highlights potential limitations or complexities in the use of conventional ignition quality metrics, such as octane number, in constraining the combustion behaviours of oxygenated (bio-derived) fuels.

Using RON and MON as reactivity indicators for oxygenated biofuels

As summarized in Table 2, according to CFR measurements both fuels have a very similar MON, according to IQT measurements both fuels have a similar DCN and according to the DCN–RON relationship, outlined by Haas *et al.*[49] and Naser *et al.*,[28] both fuels ought to have a similar RON. In applying measurement and rating methodologies historically developed for petroleum fuels to biofuels, it is important to recognize that the inclusion of oxygen atoms in the otherwise hydrocarbon chemical structure of fuels has potentially important complicating implications.

Singh *et al.* have shown that for gasoline surrogate mixtures (toluene/iso-octane/*n*-heptane/1-hexene/1,2,4-trimethylbenzene),

Table 2 Comparison of ignition properties of the El/DEE/EtOH gasoline and FACE-F

Fuel	DCN	RON	MON
EL/DEE/EtOH gasoline	22.7[a]	95.0[b]	88.3[c]
FACE-F	19.1[d]	94.4[e]	88.8[e]

[a] From eqn (2). [b] Estimated using DCN–RON relationship summarized by eqn (3).[49] [c] Measured in this work. [d] Measured by Naser *et al.*[28] [e] Measured by Sarathy *et al.*[25]

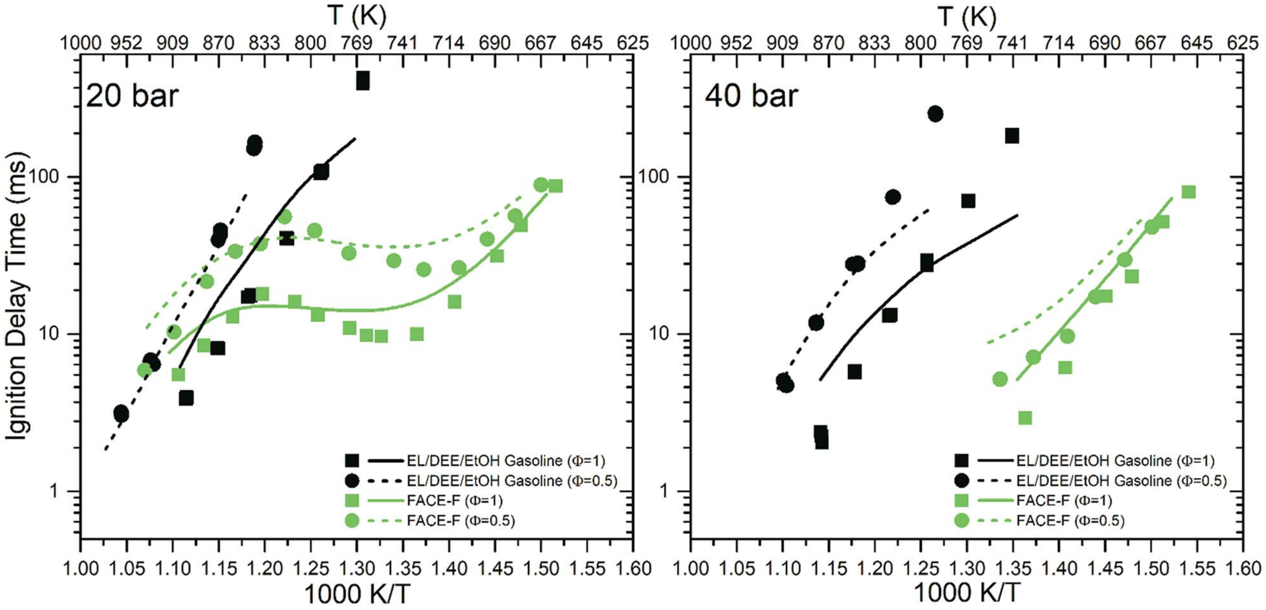

Fig. 2 RCM ignition delay times for the EL/DEE/EtOH gasoline and FACE-F.[25] Symbols correspond to measurements. Lines correspond to model simulations. FACE-F experimental data is taken from Sarathy *et al.*[25]

there is a relationship between octane sensitivity and the occurrence of NTC autoignition behaviour.[53] They show that fuels with significant NTC behaviour (like FACE-F) have a lower octane sensitivity and fuels with lesser or no NTC behaviour (like the EL/DEE/EtOH gasoline) have a higher octane sensitivity. Therefore, based solely on the observed gas phase reactivity, as the EL/DEE/EtOH gasoline has no NTC behaviour one could expect it to have a much higher octane sensitivity than FACE-F. On this basis, the EL/DEE/EtOH gasoline ought to have a higher RON than FACE-F, *i.e.*, higher than the predicted value of 95.

This argument would point to a potential limitation in the use of the specific DCN–RON estimation method employed. For use with oxygenated biofuels, a potential infidelity in the method is that it uses *n*-heptane/iso-octane/toluene reference fuels as the calibration factor to translate DCN to RON.

It is well established[29,30,54–58] that both the DCN and the RON ignition propensity metrics are influenced by different combinations of four broad physical processes:

(1) Gas phase reaction kinetics: the chemical reactivity is determined by the reaction mechanism and associated chemical thermodynamics and reaction kinetics of the fuel/air mixtures.

(2) Fuel/air equivalence ratio: the fuel/air ratio in the RON measurement is variable within the test method. This is also different to that in the DCN measurement. For RON determinations, a fuel/air ratio is selected to maximize the knocking intensity of the test fuel.[50] Whereas, DCN determinations are performed in a fixed volume of pressurized air, into which a fixed volume of liquid fuel is injected. As such, the overall equivalence ratio is variable with liquid fuel properties, notably, fuel density and empirical formula (C/H/O) defining the effective equivalence ratio.[29,59] Furthermore, ignition in the IQT occurs in locally rich equivalence ratio regions, as discussed below,[60,61] whereas equivalence ratio is homogeneous throughout the cylinder in RON measurements.

Therefore, in both metrics, the fuel/air ratio is dependent on the test fuel and experimental conditions. As the reaction rate is dependent on the equivalence ratio, this can consequently produce unequal reaction kinetic regimes.

Secondly, as different quantities of fuel are employed, the vaporization enthalpy per unit mass is also consequently variable.

(3) Enthalpy of vaporization: in both IQT and CFR measurements, the fuels are supplied to the system in the liquid phase and must vaporize into the gas phase for the combustion reaction to occur. Thus, the reacting temperature of the system, and therefore to some extent the combustion kinetic regime, is dependent on the enthalpy of vaporization of the fuel mixture.[54]

(4) Liquid fuel – air mixing: for DCN determinations, fuels are charged into the IQT reaction chamber as liquid components using a pneumatically driven fuel pump and a single-hole S-type delayed pintle nozzle.[59] The dispersion of the fuel is influenced by properties such as spray breakup, surface tension, air entrainment, among others; all of which vary between fuel mixtures.[55] Osecky *et al.* have shown that these spray and dispersion parameters impact on the fuel air inhomogeneities during the early stages of ignition, and can lead to local regions where the equivalence ratio is 50% larger than the global equivalence ratio, depending on the fuel.[56,62] This of course can have a significant effect on the resulting ignition delay.

Clearly, each one of these properties is fuel dependent. Each of these properties also have a significant impact on the resultant measurement. In the case of the EL/DEE/EtOH gasoline, the physical properties of the heavily oxygenated molecules can be widely different from those of hydrocarbons. The premise of the DCN–RON relationship proposed by Haas *et al.* is that the combination of these parameters in influencing the IQT measurement is captured by an empirical correlating function as determined by relating ignition propensity observations of toluene/iso-octane/*n*-heptane reference fuels made in a CFR engine to those made in the IQT. It stands to reason that so long as the properties of the test fuel fall within the range afforded by the properties of the reference mixtures, the estimation procedure ought to be accurate. Therefore, though the RON estimations are state of the art, it is reasonable to expect some inaccuracy on the basis of the discussion above.

Detailed gas phase reactivity differences between the EL/DEE/EtOH gasoline and FACE-F

It is important to understand what factors contribute to this strikingly different fundamental reactivity observed in the measured RCM ignition delay times. Toward this end, the underlying reaction behaviours are analyzed using detailed chemical kinetic models. FACE-F was simulated as a surrogate composed of: *n*-butane (6.9 mol%), 2-methylbutane (9.8 mol%), 2-methylhexane (7.0 mol%), cyclopentane (15.8 mol%), 1,2,4-trimethylbenzene (8.4 mol%), 1-hexene (8.4 mol%), 2,2,4-trimethylpentane (43.7 mol%) as recommended by Sarathy *et al.*, using the model developed in the same work.[25] The EL/DEE/EtOH gasoline mixture was simulated using the model developed in this work. These calculations are presented in Fig. 2. For the EL/DEE/EtOH gasoline, this is the first time such a multi-component biofuel system has been studied. This initial model lacks complete quantitative replication of the measured data, more significantly at higher pressures. However, what is important is that the model replicates the general features of the experimental observation in comparison to the very different features of the FACE-F surrogate kinetic model. The

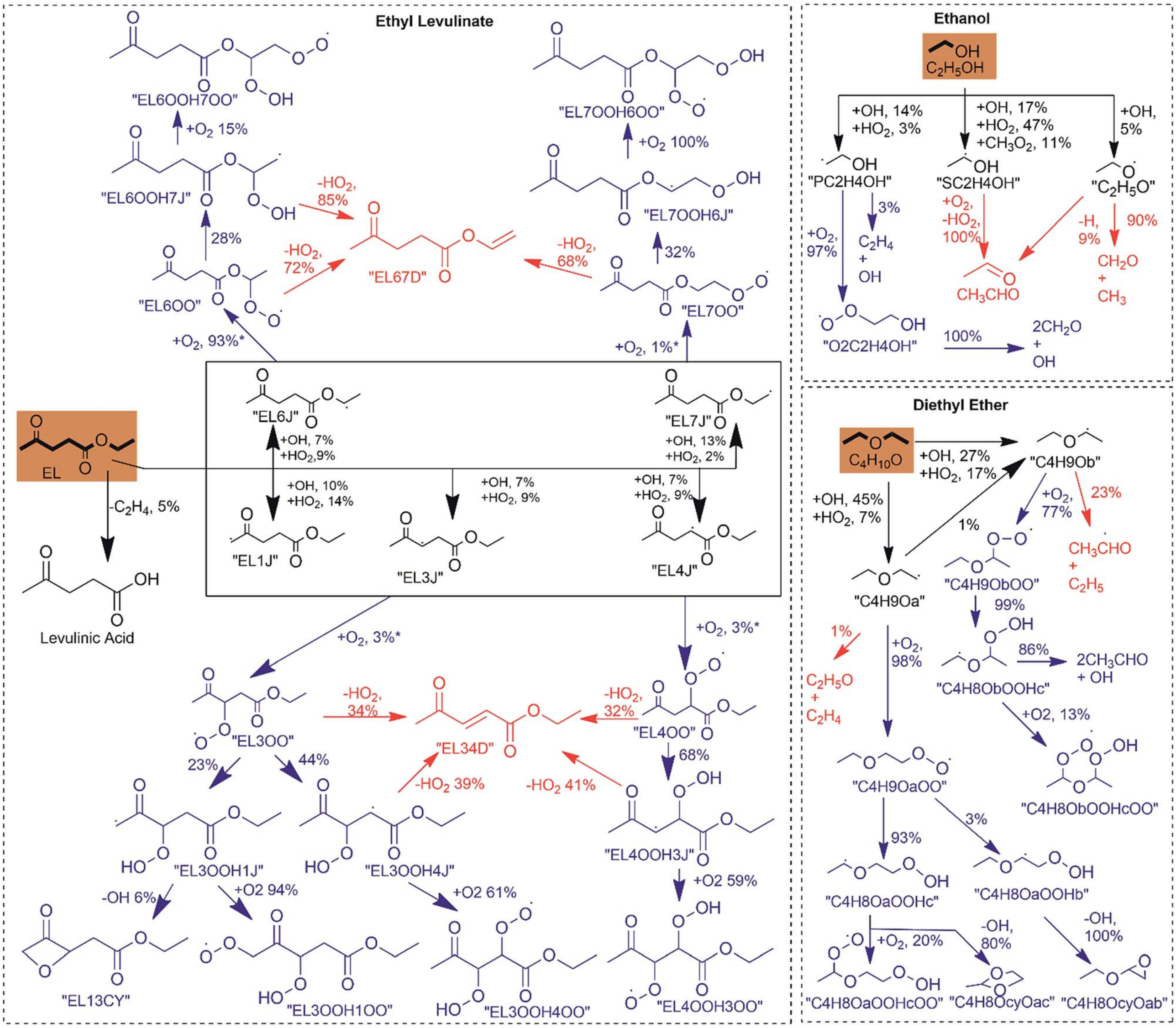

Fig. 3 Reacting flux analysis at the point of 65% of the ignition delay time for the EL/DEE/EtOH gasoline, at 750 K, 25 bar, $\Phi = 1$.Values marked with * refer to the % of consumption of total ethyl levulinate radical population, accounting for the isomerization pathways. Blue indicates pathways that reproduce or increase the $\dot{O}H$ population, red indicates chain termination pathways.

model replicates the effect of equivalence ratio and pressure but also, significantly, the truncated range of reactivity of the EL/DEE/EtOH gasoline blend. Here, it is important to note that the simulations have been performed to a test time of 500 ms. As the essence of each fuel's behaviour is replicated by the models, analyses of the models may allow for education on the fundamental reasons for the very different combustion behaviours observed for these gasoline fuels.

Singh *et al.* recently reported that constant volume simulations at 750 K and 25 bar show the best correlation between ignition delay times and RON.[53] Furthermore, analysis at these conditions is useful to highlight the role of chemical interactions between reactive and non-reactive components in a fuel mixture, as was done previously for fuel mixtures with 2-methylfuran.[63,64] Chemical flux and sensitivity analyses for each gasoline fuel are therefore performed at this condition and presented in Fig. 3, 5 and S3.†

The mode of consumption of all three fuel components of the EL/DEE/EtOH gasoline is similar. Hydrogen abstraction by $\dot{O}H$ radical is the dominant pathway for diethyl ether (72%); however, it is less significant for both ethyl levulinate and ethanol, accounting for only 44% and 36% consumption, respectively. For both of these high RON components, abstraction by HO_2 radical is more significant, accounting for 43% and 50% in ethyl levulinate and ethanol respectively and only 25% in diethyl ether. As will be show below, HO_2 is the dominant radical produced from the oxidation of ethyl levulinate and ethanol, and so is present in higher concentrations for the EL/DEE/EtOH blend. Hydrogen abstraction by HO_2 radicals is very different to the competing process of hydrogen abstraction by $\dot{O}H$ radicals. Hydrogen abstraction by HO_2 leads to the formation of H_2O_2 which, as summarized by Westbrook,[65] is accumulated until the system reaches a sufficient temperature for the H_2O_2 to decompose to two $\dot{O}H$ radicals. Thus, this process consumes a reactive radical to form H_2O_2 which does not decompose until high temperatures are reached, and as such this is one contributing factor to the reduced reactivity of the EL/DEE/EtOH gasoline. This is quite different to the FACE-F surrogate, where abstraction by $\dot{O}H$ radicals is most dominant (89–98%). For ethyl levulinate, this synergistic blend behaviour, consumption by hydrogen abstraction, is very significant. As a pure component fuel,[33] ethyl levulinate decomposes by molecular elimination to levulinic acid and ethylene. When in a mixture at these lower temperatures, a large radical pool of reactive radicals is formed from the rapid decomposition diethyl ether and thus promotes the H-abstraction of ethyl levulinate. Therefore, as part of this ternary blend, ethyl levulinate is consumed by radical chemistry as opposed to molecular elimination which is observed when ethyl levulinate is utilized as a standalone fuel at higher temperatures. This, therefore, rules out the elimination reaction to levulinic acid and ethylene as a principal reason for the high-octane behaviour of ethyl levulinate, as suggested by Tian *et al.*[15]

For FACE-F, 72% of the fuel undergoes hydrogen-abstraction followed by addition of oxygen to form alkyl radicals, referred to as "oxidation". For the radicals of the EL/DEE/EtOH gasoline, a greater level of oxidation is observed, where 97% of the total fuel undergoes oxidation following hydrogen abstraction. The greatest competition between oxidation and radical beta bond scission is observed for the secondary radical of diethyl ether ("$C_4H_9O_b$"), where only 77% of the radical is oxidized and 23% undergoes beta-bond scission to acetaldehyde and ethyl radical. In the case of ethanol, the primary hydroxyalkyl radical and secondary hydroxyalkyl radical are oxidized, with the latter (α-hyodroxyethyl) undergoing the concerted elimination to form HO_2 and acetaldehyde, a pathway important in alcohol combustion chemistry.[66] However, the ethoxy radical undergoes decomposition. For ethyl levulinate, following isomerization between radicals, 93% of the total ethyl levulinate radical pool undergoes oxidation from the EL6J radical and 3% undergoes oxidation from both the EL3J radical and the EL4J radical (see Fig. 3).

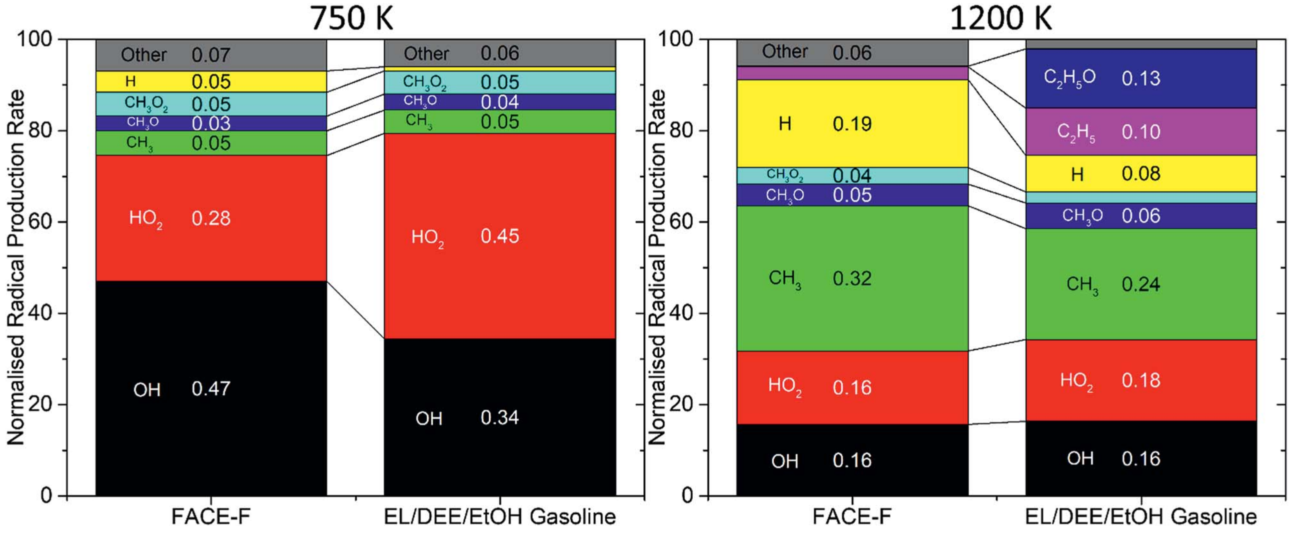

Fig. 4 Normalized small radical rate of production for the EL/DEE/EtOH gasoline and FACE-F[25] after 65% of the computed ignition delay time at 750 K and 1200 K, 25 bar, and $\Phi = 1$.

Reactivity at low temperatures is dictated by the pathways that consume these peroxy radical species (RO_2). Isomerization of the RO_2 species to the alkylhydroperoxide radicals and subsequent decomposition to cyclic ether or oxidation to the peroxy alkylhydroperoxide radicals can lead to the propagation of $\dot{O}H$ radicals, increasing the reactivity. However, elimination of HO_2 and olefins from either RO_2 or alkylhydroperoxide radicals can significantly reduce the reactivity of a fuel, as it results in an effective "termination" of the radical chain. For the fuel species in the FACE-F surrogate, only 25% of the RO_2 species undergo elimination to olefins and HO_2, and 75% isomerize to alkylhydroperoxide radicals. For the EL/DEE/EtOH gasoline fuel, a larger competition between the isomerization and elimination pathways is observed; 57% of the RO_2 species eliminate to olefin species and HO_2 and only 43% isomerize. Unsurprisingly, ethyl levulinate and ethanol contribute largely to this propensity for HO_2 production. In total, elimination accounts for 69% and 81% of the consumption of RO_2 species in ethyl levulinate and ethanol, respectively.

For diethyl ether, isomerization to alkylhydroperoxide radicals dominates in the consumption of RO_2 species (99%). Examination of the alkylhydroperoxide radical consumption for FACE-F shows that 14% eliminates to olefins and HO_2, with the remainder being further oxidized (47%) or converted to cyclic ethers with the production of $\dot{O}H$ (35%), which repopulates the reactive $\dot{O}H$ radical pool. Again, for the EL/DEE/EtOH gasoline fuel, a larger proportion produces HO_2 and olefins than FACE-F

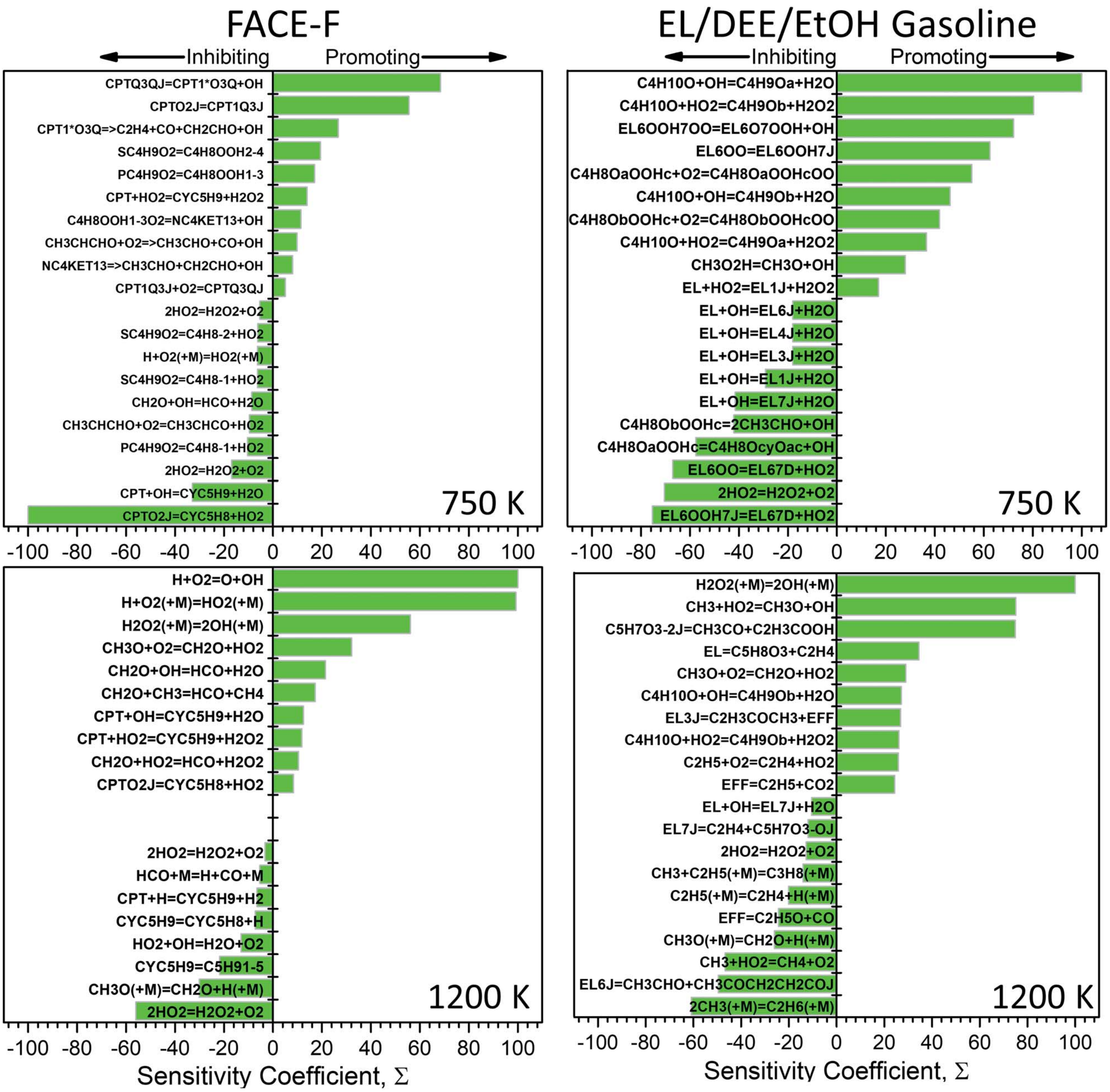

Fig. 5 Sensitivity analysis to ΔT for the EL/DEE/EtOH gasoline and FACE-F[25] at 750 K and 1200 K, 25 bar, and $\Phi = 1$. Top 20 sensitivity coefficients are shown, normalized to the absolute most sensitive reaction. Reactions are described in the direction of their net flux from left to right.

– 25% of the alkylhydroperoxide radical consumption. A smaller proportion (25%) undergoes further oxidation, thus the potential to grow the $\dot{O}H$ radical pool is limited. The $\dot{O}H$ radical pool is only maintained by the formation of cyclic ethers which accounts for 57% of the alkylhydroperoxide radical consumption. This prevalence of elimination is a key aspect of the reduced reactivity of the EL/DEE/EtOH gasoline fuel at low temperatures.

These distinctive ignition chemistries are also evident in the make-up of the reactivity-controlling small species radical pool, presented in Fig. 4. The radical rate of production, at 65% of the ignition delay time, is used for comparison, as it better accounts for the most important radicals formed, including reactive radicals with short life spans which are not captured when comparing the mole fractions of radicals. At 750 K, as expected, the most dominant radicals in FACE-F combustion are $\dot{O}H$ and HO_2, accounting for 47% and 28% of the small radical production, respectively. Similarly, for the EL/DEE/EtOH gasoline, these radicals make up the largest proportion; however, the prominence of HO_2 radicals is significantly higher, making up 45% of the population and $\dot{O}H$ radicals only make up 34% of the population. This augmented rate of production of HO_2 for the EL/DEE/EtOH gasoline, in comparison to FACE-F, stems from the dominance of RO_2 and alkylhydroperoxide radical elimination pathways.

The competition for $\dot{O}H$ radicals is clearly apparent in the sensitivity analysis (see Fig. 5) of the EL/DEE/EtOH gasoline fuel. Hydrogen abstraction by $\dot{O}H$ from ethyl levulinate inhibits the reactivity whereas hydrogen abstraction from diethyl ether by $\dot{O}H$ promotes reactivity. The alkyl radical elimination pathways dominate for ethyl levulinate, thus ethyl levulinate consumes the reactive $\dot{O}H$ radical and produces a reactivity inhibiting HO_2 radical. On the other hand, for diethyl ether, $\dot{O}H$ propagation and branching pathways are much more prominent; thus, when diethyl ether consumes an $\dot{O}H$ radical it either produces two more $\dot{O}H$ radicals through the propagation pathways or at the very least it recycles the $\dot{O}H$ radical with the formation of cyclic ethers from the alkyl radicals, thus maintaining or enhancing the population of the reactivity driving $\dot{O}H$ radicals.

The radical pool and sensitivity analyses were also examined at an exemplar high-temperature condition to compare the difference in ignition processes between the ethanolic gasoline and the petroleum-derived gasoline. At high temperatures (>850 K), while the EL/DEE/EtOH gasoline produces a similar ignition delay time as the FACE-F gasoline, examination of the radical pool population and sensitivity analyses show that a very different ignition process is occurring despite the similar time scale. At high temperatures, for both FACE-F and the EL/DEE/EtOH gasoline, $\dot{O}H$ and HO_2 still play a significant role in ignition, however slightly diminished with a larger population of methyl radicals being formed in comparison to the ignition process at low temperatures. It is interesting to note that for the EL/DEE/EtOH gasoline fuel, a significant portion of ethyl-based radicals (C_2H_5 and C_2H_5O) are formed, which is not observed in the combustion of FACE-F. The sensitivity analysis also shows a disparity in the mode of combustion. Ignition is dictated by the fate of the $\dot{O}H$ and HO_2 radicals for FACE-F, as one would expect. The combination of HO_2 to H_2O_2 and O_2 inhibits the reactivity and the decomposition of H_2O_2 to $\dot{O}H$ radicals promotes combustion. However, for the EL/DEE/EtOH gasoline fuel, ignition is more sensitive to reactions involving methyl and ethyl related radicals which dominate the radical pool. The combination of methyl radicals to form ethane being the most inhibiting reaction and the bimolecular reaction between methyl radicals and HO_2 being the second most promoting reaction, behind the decomposition of H_2O_2 to two $\dot{O}H$ radicals. While the net effect of these differences results in a similar ignition delay time, clearly, the dominance of the methyl and ethyl radicals over $\dot{O}H$ radicals indicates a different combustion mechanism for the "ethanolic" gasoline compared to the petroleum gasoline.

Conclusions

Ignition properties of EL/DEE/EtOH mixtures are determined with ignition quality tester and rapid compression machine measurements. Ignition quality tester measurements highlight the flexible range of fuels, of varying ignition quality, that are capable of being produced from blending ethyl levulinate, diethyl ether and ethanol. According to the conventional ignition quality metrics of research octane number, motor octane number and derived cetane number, it is even possible to produce mixtures of equivalent ignition quality of both EURO VI gasoline and diesel. This flexibility is a significant advantage for the acid hydrolysis of lignocellulosic biomass in alcohols over other potential biofuel technologies.

One specific mixture formulated to have an estimated RON of 95, typical of market gasoline, is selected for detailed study. The rapid compression machine measured ignition delay behaviour of the EL/DEE/EtOH gasoline mixture demonstrates a significantly limited temperature range of ignition, relative to the petroleum-derived gasoline, FACE-F, which has a similar RON of 94.4. The ignition delay times of both fuels at temperatures higher than $\sim$800 K are closely equivalent but deviate largely at lower temperatures. This indicates that conventional ignition quality indicators, such as RON/MON should be applied with caution to fuels containing significant fractions of biofuels. Examination of the detail kinetic modelling results shows that a very different ignition process occurs in the "ethanolic" gasoline (EL/DEE/EtOH gasoline) in comparison to the petroleum derived gasoline (FACE-F). The reduced reactivity of the EL/DEE/EtOH gasoline mixture is shown to originate from the propensity of ethyl levulinate and ethanol alkyl radicals to eliminate to olefins and HO_2, thus terminating the chain branching pathways, which are much more prevalent in the combustion of petroleum gasolines. Awareness of such important kinetic differences is vital for the future development and implementation of advanced biofuel mixtures from lignocellulosic biomass.

Conflicts of interest

There are no conflicts to declare.

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